ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF POLY(VINYL CHLORIDE) BLENDS: SPECTROSCOPIC, THERMAL, VISCOSIMETRIC, MECHANICAL AND SURFACE CHARACTERIZATIONS

Ph.D. THESIS

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POLİ(VİNİL KLORÜR) KARIŞIMLARININ HAZIRLANMASI: SPEKTROSKOPİK, ISIL, VİSKOZİMETRİK, MEKANİK VE YÜZEY KARAKTERİZASYONLARI

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LIST OF SYMBOLS

A : Cross-sectional area

b : Interaction coefficient

b_{12} : Interaction coefficient between two polymers

Δb : Interaction parameter

C : Concentration

c_p : Heat capacity

Δc_{pi} : The glass transition increment of the heat capacity of the specimen.

D : Diffusion coefficient

D_0 : Preexponential factor of diffusion

E : Tensile modulus

E' : Storage modulus

E'' : Loss modulus

E^* : Complex tensile modulus

E_d : Activation energy of diffusion

E_p : Activation energy of permeation

F : Tensile force

G' : Shear modulus

ΔG_m : Free energy of mixing

H : Enthalpy

ΔH_f : Enthalpy of fusion

ΔH_m : Enthalpy of mixing

ΔH_v : Molar enthalpy of vaporization

k : Boltzman constant

k' : An empirical parameter for miscibility

K : Bulk modulus

l : Length of specimen

l' : Thickness of polymer film

Δl : Amplitude of elongation

M : Molecular weight of polymer

M_n, M_w, M_v : number, weight and viscosity average molecular weights, respectively

N_1 : Mole fraction of solvent molecules in a solution

N_2 : Mole fraction of polymer in a solution

p : Pressure

P : Permeability coefficient

P_0 : Preexponential factor of permeability

q : Permeability

r_d : Distance between the molecules

r : Effective number of segments between components

R : Gas constant

S : Entropy

ΔS_m : Entropy of mixing

S' : Solubility constant

S_0 : Preexponential factor of solubility

T : Temperature

T_1 : Relaxation time

T_2 : Spin-spin relaxation time

T_g : Glass transition temperature

T_m : Equilibrium melting point of the semicrystalline polymer in the blend

T_m^0 : Melting point of the semicrystalline polymer in the pure form

U : Total energy of the system

V : Volume

V_i : Molar volume of component i

V_s : Interacting segment volume

w_i : Weight fraction of component i

Δw_{12} : The energy change due to the formation of the 1-2 contact pair

x_i : Mole fraction of component i

z : Lattice coordination number of cells

ε : Elongation at break

ε' : Dielectric constant

η_{sp} : Specific viscosity

η_{spm} : Specific viscosity of mixture

$[\eta]$: Intrinsic viscosity

ϕ_i : Volume fraction of component i

δ : Solubility parameter of component i

σ : Ultimate tensile strength

χ . Thermodynamic interaction parameter

μ : Dipole moment

μ_i : Chemical potential of component i

Ω : Total number of ways of arranging N_1 and N_2 molecules

δ : Phase angle

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PREPARATION OF POLY(VINYL CHLORIDE) BLENDS: SPECTROSCOPIC, THERMAL, VISCOSIMETRIC, MECHANICAL AND SURFACE CHARACTERIZATIONS

SUMMARY

In this work, binary and ternary blends of poly(vinyl chloride) were prepared by solvent casting method. Poly(vinyl chloride)/Tegomer (PVC/Tegomer), poly(vinyl chloride)/poly(2-ethyl hexyl acrylate) (PVC/PEHA) and poly(vinyl chloride)/poly(2-ethyl hexyl acrylate)/Tegomer (PVC/PEHA/Tegomer) blend systems were studied. The influence of small amounts (1-10 wt %) Tegomer on homopolymer PVC, and PVC/PEHA blends were investigated by a number of different characterization techniques.

Miscibility, thermal, mechanical, viscosimetric, morphological, surface and gas permeation properties of polymer blends based on PVC were determined by Fourier Transform Infrared (FTIR) Spectroscopy, Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), Stress-Strain Tests, Scanning Electron Microscopy (SEM), Viscometry, Contact Angle and Gas Permeability Testing Appliance.

Binary blends of PVC/Tegomer were found to be miscible according to FTIR, DSC, DMTA and Viscosity measurements. Stress-strain measurements showed that Tegomer is a very effective plasticizer for PVC. Gas permeability of the blends increased with Tegomer content and the temperature. According to SEM micrographs, pure PVC and PVC/Tegomer blends have slightly different fractured surfaces, however no two-phase morphology could be observed. Contact angle measurements showed that the addition of small amounts of Tegomer may change surface properties of pure PVC homopolymer dramatically.

The results of the characterization techniques also showed that although binary blends of PVC/PEHA are immiscible at the composition range of 1-10 wt % PEHA, Tegomer addition makes a synergetic effect on the miscibility and the properties of these binary blends. Ternary blends of PVC/PEHA/Tegomer exhibited single T_g behaviour and viscosity experiments indicated some compatibility. Even at very low percentages of copolymer content, the stress-strain behaviour of the blends changes dramatically. SEM micrographs indicated that PEHA component seems to cause voids on the surface during fracture. However at higher magnifications of SEM images, no two-phase morphology could be observed.

POLİ(VİNİL KLORÜR) KARIŞIMLARININ HAZIRLANMASI: SPEKTROSKOPİK, ISIL, VİSKOZİMETRİK, MEKANİK VE YÜZEY KARAKTERİZASYONLARI

ÖZET

Polimer karışımları (blend) son yıllarda, endüstride giderek artan ölçülerde kullanılmakta ve bu nedenle geniş bir araştırma konusu olarak ilgi çekmektedir. Polimer karışımlarının en önemli üstünlüğü, ticari bir polimerin özelliklerinin kolaylıkla değiştirilebilmesine olanak sağlamasıdır. Ayrıca istenen özelliklerde yeni maddelerin elde edilmesinde oldukça ucuz bir yöntemdir. Karışımların üstün özellikler göstermesi, homopolimerlerinin moleküler düzeyde uyumlu olmasına bağlıdır.

Polimer uyumluluğunu (miscibility) incelemek için pek çok deneysel ve kuramsal yöntemler kullanılır. Infrared spektroskopisi, camsı geçiş sıcaklığı ölçümleri, gerilme-uzama testleri, elektron mikroskobu ile morfoloji analizi, viskozite ölçümleri, nükleer manyetik rezonans spektroskopisi vb. teknikler literatürde polimer karışımlarının uyumluluğunu araştırmada kullanılan tekniklerden bazılarıdır.

Polimer karışımları arasındaki özgül etkileşimler uyumluluğu sağlar. Genellikle polimer karışımları uyumlu değildirler. Bu tür polimerler zayıf fiziksel ve kimyasal etkileşimler ile çok fazlı (karışmayan) (immiscible) sistemler oluştururlar. Uyumlu olmayan bu tip polimer karışımları zayıf mekanik özellikler gösterirler. Bazı durumlarda, sınırlı uyumluluk sağlayan bir polimer (compatibilizer) eklenmesi ile (örneğin, blok yada graft kopolimerler) uyumluluk sağlanabilir.

Üçlü polimer karışımı sistemlerinin uyumluluk davranışları son yıllarda ayrıntılı olarak incelenmektedir. Üçlü A/B/C polimer karışımları ile ilgili bir çok çalışma literatürde rapor edilmiştir. Uyumlu olmayan B/C polimer karışımına, uyumlu A polimerinin eklenmesi ile A/B ve A/C polimer karışımı çiftleri uyumlu (miscible) yada kısmen uyumlu (partially miscible) hale getirilebilir. Bu durumda A polimeri uyumluluğu sağlayan polimer (compatibilizer) görevini görür. Üçlü poli(n-propil metakrilat) / poli(n-amil metakrilat) / poli(vinil klorür) karışım sistemi bu gruba örnek olarak verilebilir. Bu karışım sisteminde poli(n-propil metakrilat) ve poli(n-amil metakrilat) polimerleri birbirleriyle karışmayan iki polimerdir. Bu iki polimer arasında uyumluluğu sağlamak için katılan poli(vinil klorür), kompatibilizer etkisi yaparak üçlü polimerin karışabilirliğini sağlar.

Poli(vinil klorür) (PVC), vinil polimerleri olarak bilinen plastiklerin en önemli türüdür. Büyük şehirlerin alt-yapı materyali ve bina inşaat malzemesi olarak, ayrıca su borularında ve elektrik kablolarında yalıtkan olarak geniş ölçüde kullanılmaktadır. PVC ısı ve ışık etkilerine duyarlı bir polimerdir. Son ürüne dönüşmesini sağlamak ve özelliklerini geliştirmek için bazı katkı maddelerinin (plastifiyanlar) eklenmesi gerekmektedir. Plastifiyanlar PVC' yi yumuşatır ve esneklik kazandırır. Böylece kullanım alanları genişler.

Son yıllarda ticari polimerlerin özelliklerinin değiştirilmesinde silikon polimerleri başarı ile kullanılmaktadır. Silikon polimerleri, örneğin poli(dimetil siloksan) (PDMS), diğer pek çok polimerden farklı özelliklere sahiptir. Oksitlenmeye karşı dirençli, termal ve UV kararlılığı olan özellikler gösterir. Hidrofob olan bu polimerlerin gaz geçirgenlikleri yüksektir. Ayrıca, silikon polimerleri düşük camsı geçiş sıcaklığı (-125°C), düşük yüzey enerjisi ve yüksek zincir esnekliğine sahiptir. Düşük yüzey enerjisi ve düşük çözünürlük parametresi sebebiyle PDMS tek başına başka bir polimerle tam olarak karışmaz. Silikonların diğer polimerlerle uyumluluğunu sağlamak için en etkin yöntem, karbon bazlı kopolimerleri bu amaçla kullanmaktır. Üçlü polikaprolakton-poli(dimetil siloksan)-polikaprolakton (PCL-PDMS-PCL) kopolimeri bu amaç için uygun polimerlerden biridir. Bu üçlü kopolimer ticari olarak "Tegomer" diye adlandırılmaktadır. Polikaprolakton'un (PCL) her oranda PVC ile karıştığı daha önceki çalışmalardan bilinmektedir.

Bu çalışmada, PVC' nin ikili ve üçlü karışımları çözücü uçurma (solvent casting) tekniği ile hazırlandı. İkili poli(vinil klorür)/Tegomer (PVC/Tegomer), ikili poli(vinil klorür)/poli(2-etilhekzil akrilat) (PVC/PEHA) ve üçlü poli(vinil klorür)/poli(2-etilhekzil akrilat)/Tegomer (PVC/PEHA/Tegomer) karışım sistemleri üzerinde çalışıldı. Az miktarda (ağırlıkça % 1 - 10) sisteme katılan Tegomer ' in (PCL-PDMS-PCL), PVC homopolimeri ve ikili PVC/PEHA karışımları üzerindeki etkileri çeşitli karakterizasyon yöntemleri kullanılarak incelendi.

Infrared spektroskopisi (FTIR), diferansiyel taramalı kalorimetre (DSC), dinamik mekanik termal analiz (DMTA), gerilme-uzama testleri, taramalı elektron mikroskobu (SEM), viskozimetre, değme açısı ve gaz geçirgenliği ölçüm aletleri kullanılarak polimer karışımlarının uyumluluk (karışabilirlik), ısıl, mekanik, morfolojik, viskozimetrik, yüzey ve gaz geçirgenlik özellikleri incelendi.

FTIR, DSC, DMTA ve viskozite ölçümleri ikili PVC/Tegomer karışım sisteminin uyumlu olduklarını gösterdi. FTIR spektroskopi analizi, bu iki polimer arasında özgül bir etkileşim olduğunu doğrulamaktadır. Tegomer 'deki PCL 'nin karbonil grubu (-C=O-) ile PVC 'nin α-hidrojeni, hidrojen bağı yaparak özgül etkileşime sebep olmaktadır. Böylece, karbonil bandı yüksek frekanslara kaymaktadır.

Karışımların camsı geçiş sıcaklıkları, o sistemin uyumlu olup olmadığı hakkında bilgi verir. Uyumlu polimerik karışımlar tek T_g gösterirken, uyumlu olmayan karışımlar iki T_g gösterirler. DSC ve DMTA ölçümleri ikili PVC/Tegomer karışım sisteminin tek camsı geçiş sıcaklığı göstermesi sebebiyle bu sistemin uyumlu olduğunu kanıtlamaktadır. PVC homopolimerinin camsı geçiş sıcaklığı 79°C iken, PVC/Tegomer (90/10) karışımının camsı geçiş sıcaklık değeri 35°C' ye düşmektedir. Karışımdaki Tegomer oranının artması ile camsı geçiş sıcaklığındaki bu ani düşüş, Tegomer' in PVC polimeri üzerinde plastifiyan bir etki yaptığını göstermektedir.

İkili PVC/Tegomer karışımının özgül viskoziteleri 25°C de, THF içinde ölçüldü ve etkileşim parametre (Δb) değerleri hesaplandı. Etkileşim parametresinin negatif olması halinde sistemin uyumlu olmadığı söylenebilir. Etkileşim parametresinin pozitif değerleri ise, polimerler arasında bir etkileşim olduğunu ve uyumlu sistemler sağlandığını belirtir. PVC/Tegomer karışım sistemi için Δb her oranda pozitif değer taşır. Bu sonuç, sistemin uyumluluğu üzerindeki görüşleri destekler.

İkili PVC/Tegomer karışımlarının mekanik özellikleri gerilme-uzama testleri yapılarak incelendi. Karışımların PVC' ye göre daha esnek (flexible) bir davranış

gösterdiği belirlendi. Düşük Tegomer oranlarında bile gerilme-uzama davranışında oldukça önemli değişiklikler gözlenmiştir. PVC' nin mekanik özelliklerindeki iyileşme PVC' ye katılan Tegomer oranına göre değişmektedir. Karışımdaki Tegomer oranı arttıkça, kopma kuvveti (σ) ve modül (E) değerleri azalırken, kopma uzaması (ε) değeri artar. PVC' nin kopma uzama değeri % 8 iken, PVC/Tegomer (90/10) karışımının kopma uzaması % 472 ' ye çıkmaktadır. Uzamadaki bu artış Tegomer' in PVC için etkin bir plastifiyan olabileceğini göstermektedir. Mekanik özelliklerdeki benzer davranış PVC/PCL karışım sistemi içinde gözlenmiştir. PVC' ye ağırlıkça % 25 PCL eklendiğinde uzama değeri % 148 dir. Oysa, PVC' ye sadece % 10 Tegomer ilavesi ile uzama % 472 'ye ulaşmaktadır. Bu durum PVC/PCL sisteminden farklı olarak silikonun etkisini vurgular. Tegomer , PCL' ye göre PVC için daha etkin bir plastifiyan görevi görür.

Karışımın morfolojik analizi de sistemin uyumlu olup olmadığı konusunda bilgi vermektedir. Elektron mikroskobu (SEM) ölçümlerine göre, homopolimer PVC ile PVC/Tegomer karışımları farklı kırılma yüzeylerine sahiptirler. Karışımlar her oranda homojen bir morfoloji göstermektedir. İki fazlı bir davranış gözlenmemiştir.

PVC' ye az miktarda (%1-%10) eklenen Tegomerin, PVC' nin yüzey özelliklerini değiştirdiği değme açısı ölçümleri ile saptandı.Düşük yüzey enerjisi sebebiyle silikon içeren kopolimerlerin yüzeyde toplandıkları bilinmektedir. PVC' ye az miktarda silikonlu polimer yani Tegomer eklenmesi ile değme açısı değerlerinde PVC' ye göre bir artış gözlenmektedir. Bu davranış çok az miktarda silikonlu kopolimerin PVC' ye eklenmesi ile PVC' nin yüzey özelliklerinin modifiye edilebileceğini göstermektedir.

Son olarak, PVC/Tegomer karışımlarının değişik sıcaklıklarda (5-50°C) ve değişen Tegomer oranlarında gaz geçirgenliği davranışı incelendi. Tegomer' in PVC' ye esnek bir yapı kazandırması ve o nedenle uygun bir plastifiyan olması sebebiyle, bu karışımların pratik uygulamada paketleme malzemesi olarak kullanılabilecekleri düşünüldü. Bu nedenle, gaz geçirgenlik özellikleri araştırıldı. Bu amaçla, hazırlanan polimer karışım filmlerinin 5°C ile 50°C arasında değişen sıcaklıklarda karbondioksit (CO_2), oksijen (O_2) ve azot (N_2) gazı geçirgenlikleri incelendi. Karışımdaki Tegomer oranı ve sıcaklık arttıkça gaz geçirgenliklerinin arttığı gözlendi. Tegomer oranı arttıkça gaz geçirgenlik sabitindeki artış PDMS' in yüksek gaz geçirgenliğine sahip olması ile açıklanabilir. Fakat bu artış, değişik oranlarda hazırlanan polimer karışım filmlerinin paketleme malzemesi olarak kullanılmasına engel teşkil edecek şekilde fazla değildir. Ayrıca geçirgenlik sabiti ile karışımdaki Tegomer oranı arasında çizilen grafiğin doğrusal olması bu sistemin uyumlu olduğunu ispatlayan karakterizasyon yöntemlerinden biridir.

Bazı polimer karışımları ise zayıf özgül etkileşimler sebebiyle uyumlu polimer çiftleri oluşturmazlar. Bu sebeple, uyumluluğu sağlayan üçüncü bir polimerin eklenmesi gerekir. PVC ile polimetakrilat ve poliakrilat karışımlarının uyumluluk davranışı literatürde incelenmiştir. Polimetakrilatlar, PVC ile uyumluluk gösterirken, yüksek zincirli (karbon sayısı fazla) poliakrilatlar PVC ile uyumluluk göstermezler. Bu bilgiler doğrultusunda, PVC ile poli(2-etilhekzil akrilat) (PEHA) polimer karışımının uyumlu olmadığını söylemek mümkündür. Deneysel karakterizasyon yöntemlerinden yararlanarak yapılan ölçmeler bu sistemin uyumlu olmadığını gösterdi. Uyumlu olmayan ikili PVC/PEHA sistemine, uyumluluğu sağlayıcı üçüncü bir polimer olarak karbon bazlı silikon kopolimeri olan Tegomer' i ekleyerek, sistem üzerindeki etkisini benzer karakterizasyon yöntemleri ile inceledik.

FTIR, DSC ve viskozite ölçümleri , ikili PVC/PEHA karışımlarının incelenen bileşimlerde (ağırlıkça % 1 - 10 PEHA) uyumlu olmadıklarını gösterdi. FTIR spektroskopisi ile uyumluluk davranışı incelendiğinde, PVC ile PEHA polimerleri arasında özgül bir etkileşim saptanmamıştır. PEHA homopolimerinin karakteristik karbonil bandı (C=O) 1738 cm^{-1} de gözlenmiştir. Karışımlar da her oranda aynı değeri göstermektedir. Oysaki, bu sisteme Tegomerin eklenmesi (PVC/PEHA/Tegomer karışımları) ile karbonil (-C=O-) bandında kayma gözlenmiştir. Bu kayma, üçlü polimer sisteminde polimerler arası hidrojen bağı etkileşimi olabileceğinin göstergesidir.

İkili PVC/PEHA ve üçlü PVC/PEHA/Tegomer karışımlarının camsı geçiş sıcaklıklarındaki değişim DSC tekniği kullanılarak incelendi. PVC homopolimerinin camsı geçiş sıcaklığı 79°C de, PEHA homopolimerinin ise -30°C de gözlendi. PVC/PEHA karışımları her oranda aynı T_g değerine sahiptir. İkili sistemin uyumlu olmadığı bilinmesine rağmen, 67°C civarında tek T_g gözlenmektedir. Oysa, uyumlu olmayan karışım sistemlerinin iki T_g göstermesi beklenirdi. Tek T_g gözlememiz, PEHA' nın PVC' ye çok az miktarda (% 1 - 10) katılmış olması ile açıklanabilir.

İkili PVC/PEHA karışımlarına (oranlar: 99/1, 95/5, 90/10) ağırlıkça %1-%10 arasında değişen miktarlarda Tegomer ilave edildiğinde tek T_g gözlenir. Ancak, Tegomer oranı arttırılırsa, gözlenen T_g değerleri de daha düşük sıcaklıklara kayar. Üçlü karışımların T_g değerleri, Fox eşitliği kullanılarak hesaplandı. PVC/PEHA oranı 99/1 olan karışımda, deneysel olarak bulunan T_g değerleri hesaplanandan bir miktar daha düşüktür. Üçlü karışımdaki T_g değerleri, sisteme az miktarda katılan bileşen göz önüne alınmadan hesaplandı. 99/1 PVC/PEHA sistemine %1 ile %8 arasında değişen oranlarda Tegomer ilave edildi ve PEHA' nın (az olan komponent) T_g değeri dikkate alınmadan teorik değerler hesaplandı. PEHA' nın az miktarda katılması sebebiyle karışımların T_g değerlerinde fazla bir etki gözlenmedi. Bununla birlikte deneysel olarak üçlü karışımlar için bulunan T_g değerleri hesaplanan teorik değerlerden daha düşüktür.Üçlü karışımların deneysel T_g değerleri ile ikili PVC/Tegomer karışımlarının değerleri daha önce karşılaştırıldığında da benzer davranış gözlendi. PVC/PEHA/Tegomer karışım sisteminin T_g değerleri, PVC/Tegomer sistemi için elde edilen T_g değerlerinden daha düşüktür. Örneğin, ikili PVC/Tegomer (92/8) karışımı için T_g, 50°C iken, üçlü PVC/PEHA/Tegomer (91.08 / 0.92 / 89) karışımı için 40°C gözlenmiştir. Üçlü karışımda PEHA miktarı çok az (< %1) olmasına rağmen T_g' de etkin bir düşüş gözlenmektedir. PEHA' nın sistemin T_g' si üzerindeki bu etkisi düşük PEHA konsantrasyonları için geçerlidir. PEHA konsantrasyonu % 5 den fazla iken bu davranış gözlenmemektedir.

Sadece DSC karakterizasyonu yöntemini kullanarak yukarıda belirtilen üçlü karışım sisteminin uyumlu olup olmadığını anlamak mümkün değildir. Bu sistem için viskozite ölçümleri yaparak uyumluluk davranışı üzerindeki görüşler desteklendi. İkili PEHA/PVC ve üçlü PVC/PEHA/Tegomer karışımlarının özgül viskoziteleri 25°C' de THF çözeltilerinde ölçüldü. İkili karışım için etkileşim parametresi değerleri her kompozisyonda negatif, üçlü karışım için ise pozitif bulunmuştur. Etkileşim parametre değeri karışımdaki Tegomer oranına bağlı olarak değişmektedir. Bu sonuçlar, Tegomerin, uyuşmayan PVC/PEHA sistemini uyuşabilir hale getirdiği görüşünü destekler.

İkili PVC/PEHA ve üçlü PVC/PEHA/Tegomer karışımlarının mekanik özellikleri incelenerek, Tegomerin karışmayan ikili PVC/PEHA sistemine etkisi gözlendi.

PVC/PEHA karışım sisteminde moleküler düzeyde bir etkileşim olmamasına karşın, bu sistem PVC homopolimerine göre daha esnek bir davranış göstermektedir. PEHA konsantrasyonunun artması ile kopma kuvveti azalırken, kopma uzaması oldukça artmaktadır. İkili PVC/PEHA (99/1 ve 95/5) karışımlarına Tegomerin eklenmesiyle uzamada artış gözlenir. Kopma kuvveti (σ) ve modül (E) değerleri üçlü sistem için ikili sisteme göre daha düşüktür. Ancak, düşük Tegomer konsantrasyonlarında bile, karışımların gerilme-uzama davranışları dramatik bir değişim göstermektedir.

Elektron mikroskobu ile yapılan incelemeler, PVC/PEHA karışımlarının kırılma davranışlarının PVC' ye göre oldukça farklı olduğunu gösterir. PVC/PEHA karışımının kırılma yüzeyinde boşluklar (voids) gözlendi. Bu boşluklar, sisteme Tegomerin ilave edilmesi ile kaybolmuş ve tek fazlı bir yapıya dönüşmüştür.

Sonuç olarak, bu tezde yapılan deneylerle, silikon-kaprolakton kopolimerinin (Tegomer), geniş bir uygulama alanı olduğu için önemli bir endüstriyel materyal olarak bilinen PVC ile uyumlu olduğunu ve uygun bir plastifiyan olarak kullanılabileceğini gösterdik. Ayrıca, karışmayan ikili PVC/PEHA sistemine katılan bu kopolimerin az miktarlarda (%1-%10) ikili sistemi uyuşabilir hale getirdiğini ve mekanik özelliklerinde önemli gelişmeler sağladığını saptadık..

CHAPTER 1

INTRODUCTION

A polymer blend can be defined as a combination of two or more polymers resulting from common processing steps, e.g. mixing of two polymers in the molten state, casting from common solvent etc.[1,2].

In recent years the blending of polymers has gained significant interest, because of their growing industrial use. The advantage of blending polymers is that properties of commercially available polymers may be modified by using an inexpensive route. Blending is the least expensive and the most versatile way of achieving materials with new desirable properties. However, the manifestation of superior properties depends upon miscibility of the homopolymers at the molecular level[3-6].

Many experimental and theoretical methods have been used to investigate polymer miscibility[4]. Heat of mixing, infrared spectroscopy, glass transition temperature measurements, morphology by optical and electron microscopy, viscometry, light scattering, nuclear magnetic resonance spectroscopy, neutron scattering, fluorescence spectroscopy, and dynamic mechanical response are some of the methods extensively reported in the literature[3,4,7].

It is known that miscible binary blends most often result from favorable, exothermic interactions between the blend components. More precisely, miscibility arises from the "complementary dissimilarity" between two polymer structures and is related to the presence of specific interactions between them[3,4,8-12].

As most polymer pairs are immiscible, they form multiphase systems with weak physical and chemical interactions across the phase boundaries. As a consequence, the rheology of the material will be strongly dependent on both the morphology and the interactions between the phases. Immiscible blends therefore

often exhibit poor mechanical properties. In some cases, addition of small amounts of compatibilizers, e.g., block or graft copolymers which interact favorably with both major constituents, may relieve this problem[13-19].

Ternary blends are gaining an important share in the field of polymer property diversification through blending. From the practical viewpoint these systems offer the possibility of extending the list of miscible or mechanically compatible blends frequently utilizing scrap or recycled plastic material. Theoretically their study offers the possibility to explore the important principles governing the compatibilization of immiscible or nearly miscible blends[13-36].

Most studies of ternary A/B/C systems reported in the literature[21-36], deal with the addition of a miscible polymer A to an immiscible B/C pair, the A/B and A/C pairs being miscible or at least partially miscible. For example, PVC was used to solubilize totally immiscible system of poly(n-propyl methacrylate) and poly(n-amyl methacrylate)[22].

Poly(vinyl chloride) (PVC) is one of the most important thermoplastics. Several polymers are currently mixed with PVC to alter its properties, such as high impact behaviour, heat resistance temperature and processability. The miscibility behaviour of PVC blended with these polymers have been investigated[37-99]. The methacrylate and acrylate polymers with PVC are reported that polymethacrylates up to poly(n-hexyl methacrylate), and poly(n-propyl acrylate) and poly(n-butyl acrylate) are compatible with PVC[26,39-43]. Higher chain acrylates are incompatible. In comparison, the polyacrylates seem to be less miscible with chlorinated polymers than are the corresponding polymethacrylates [40,41]. Several polyesters are reported to form miscible blends with chlorinated polymers[1-5,8,51-75]. Among the most important and intensively studied in this group are the blends of polycaprolactone(PCL) and PVC [8,51-62]. The use of PCL-b-PDMS copolymers as surface modifying additives in polymer blends were investigated[100].

The modification of conventional polymers through the addition of small amounts of siloxane polymers have received increasing attention in the last decade. While its surface properties render poly(dimethylsiloxane) (PDMS) very attractive for modification of other surfaces and interfaces, its low solubility parameters cause it

to be highly immiscible with most other materials. Whereas it possesses exceptional properties, such as good oxidative, thermal and ultraviolet stability, hydrophobicity, biocompatibility and low glass transition temperature (T_g, -123°C), low surface energy and high chain flexibility. An effective way to increase the compatibility of PDMS in blends is to form copolymers of siloxanes with carbon based polymers. Triblock polycaprolactone-poly(dimethylsiloxane)-polycaprolactone (PCL-PDMS-PCL) copolymer, Tegomer is a good example to combine the compatibilizing effect of PCL and the surface modifying and toughening characteristics of PDMS[100-106].

In this work, we have examined the miscibility of PVC blends containing small amounts (1-10%) Tegomer[101]. Then the effect of the PCL-PDMS-PCL triblock copolymer on the properties of immiscible binary PVC/poly(2-ethylhexyl acrylate) blends was studied[106].

Miscibility, thermal, mechanical, morphological, viscosity, surface properties, gas permeation and density measurements of PVC blends were investigated by using several techniques; Fourier Transform Infrared spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Stress-Strain measurements, Scanning Electron Microscopy (SEM), Viscosity experiments, Contact Angle measurements, Gas Permeability and Density measurements.

CHAPTER 2

POLYMER / POLYMER MISCIBILITY

2.1 TERMINOLOGY

Polymer blends are mixtures of at least two macromolecular species, polymers and/or copolymers. For practical reasons the name blend is given to a system only when the minor component content exceeds 2 wt %. Depending on the sign of the free energy of mixing, blends are either miscible or immiscible[1,p 21].

Miscible polymer blend is a polymer blend homogeneous down to the molecular level, associated with the negative of the free energy of mixing ($\Delta G_m \approx \Delta H_m \leq 0$). Immiscible polymer blend is any polymer blend whose $\Delta G_m \approx \Delta H_m > 0$[1, p 2].

Before proceeding, clarification of the use of the term "miscibility" to describe single phase, polymer-polymer blends is necessary. Prior studies and reviews have generally used the term compatible to describe single phase behavior[3,p 2]. However, compatible polymer blend is a utilitarian term indicating a commercially attractive polymer mixture, normally homogenous to the eye, frequently with enhanced physical properties over the constituent polymers. Polymer alloy is an immiscible polymer blend having a modified interface and/or morphology. Most blends are immiscible, and need to be compatibilized. The compatibilization is a process of modification interfacial properties of an immiscible polymer blend, leading to the creation of a polymer alloy[1,p 21].

2.2 THE METHODS OF BLENDING

Preparation of polymer blends can be accomplished by:

(i) mechanical mixing: For economic reasons mechanical blending predominates. It is important that the size of the dispersed phase is optimized considering the final performance of the blend. In order to avoid streaking and delamination peeling during injection molding the size of the dispersed phase is normally reduced to a sub-micron[1,p 16].

(ii) dissolution in co-solvent then film casting: films of pure polymers and their blends are cast from the solution at room temperature. Evaporation of solvent is done slowly and the resulting films are dried until the films reached constant weight[107].

(iii) Coprecipitated blend: In this method, pure polymers and their blends are dissolved in a solvent and then precipitated using the nonsolvent methanol. The precipitated powder is allowed to dry[107].

(iv) Interpenetrating Networks (IPNs): IPNs can be considered a unique subset of polymer blends for which many variations and methods of preparation can be devised. An IPN is an intimate combination of two polymers both in network form, at least one of which is synthesized or cross-linked in the immediate presence of the other[108]. There are no induced covalent bonds between two polymers[3,109].

2.3 ECONOMY OF BLENDING

There is no doubt that the main reason for blending, compounding and reinforcing is economy. In general the following economy related reasons can be listed[1,p 15]:

1.Extending engineering resin performance by diluting it with a low cost polymer.
2.Developing materials with a full set of desired properties.
3.Forming a high performance blend from synergistically interacting polymers.
4.Adjusting the composition of the blend to customer specifications.

5.Recycling industrial and/or municipal plastics scrap.

2.4 THERMODYNAMICS OF POLYMER SOLUTIONS

A solution can be defined as a homogeneous mixture of two or more substances, i.e. the mixing is on a molecular scale. Under the usual conditions of constant temperature T and pressure P, the thermodynamic requirement for formation of a two component solution is that the Gibbs free energies G_1 and G_2 of the pure components in isolation. This requirement is defined in terms of the Gibbs free energy of mixing

$$\Delta G_m = G_{12} - (G_1 + G_2) \tag{2.1}$$

which must be negative (i.e. $\Delta G_m<0$) for a solution to form. Since Gibbs free energy is related to enthalpy H and entropy S by the standard thermodynamic equation

$$G=H-TS \tag{2.2}$$

a more useful expression for ΔG_m is

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2.3}$$

where ΔH_m is the enthalpy (or heat) of mixing and ΔS_m is the entropy of mixing[110, p 138-140].

2.4.1 Ideal Solutions

Ideal solutions are mixtures of molecules (i) that are identical in size and (ii) for which the energies of like (i.e. 1-1 or 2-2) and unlike (i.e. 1-2) molecular interactions are equal. The latter condition leads to athermal mixing (i.e. $\Delta H_m = 0$), which also means that there are no changes in the rotational, vibrational and translational entropies of the components upon mixing. Thus ΔS_m depends only upon the combinatorial (or configurational) entropy change, ΔS_m, which is positive because the number of distinguishable spatial arrangements of the molecules increases when they are mixed. The combinatorial entropy is given by

$$\Delta S_m = -k (N_1 \ln x_1 + N_2 \ln x_2) \quad (2.4)$$

where x_i is the mole fraction of component i. Ideal solubility precludes volume changes on mixing, and the enthalpy of mixing, ΔH_m, must be zero. This applies to a mixing of two materials that are effectively identical except for a tag on one. Changing the relative size will reduce the number of possible combinations and the entropy will be less than that above.

These ideas are depicted in Figure 2.1, which illustrates the lattice picture with a cell size equal to the volume occupied by these identical molecules. This conception aids in the derivation of Equation 2.4, which is based on the Boltzman law for the entropy of mixing

$$\Delta S_m = k \ln \Omega \quad (2.5)$$

where Ω is the total number of ways of arranging N_1 and N_2 molecules on a regular lattice comprising $N = N_1 + N_2$ cells.

$$\Omega = N! / N_1! N_2! \quad (2.6)$$

Recalling Sterling's approximation

$$\ln N! = N \ln N - N \quad (2.7)$$

and substituting Equation 2.6 into 2.5 gives the result, Equation 2.4. The activity a_i of each component in the ideal solution is equal to its mole fraction; it will obey Raoult's law if the vapors form ideal gases. Because of the relationship,

$$\Delta G = \Delta H - T\Delta S \qquad \Delta H = 0, \text{ ideal} \quad (2.8)$$

The components forming an ideal solution will always be completely miscible[3,p 22].

2.4.2 Regular Solution

"Regular" solutions, in which ΔS has the ideal value but ΔH is finite[111]. The latter can be developed most simply in terms of an exchange energy Δw,

$$\Delta w = w_{12} - (1/2)(w_{11} + w_{22}) \tag{2.9}$$

where w_{ij} is the energy of a contact between components i and j. Because the mixing must be close to random in order to have ideal entropy, the total enthalpy can be closely approximated by

$$\Delta H_m = z\, \Delta w_{12}\, N_1\, x_2 \tag{2.10}$$

where z is the lattice coordination number.

$$\Delta G_m = z\, \Delta w_{12}\, N_1\, x_2 + kT\ (N_1 \ln x_1 + N_2 \ln x_2) \tag{2.11}$$

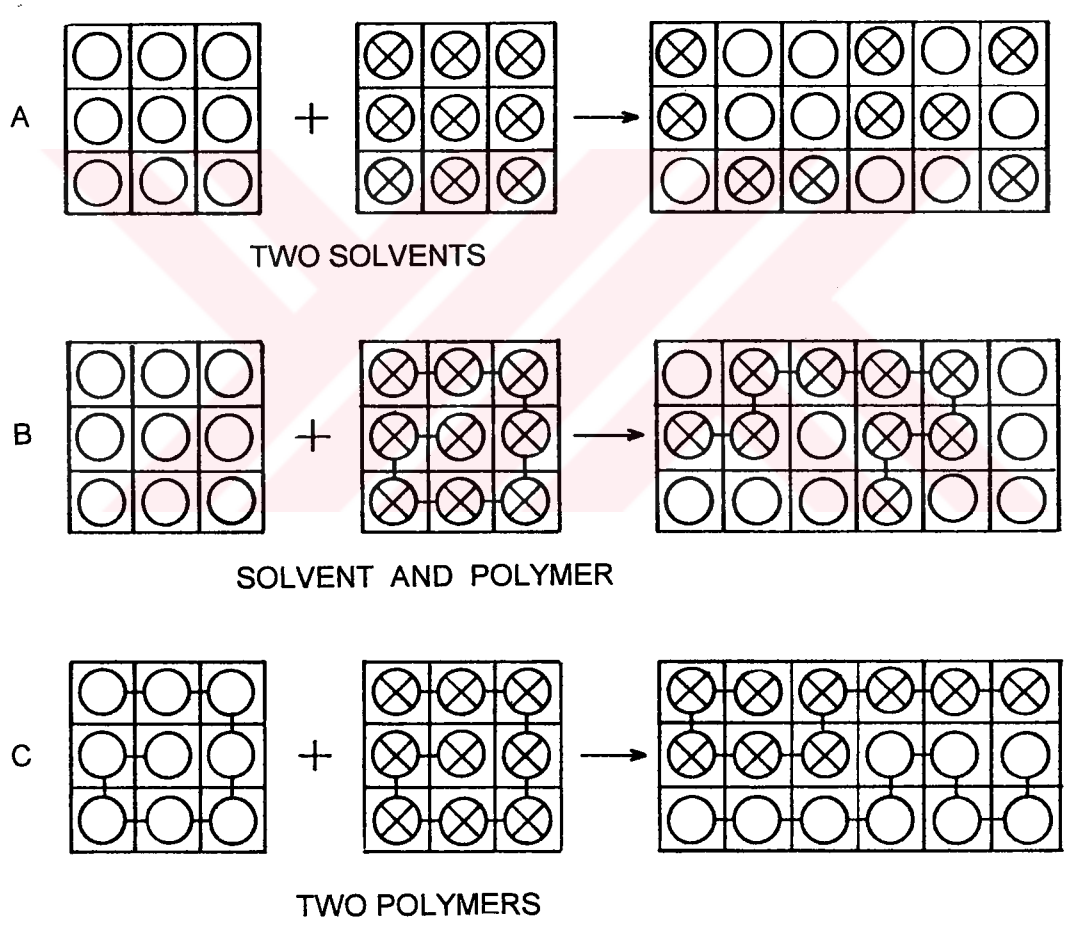


Figure 2.1 Schematic illustration of the numbers of possible arrangements in a small molecule mixture(A), a polymer solution(B), and a polymer mixture(C). The polymer chains each contain nine segments of the size of the solvent molecules.

2.4.3 Polymer-Solvent Systems

Solvent vapor pressure was found to be far lower than predicted by the above free energy relation using mole fractions, even for solutions of polymers in liquids with very similar structures (e.g. polystyrene in ethylbenzene). Such solutions are expected to be nearly athermal; that is, w should be zero and the solvent vapor pressure above the polymer solution should be proportional to the solvent mole fraction multiplied by the pure liquid vapor pressure (Raoult's law). It seemed evident, therefore, that the mole fraction, would have to be replaced by some sort of fraction characteristic of chain molecular systems. Thus arose the concept of a lattice where the sites of the lattice would represent the exchangeable units for the calculation of entropy. Consider a polymer chain consisting of r covalently bonded segments whose size is the same as the solvent molecules, i.e. $r = (V_2/V_1)$ where V_1 is the molar volume of component i. There are a total of $(N_1 + r\ N_2) = N$ lattice sites. The N_2 polymer molecules are added one by one to the lattice before adding the solvent molecules. The picture is schematically shown in Figure 2.1 B. Taking into account that the polymer segment must have at least two adjacent sites occupied by polymer segments yields the famous Flory-Huggins expression for the entropy of mixing of polymer with solvent:

$$\Delta S_m = -k\ (N_1 \ln \phi_1 + N_2 \ln \phi_2) \qquad (2.12)$$

where k is Boltzmann's constant and ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer respectively and are given by

$$\phi_1 = N_1 / (N_1 + r\ N_2) \quad , \quad \phi_2 = r\ N_2 / (N_1 + r\ N_2) \qquad (2.13)$$

Comparison of Equation 2.12 with Equation 2.4 reveals an interesting analogy to the ideal entropy of mixing; mole fractions occuring in the ideal expressions are replaced with volume fractions in the formula for mixing of molecules dissimilar size.

The enthalpy of mixing must also undergo a similar modification because it is the segments of the polymers which are presumed to interact according to the expression of Equation 2.9. The enthalpy is obtained from Equation 2.10 simply by substituting ϕ_2 for x_2

$$\Delta H_m = z\, \Delta w_{12}\, N_1\, \phi_2 \qquad (2.14)$$

where z is the lattice coordination number or number of cells that are first neighbours to a given cell. Since z and Δw have the character of emprical parameters, it is convenient to define a single energy parameter called Flory interaction parameter, χ, given as

$$\chi = z\, \Delta w_{12} / k\, T \qquad (2.15)$$

The interaction parameter is a dimensionless quantity that characterizes the interaction energy per solvent molecule divided by kT. As Equation 2.15 indicates, χ is inversely related to temperature but is independent of concentration.

The expression for the enthalpy of mixing then be written by combining Equations 2.14 and 2.15 as

$$\Delta H_m = k\, T\, \chi\, N_1\, \phi_2 \qquad (2.16)$$

Well known Flory-Huggins expression for the Gibbs free energy of mixing is simply obtained by combining Equations 2.4 and 2.16. That is

$$\Delta G_m = kT\, [N_1 \ln \phi_1 + N_2 \ln \phi_2] + \chi\, N_1 \phi_2 \qquad (2.17)$$

Using the Flory Huggins equation it is possible to account for the equilibrium thermodynamic properties of polymer solutions, particularly phase-separation and fractionation behaviour, melting point depression in crystalline polymers and swelling of networks[3,6,110].

2.4.4 Polymer-Polymer Systems

The conceptual changes on going from a solvent(1)+polymer(2) system to a polymer(1)+polymer(2) system can be either insignificant or immense. The lattice concept cannot be rejected offhand although it will be difficult to use a lattice of "solvent size" without leaving many vacant sites, because both components must retain their chain character. But, as we have seen, lattice parameters do not enter directly and Equation 2.14 can be written in terms of an interacting segment volume V_s which conveniently preserves the interaction energy w given in

Equation 2.9 at around the same value. The enthalpy is then obtained from Equation 2.14 simply by substituting

$(N_1 + r N_2) \phi_1$ for N_1

$$\Delta H_m = V z \Delta w_{12} \phi_1 \phi_2 / V_s \quad , \quad \Delta S_m = -k [N_1 \ln \phi_1 + N_2 \ln \phi_2] \qquad (2.18)$$

Combination to give the free energy on a volume basis yields

$$\Delta G_m / V = kT [(\phi_1 / V_1) \ln \phi_1 + (\phi_2 / V_2) \ln \phi_2] + (z \Delta w_{12} / V_s) \phi_1 \phi_2 \qquad (2.19)$$

2.4.5 Molecular Forces of Attraction

(i) Random Dipole-Induced Dipole: This type of interaction is possible between any two molecules, regardless of structure, because the only requirement is the ground state oscillation of charge in the molecule. The result of such oscillation is a temporary dipole moment, which immediately induces dipoles in all other neighboring molecules. These dipoles then interact[3,p 26].

(ii) Dipole-Induced Dipole: If one component of a solution has a permenant dipole moment, it will induce a dipole in neighboring symmetrical molecules, leading to an interaction[3,p 27].

(iii) Dipole-Dipole: The energy due to the interaction of randomly oriented dipoles is given by the following expression:

$$U = -2\mu_1^2\mu_2^2 / 3kTr_d^6 \qquad (2.20)$$

U is the energy, μ is the dipole moment and r_d is the distance between the molecules. The $1/r_d^6$ dependence emphasizes a significance of the constant volume of mixing approximation in that the geometric mean rule will not hold if the interaction distance changes on mixing. However, positive or negative deviations of large magnitude are possible because of the strong dependence of the interaction energy on the spacing between the segments[3,p 28].

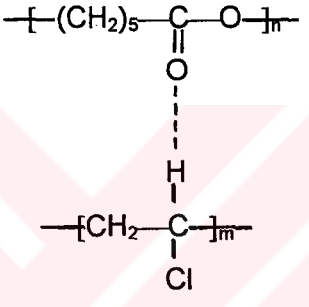
(iv) Ion-Dipole Interactions: This interaction is responsible for the solubility of polyacrylonitrile and polyamides in salt solutions. Ions can also induce a dipole in an isotropic molecule, leading to a weaker interaction[3,p 28].

(v) Hydrogen Bonding: The prerequisites for a hydrogen bond of significant strength are:

(1) a hydrogen atom covalently bound to an electron-withdrawing atom

(2) a structure with donatable electrons as the acceptor must situate at about 180° with respect to the first bond[3].

Specific interactions, particularly hydrogen bonds, are of central importance to a large number of polymer blend systems. As an example, the large number of miscible systems in which PVC is a component can probably be ascribed to the donating character of the Cl-C-H groups shown below in an interacting situation with polycaprolactone[3,112].



(vi) Acid-Base Interactions: The reaction A + B=A^- + B^+ is common among the low molecular weight organic compounds. Adipic acid reacted with hexamethylene diamine to form the salt precursor to Nylon 6,6 is a famous example[3,p 29].

(vii) Charge Transfer: This term is used to describe many types or degrees of electronic delocalization but is generally considered to mean the existence of a two molecule entity with complete removal of one electron from the orbitals of one molecule to those of the other. The interaction is thus electrostatic in nature. Usually color changes accompany in the interaction and the complex exhibits paramagnetism[3,p 30].

2.5 THE SOLUBILITY PARAMETER

The solubility parameter was probably first identified by Hildebrand as being a useful quantity for the characterization of the strength of interactions in simple liquids[3,p 47]. The equation employed is

$$\Delta H_{m\ contact} = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \qquad (2.21)$$

where V_m is the molar volume if the mixture, and δ_1 and δ_2 are the solubility parameters of components 1 and 2 respectively. The solubility parameter, δ, of a liquid is the square root of the energy of vaporization per unit volume and is given by

$$\delta = [(\Delta H_v - RT) / V_i]^{1/2} \qquad (2.22)$$

where ΔH_v is its molar enthalpy of vaporization and V_i is its molar volume. The quantity δ^2 is called the cohesive energy density (CED) since it characterizes the strength of attraction between the molecules in unit volume. For a volatile liquid CED, and hence δ, can be determined experimentally by measuring ΔH_v and V.

Equation 2.21 yields only zero or positive values for ΔH_m and predicts that mixing becomes more favourable (i.e. ΔH_m becomes less positive) as the difference between the solubility parameters of the two components decreases, with ΔH_m=0 when $\delta_1 = \delta_2$. Specific effects such as hydrogen bonding and charge transfer interactions can lead to negative ΔH_m but are not taken into account by Equation 2.21 and so a separate qualitative judgement must be made to predict their effect upon miscibility[110,p 150].

2.6 PHASE SEPARATION BEHAVIOUR OF POLYMER BLENDS

2.6.1 General Principles of Phase Equilibria Calculation

The total energy of the system, U, can be expressed as the difference between the heat content, H, and the compressive energy, PV. (U = H - PV). Note that for closed system where U is constant any change in enthalpy is compensated by an increase of either pressure, P, or volume V:

$$dH = P\,dV + V\,dP \;;\quad U=\text{const.} \tag{2.23}$$

At equilibrium the Gibbs free energy is given by: G = H - TS where S and T are entropy and absolute temperature respectively. The change in G can be written as:

$$dG = V\,dP - S\,dT + \Sigma\,\mu_i\,dn_i \;;\quad \mu_i = (\partial G / \partial n_i)_{P,T,nj} \tag{2.24}$$

where n_i represents the number of moles of the substance i having the chemical potential μ_i. The free energy, enthalpy, entropy and chemical potential of mixing are respectively defined as a difference:

$$\Delta F_m = F - F_0 \;;\quad F \equiv G, H, S, \mu_i \tag{2.25}$$

where F and F_0 represent the mixture and pure state respectively. The conditions of miscibility in a binary system are described in terms of binodal:

$$\Delta\mu_i' = \Delta\mu_i'' \qquad i=1,2 \tag{2.26}$$

(where the superscripts ' and " indicate the two phases), spinodal:

$$D \equiv (\partial^2 \Delta G_m / \partial x_2^{\,2})_{P,T} = 0 \tag{2.27}$$

and the critical point:

$$CST \equiv (\partial^3 \Delta G_m / \partial x_2^{\,3})_{P,T} = D' = 0 \tag{2.28}$$

where x_2 is the mole fraction of component 2. The dependencies (2.26) to (2.28) are illustrated in Figure 2.2; the upper part shows the isothermal and isobaric variation of ΔG_m with x_2 whereas the lower part represents the isobaric phase diagram for binary mixtures with the upper critical solution temperature, UCST. Note that the equilibrium variation of ΔG_m with x_2 follows the solid line, i.e. the line b'b", which corresponds to Equation 2.26. The points of contact define the limiting conditions for miscible system, $x_2<b'$ or $x_2>b''$. The inflection points, s' and s", define the spinodal conditions, i.e. for $s'<x_2<s''$ the system is phase separated. Within the concentration range between the b and s curves the system is metastable[1,p 30].

In polymer blends two other types of phase diagrams, illustrated in Figure 2.3 are also observed; the LCST, is more frequent than UCST[1,p 32].

2.6.2. Phase Separation Phenomena

As shown in Figure 2.2, there are three regions of phase separation of a binary system: miscible, metastable and immiscible. Phase separation occurs in two latter systems although by different mechanisms. In the metastable region between binodal and spinodal some form of activation mechanism must trigger the phase separation. In the immiscible region such a triggering is not needed the phases separate spontaneously[1,p 43].

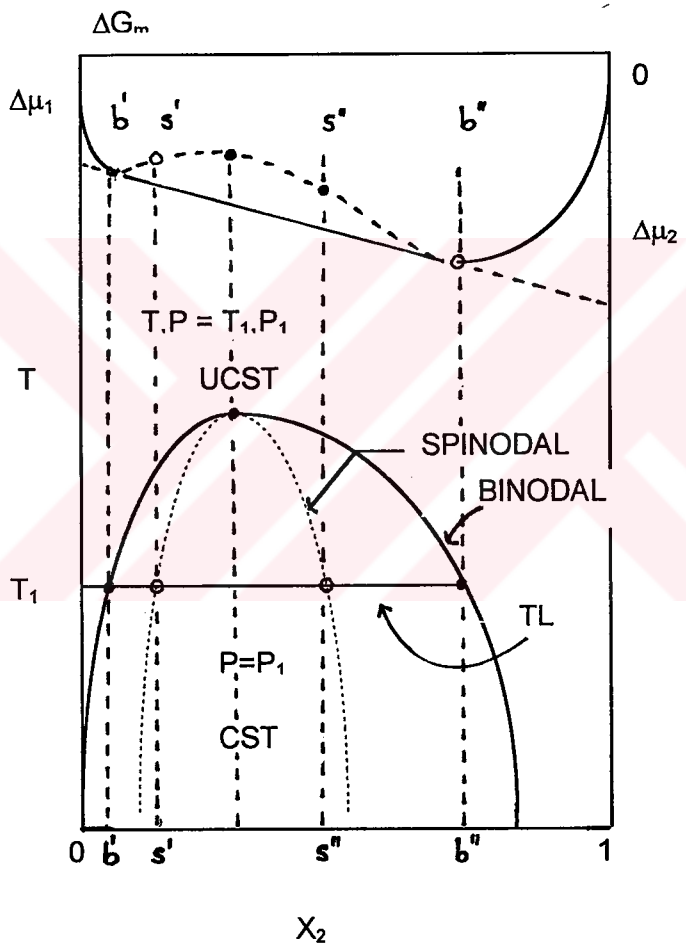


Figure 2.2 Upper part: Gibbs free energy of mixing as a function of concentration in a binary liquid system at constant temperature and pressure, T,P = T_1,P_1. Lower Part: Phase diagram at P = P_1. The points marked b,s and CST represents binodal, spinodal, and critical solubility temperature, respectively.

Because of the different ways by which the energy state of the homogeneous mixture responds to composition changes, the rate processes that accompany phase transformation in the two regions are radically different. Inside the spinodal where the mixture is unstable to infinitesimal fluctuations, there is no thermodynamic barrier to phase growth, and thus, separation should occur by a continous and spontaneous process. Since the mixture is initially uniform in composition, this spontaneous reaction must occur by a diffusional flux against the concentration gradient, that is, by "uphill" diffusion with a negative diffusion coefficient. This process is called spinodal decomposition.

In the metastable region, on the other hand, all small fluctuations tend to decay and hence separation can proceed only by overcoming the barrier with a large fluctuation in composition. This fluctuation is called a nucleus and, once such a nucleus is formed, it grows by a normal diffusion process. This is the nucleation and growth mechanism[3,p 31-34; 4,p 152-154].

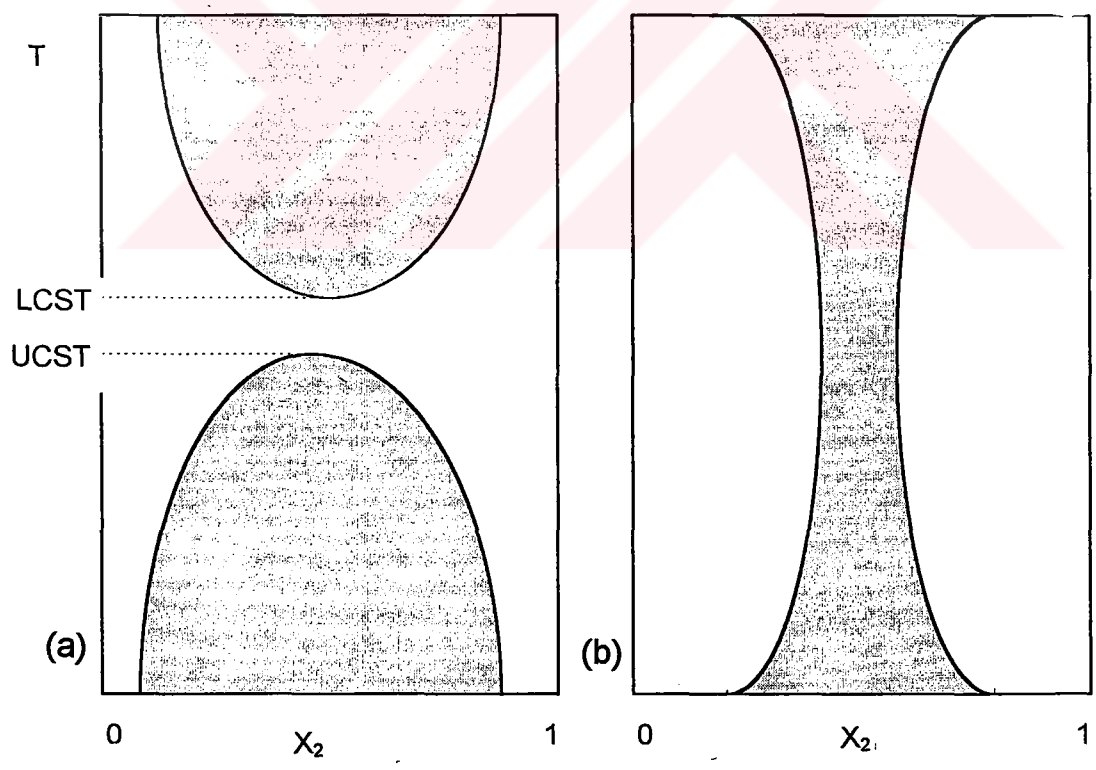


Figure 2.3 Schematic phase diagrams, T vs. x_2, for polymer/polymer systems; shaded areas represent two phases. In figure (a) the lower and upper critical solution temperatures are indicated. Diagram (a) or (b) can be generated by varying either the interaction parameter or molecular weight of the ingredients.

2.6.3 Compatibilization Methods

It is advantageous to produce heterogeneous blends which will be as easy to handle and as stable and reproducible as homopolymers. The way to obtain such systems is by stabilization of the phases, by "compatibilization".The prevailing methods of stabilization , and compatibilization involve addition or generation of an agent which will modify the interfacial properties in polymer systems[1,p 124;113,p 49].

Compatibilization has been achieved by,
(i)Achievement of thermodynamic miscibility, (ii)Addition of block and graft copolymers, (iii)Addition of functional/reactive polymers, (iv)In situ grafting/polymerization (reactive blending)
Achievement of thermodynamic miscibility was reported in Section 2.4.

2.6.3.1 Addition of Block and Graft Copolymers

Block and graft copolymers containing segments chemically identical to the blend components are obvious choices as compatibilisers, given that miscibility between the copolymer segments and the corresponding blend component is assured, provided the copolymer meets certain structural and molecular weight requirements, and that the copolymer locates preferentially at the blend interfaces. The classical view of how such copolymers locate at interfaces is shown in Figure 2.4.

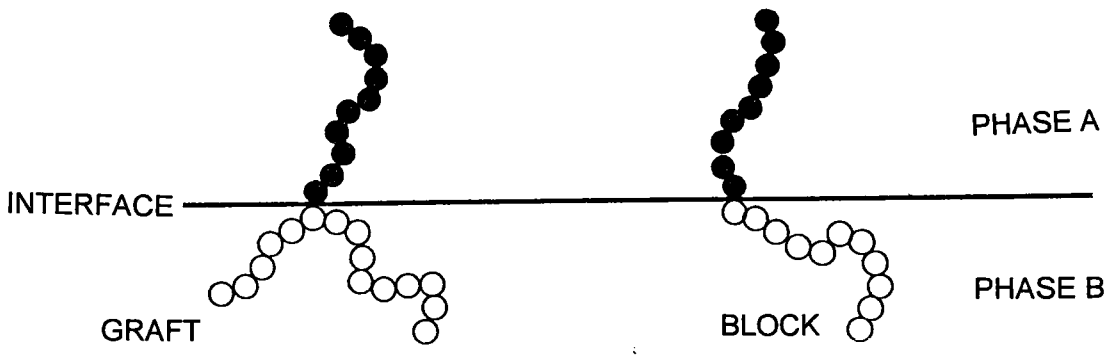


Figure 2.4 Schematic diagram showing location of block and graft copolymers at phase interfaces.

Calculations indicated that (1) block copolymers were more effective than graft copolymers (2) diblock copolymers were more effective than triblock or star-shaped copolymers (3) "tapered" diblock copolymers were more effective than pure diblock copolymers[15,21,113].

Most blends are immiscible, and need to be compatibilized[21]. The effect of compatibilizers on the phase structure of immiscible polymer blends has been investigated for many years[13]. Early investigations focused mainly on immiscible binary blends of A and B homopolymers to which A-B block or graft copolymers were added, which is still of great interest today[114-116].

2.6.3.2 Addition of Functional Polymers

The addition of functional polymers as compatibilizers has been described by many workers. Usually a polymer chemically identical to one of the blend components is modified to contain functional (or reactive) units, which have some affinity for the second blend component, but other types of interaction (e.g. ionic) are possible[113,p 53].

2.6.3.3 Reactive Blending

A comparatively new method of producing compatible thermoplastic blends is via reactive blending, which relies on the in situ formation of copolymers or interacting polymers. This differs from other compatibilisation routes in that the blend components themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibiliser.

The area of reactive blending is one in which there is currently a great deal of development activity, and much proprietary knowledge[113,p 53].

2.7 DETERMINATION OF POLYMER/POLYMER MISCIBILITY

2.7.1 Criteria for Establishing Miscibility

Small-angle neutron scattering in one-component amorphous polymers has established that the polymer chain in bulk state is essentially randomly placed[117,118]. This conclusion supports the vast body of other evidence for random statistics. An example from this evidence is the high dependence of viscosity on molecular weight above a critical molecular weight, implying the presence of highly entangled chains. The appropriate picture for one-component, amorphous polymers is that of A rather than B or C in Figure 2.5.

Polymers dissolved in solvents usually are "expanded" by the interaction of the solvent with the chain segments. Expanded means simply that the average end-to-end distance is increased over that of the bulk. A polymer dissolved in a polymer solvent might be expanded by favorable interactions, in which case a structure represented by Figure 2.5C would result. The situation in Figure 2.5B implies some segregation on a segmental scale, but a random dispersing of molecular centers. Methods with high resolution, such as X-ray scattering, small-angle neutron scattering, nmr relaxation, and electron microscopy, suggest that many miscible systems fall between A and B or A and C; i.e., the components are not as randomly mixed as the molecules in a single-component system[3,p 117].

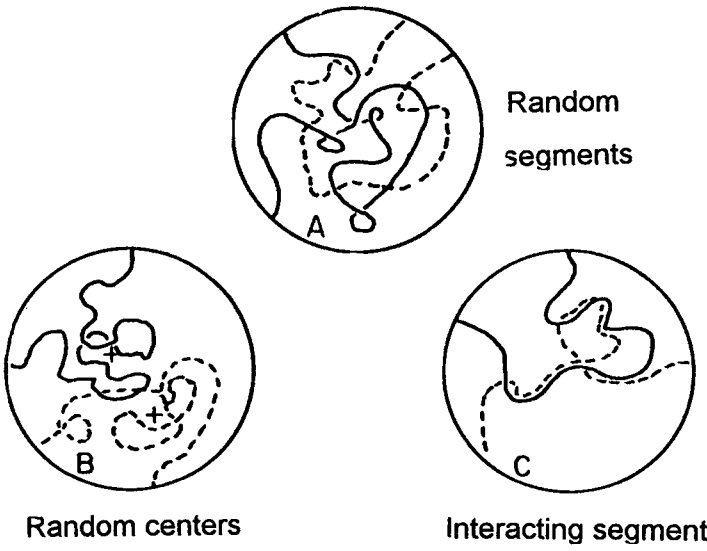


Figure 2.5. Variations in the placement of two different polymer molecules in a miscible system.

As pointed out by Yu[119], the homogeneity of the polymer-polymer solution, because of its high viscosity, will depend a great deal on the methods of preparation and the time and temperature (energy) to which the mixture is subjected. More recent evidence shows that, with reasonable care, thermodynamic equilibrium can be bracketed fairly easily. By taking advantage of spinodal decomposition, a one-phase mixture can be transformed into a two-phase mixture regardless of the diffusional barriers. Returning to the one-phase region involves a longer wait or gentle mixing in the melt. Preparation of mixed polymer systems with the aid of solvents can lead to spurious results[12,121].

Shown schematically in Figure 2.6 is an extreme case, demonstrated by Robard et al.[121], for the system polystyrene-poly vinyl methyl ether-chloroform. Removal of solvent during the preparation of polymer mixtures should be accompanied by annealing at a suitable temperature[122].

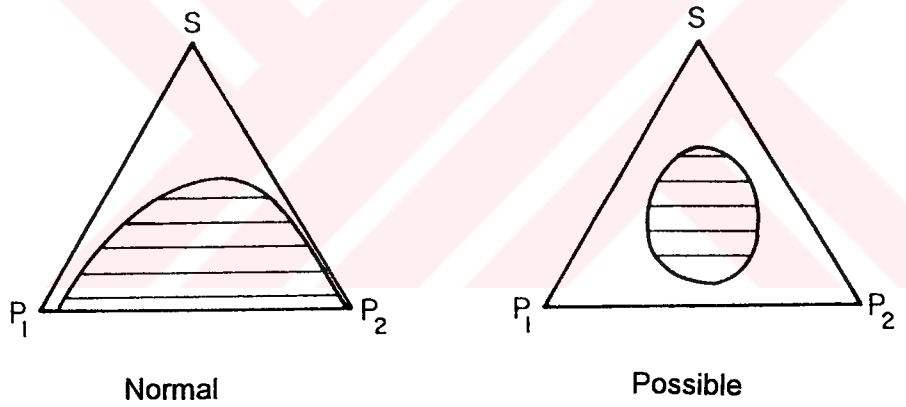


Figure 2.6. Schematic represantation of ternary phase behaviour of a system containing two polymers and a solvent

It must be emphasized that any experiments on polymer mixtures performed at temperatures other than the temperature of equilibration will be subject to unknown effects due to the slow process of reequilibration at the test temperature. For example, the presence of two glass transition temperatures,T_gs,(or two phases by microscopy) for a glassy sample quenched to room temperature from the melt does not mean that the components were immiscible in the melt. Of course, the reverse situation is true as well[3,p 117-119].

2.7.2 Infrared Spectroscopy

Infrared spectroscopy has most often been used in the analysis of polymer mixtures[3,p 188]. Application of infrared spectroscopy in characterization of polymer blends is extensive[112].

Fourier transform interferometer (FTIR) were used to study hydrogen bonding in polymer blends[52-54,123-125]. These interactions not only affected the -OH absorption region (3500 to 3600 cm^{-1}) but also the (-C=O-) stretching (1737 cm^{-1}), the $-CH_2-$ symmetric stretching (2886 cm^{-1}) as well as the finger printing frequency region (1300 to 650 cm^{-1}) and others. The results indicate that macromolecular conformation in hydrogen bonding blends is affected.

In a series of articles Coleman and collaborators discussed the interactions in blends of polyesters with chlorinated polymers[52-54,123]. Shift of the polyesters carbonyl stretching absorption (1700 to 1775 cm^{-1}) was observed in miscible blends and its absence in macroscopically immiscible ones. Hydrogen bonding between C=O and α- or β- hydrogen were proposed as well as a dipolar C=O with C-Cl interactions. There is some indication that mechanisms may vary from system to system within the polyester/chlorinated polymer group.

2.7.3 Glass Transition Temperature

Glass transition is a second-order transition existing between glass and a liquid supercooled below its melting point. The temperature at which the transition occurs is the glass transition temperature, T_g, dependent on: sample preparation, rate of scanning, pressure, frequency, additives (plasticizers as well as fillers), molecular parameters (molecular weight and its distribution, tacticity, branching), crystallinity, etc. It can be determined in nearly any physical test , viz. dilatometric, calorimetric spectroscopic, diffractional, rheological, dielectric or electric[1,p 93].

The most commonly used method for establishing miscibility in polymer-polymer blends or partial phase mixing in such blends through determination of the glass transition (or transitions) in the blend versus those of the unblended costituents[3]. In polymers the glass transition is related to cooperative segmental motion. The use of T_g in determination of polymer/polymer miscibility is based on the premise

that a single T_g indicates that the domain size is below d_d (domain with diameter), where $2 \leq d_d \leq 15$ nm.

There are several equations relating T_g to composition. Couchman (1978) proposed the following:

$$\ln T_g = [\Sigma w_i \Delta c_{pi} \ln T_{gi}] / [\Sigma w_i \Delta c_{pi}] \quad (2.29)$$

where w_i and T_{gi} are respectively weight fraction and glass transition temperature of polymer i in the blend. The symbol Δc_{pi} designates the glass transition increment of the heat capacity of the specimen, originally assumed to be independent of T. Equation 2.29 was derived for intimately miscible blends considering the entropic contribution of pure components and neglecting the enthalpy of mixing. From this relationship several empirical formulas can be recovered.

(i) Gordon-Taylor (1952) equation:

$$\Sigma w_i c_{pi} (T_{gi} - T_g) = 0 \quad (2.30)$$

For two component systems Equation 2.29 is frequently written in the form:

$$w_1(T_{g1} - T_g) + k' w_2(T_{g2} - T_g) = 0 \quad (2.31)$$

where k' (formally equal $\Delta c_{p2} / \Delta c_{p1}$) can be used as an empirical parameter a measure of miscibility.

(ii) Fox equation (1956):

$$\Sigma w_1 (1 - T_g / T_{gi}) = 0 \quad (2.32)$$

(iii) Utracki and Jukes equation (1984):

$$(\ln T_g) / T_g = \Sigma(w_i \ln T_{gi}) / T_{gi} \quad (2.33)$$

The last relation was derived assuming $T_{gi} \Delta c_{pi}$=const.

For costructing the phase diagram the blends were annealed at a temperature of interest, then quenched and either scanned in DSC or examined either in a thermo-mechanical analyzer or a torsion pendulum instrument. All three methods allowed

determination of T_g from which it was concluded whether at the annealing temperature the blend was phase separated or not [1,p 94,98].

A double glass transition obtained for systems in which the energy transfer tests indicate immiscibility, and a single T_g in those where energy transfer shows miscibility.

DSC/DTA is the most popular method of T_g determination, a close second in popularity is a group of dynamic tests: dielectric, shear, bending or tensile.
In most mechanical or dielectric spectrometers the directly measured properties are the storage modulus, F', (or dielectric constant, ε') and "damping factor" or the lost tangent, tan δ=F"/F', where F stands for shear (F≡G), bulk (F≡K), tensile or Young's (F≡E) modulus or dielectric parameter (F≡ε) and indicates storage or in-phase quantity while " indicates loss or out-of-phase quantity. While the damping factor has a direct use for some engineering applications, it only expresses the ratio of lost to stored energy. The loss tangent does not have a direct molecular meaning and it should not be used as a measure of T_g. It is quite obvious that since in the proximity of this transition both parts of the complex moduli, F' and F", change rapidly the location of the peak position of F" is different from that of tan δ.

The dynamic data are collected in two ways: (1) more often as a temperature scan at costant frequency, or (2) as the isothermal frequency scans[1,p 104].

2.7.4 Mechanical Methods

Mechanical methods for determination of the transitional behaviour of polymers and polymer blends have been cited more frequently than the other techniques to be discussed.

Dynamic mechanical testing can be accomplished using various experimental arrangements. Dynamic mechanical testing of materials subjected to a cyclic tensile strain (forced vibration) is a method commonly employed to measure polymeric transitions. The instrument, commonly referred to as a viscoelastometer, operates on the principle that an applied sinusoidal tensile strain to the specimen generates a sinusoidal stress with a phase angle δ. The horizontal specimen is attached at one end to a driver unit providing oscillatory motion while the other end

is connected to a load transducer. Outputs of the stress and strain transducers are converted to provide direct tan δ readings. The absolute value of the complex tensile modulus E* (E*=E'+iE") is given by

$$|E^*| = F.l / \Delta l.A \qquad (2.34)$$

where F=tensile force, A=cross-sectional area, l=length of specimen, and Δl=amplitude of elongation. Then E' and E" can be calculated with the following relationships.

$$E'=E^* \cos \delta \qquad (2.35)$$

$$E''=E' \tan\delta \qquad (2.36)$$

The mechanical damping, tan δ , data parallel the modulus-temperature data in that the slope of the modulus-temperature curve is roughly proportional to the value of tan δ. This is illustrated in Figure 2.7, which shows generalized relationships for heterogeneous, partially miscible, and miscible polymer blends.

For partically miscible blends, two possibilities are represented. A broad transition region can exist, indicating microheterogeneity in that an infinite number of phases of differing compositions exist. However, the distrubition of compositions is such that a dispersion maximum occurs between those of the constituents (case 3). Another possibility (case 2) exists which is expected by consideration of the phase diagram for a polymer blend. Each phase contains a certain concentration of the other component of the blend, although, for heterogeneous blends, this is negligible relative to any property change (i.e., T_g shift) which can be observed. However, in cases of marginal miscibility, the concentration of the minor component in the phase of the major component may have a finite and measurable value, thus shifting the respective transitions in the directions shown in Figure 2.7[3, p.124-125; 282]

Ultimate mechanical properties such as tensile strength, impact strength, abrasion resistance, enviromental stress crack or crazing resistance, and fatigue resistance are mechanical properties covered much less frequently in discussions of miscible polymer-polymer blends[3, p.287].

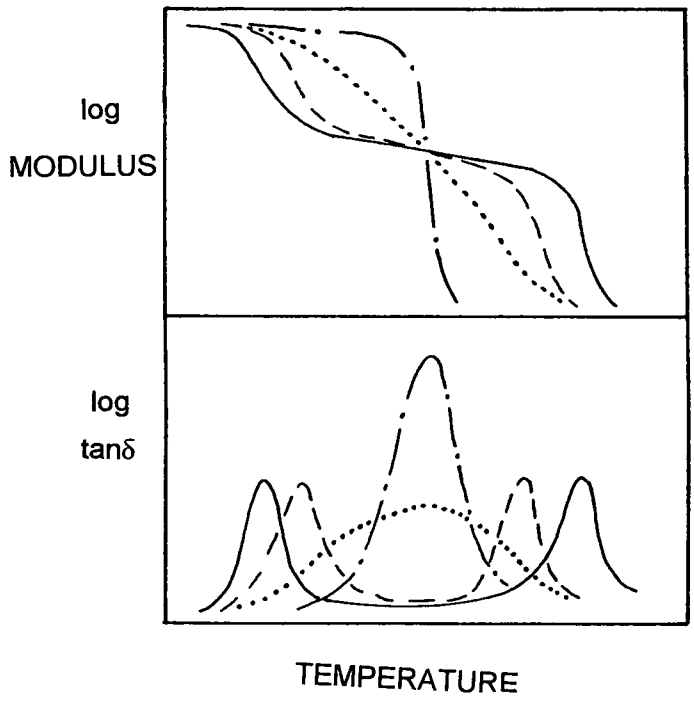


Figure 2.7 Generalized mechanical loss (tan δ) and modulus behaviour for different types of polymer blends.case 1 (dashed-dotted line), miscible; case 2 (dashed line), limited miscibility (partially miscible); case 3 (dotted line), microheterogeneous (partially miscible); case 4 (solid line), heterogeneous.

Probably the most widely used mechanical test is the stress-strain test. Stress-strain measurements made over a wide range of temperatures and speeds of testing are very important for the practical use of polymeric materials. Such measurements are among the few which tell one something about the strength of a material or the conditions under which it will break.

Figure 2.8 illustrates a possible stress-strain curve[126,p 99]. The stress-strain properties of polymers are sensitive to temperature. The modulus, yield strength, and tensile strength generally increase as the temperature decreases, The elongation usually decreases as the temperature is lowered for rigid polymers, but for rubbers the elongation may increase as the temperature decreases[126,p 108].

The addition of plasticizers to a polymeric material has an effect very similar to an increase in temperature. Plasticizers decreases the modulus and tensile strength but increases elongation[110,126,127].

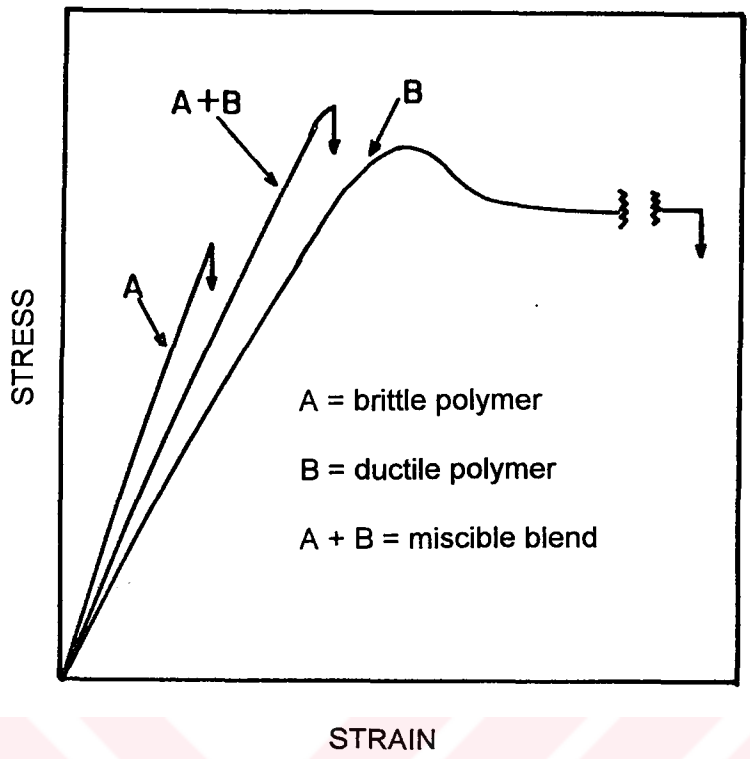


Figure 2.8 Schematic represantation of the stress-strain behaviour of a ductile (semi crystalline) polymer (b) and a brittle (glassy) polymer (a)

2.7.5 Microscopy

In polymer blends the main application of microscopy is not so much to determine miscibility but rather to study their morphology.

The microscopic methods can be divided into three categories: optical or light microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

SEM is the most popular method of observation of polymer blends. The great advantages of this technique are rapidity, range of readily accessible magnifications, depth of field and, almost universal for modern machines, the ability to perform back scattered electron imaging and X-ray elemental analysis of the observed surface.

TEM has been widely used in polymer-polymer studies. Preparation of samples for observation under TEM is more tedious and exacting. The surface morphology can also be observed under TEM by replication methods[1,p 114;3,p 137; 113,p 109].

2.7.6 Ternary Solution Methods

2.7.6.1 Mutual-Solvent Method

Probably the oldest and most used method of determining polymer-polymer miscibility is the mutual-solvent approach. It consists of dissolving and thoroughly mixing a 50/50 mixture of two polymers at low to medium concentration in a mutual solvent. By allowing the mixture to stand, usually for a few days, miscibility is said to prevail if phase separation does not occur; if phase separation does occur the two polymers are said to be immiscible with each other. The method was first used in the field of paints, varnishes, and lacquers [3,p.157,160].

Dobry and Boyer-Kawenoki [114] studied 78 mixtures made up from 14 high polymers dissolved in 13 solvents. About a decade later, Kern and Slocombe [115] undertook a similar study on 27 other mixtures. The six general conclusions reached by Dobry and Boyer-Kawenoki.

(1) Miscibility is the exception, immiscibility is the rule. (2) When two high polymers are incompatible in one solvent, they are generally also incompatible in all other solvents. This rule represents the normal situation, but it is not always fullfilled. (3) The limit of phase separation depends on the nature of the solvent. (4) The molecular weight of the polymers is of great importance. The higher it is, the less miscible are the samples and the more is the limit of phase separation shifted toward smaller (polymer) concentration. (5) Theoretical considerations make it probable that not only the molecular weight but also the shape of the dissolved molecules influences their miscibility. (6) There is no obvious relationship between the miscibility of two polymers and the chemical nature of their monomers. The similarity of the principal chain is not sufficient to insure miscibility of two polymers [3,p.160].

2.7.6.2 Inverse Gas Chromatography Method

In the recent past, gas-liquid chromatography (GLC) has received general recognition as an effective, simple technique for rapid measurement of polymer interactions and solvent activity coefficients in molten homopolymers and their mixtures. It has been used in determining such properties as the glass transition

temperature, crystallinity, adsorption isotherms, heats of adsorption, surface area, interfacial energy, diffusion coefficients[116]. For these studies, its major advantages are (i) the simplicity, speed, and accuracy with which a large number of systems can be investigated, (ii) the wide range of easily controllable temperatures, and (iii) the ability to work at a single solution concentration.

2.7.7 Viscometric Method

A viscometric method has been used by several authors[42,75-77,128,129] to study the interaction of polymers in solution and, hence, to characterize polymer blends for their compatibility. The studies of ternary polymer-polymer-solvent systems are based on the assumption that repulsive interaction may cause shrinkage of the random coils of polymer molecules, which results in the reduction of viscosity below the calculated value, while attractive interaction leads to an increase in viscosity when the system is compatible.

Compatibility investigations by viscosity are carried out in dilute solutions with total concentration of polymers between 0.1 and 2.0 g per 100 ml of solvent. Basically the dilute solution viscometry hinges on the classical Huggins equation[130]. The theoretical consideration starts from the derivation by Krigbaum and Wall[131]. This method, and Krigbaum and Wall treatment are empirical in nature and should be used caution[3,p 177].

2.7.8 Nuclear Magnetic Resonance

Nuclear magnetic resonance (nmr) is a spectroscopic method which is growing importance for studies of interactions in polymer blends[1,p 105]. Proton nmr experiments on polymers are generally confined to studying the spin-spin and spin-lattice relaxation processes as a function of temperature and composition. By convention, the latter is characterized by a relaxation time T_1 while the spin-spin relaxation time is called T_2. As with mechanical measurements, simpler results are expected with one-phase than with two-phase mixtures. But nmr has an advantage over mechanical measurements in that the signal should be independent of the shape of the phases in a two-phase mixture. This allows one to decompose a

multi-time relaxation process and analyze the phases thereby. nmr, as has been mentioned, has a particular advantage in two-phase systems[3,p 184].

2.7.9 Phase Equilibria Methods

For commercially important high molecular weight polymer blends the combinatorial entropy of mixing is negligibly small and the free volume contribution further increases the free energy of mixing. As a result, the miscibility depends either on specific interactions or on intramolecular repulsions. Various types of specific interactions are responsible for miscibility. They all contribute to the negative heat of mixing ($\Delta H_m<0$).

A simple calorimetric scan of low molecular weight analoges has been used to predict the miscibility of polymer blends. To know if the pair is miscible one has to determine the conditions of miscibility, i.e. study the phase equilibria [1,p 64,65].

2.7.9.1 Turbidity Measurements

This is the oldest method of determination of phase relationships. It consists of preparation of a series of mixtures near the phase separation condition then causing the separation to occur. The precipitation is observed by onset of turbidity either visually or in a photoelectric cell. The method has been used to study the phase separation in polymer solutions. The ensemble of the turbidity (or cloud) points defines the cloud-point curves, CPC. For strictly binary mixtures at equilibrium, CPC should follow the binodal equation[1,p 66;3,p 140].

2.7.9.2 Light Scattering Methods

Light scattering is a very simple technique which in principle consists of a good light source (laser) and a sensitive detector. The detector can be fixed at 45 or 90° or be movable through a range of angles. The light entering the sample cell will be scattered on heterogeneities such as large molecules. The transmitted intensity will thus be reduced and the scattered intensity increased. This technique can detect segregation of phases in solutions with temperature changes (e.g. spinodal decomposition, cloud point), but can also be used for detection and even

measurement of phase size and dispersion in thin films. The simplicity of this technique is an attraction but the interpretation of the data is not always straightforward[113,p 123].

2.7.9.3 SAXS and SANS

Small angle X-ray scattering, SAXS, and small angle neutron scattering, SANS, are used with increasing frequency to study polymer blend structure. Since the light, X-ray and neutron scattering depend on differences in refractive indices, electron densities and atomic number respectively, these techniques complement each other. These techniques are therefore rather specialised and are not commonly used for polymer blends. The methods can be used for systems in liquid, glassy or crystalline states to study the molecular weight and molecular sizes of polymer as well as particle or crystalline morphology[113,p 123].

SAXS has been used by Stein and his coworkers to study the morphology of polymer blends in the solid state. The authors concluded that in the interlamellar regions of poly-ε-caprolactone (PCL) blend with polyvinylchloride (PVC) the system is miscible on a molecular scale[53,55].

SANS has been used to determine the phase diagram in polyvinylmethylether/deuterated polystyrene[132]. SANS is one of the most important tools for studying macromolecular sizes, conformation and morphology. The method has been used to study a single or multicomponent system in its molten or solid state[1,p 72].

2.7.9.4 Fluorescence Techniques

Scattering techniques are applicable only at relatively high concentration of the scattering ingredient as well as are not being specific enough regarding the nature of the polymer/polymer interface. Fluorescence techniques show promise in overcoming these disadvantages. The application of these methods to characterize polymer blends has been discussed in several reviews[1,p 78].

2.7.10 Transport Properties

Permeability (P) is a product of solubility of penetrant and its diffusion through the barrier material; reduction of solubility or increase of the diffusion path caused by the lamellar blend structure can decrease permeability[1,p 207]. The permeability constant, P, is related to the solubility constant, S', and the diffusion coefficient, D, by the simple equation

$$P=D.S' \tag{2.37}$$

P can be expressed by mass, moles, or gaseous volume at standard temperature and pressure (STP). These can readily be converted from one unit into another.

The temperature dependence of the permeability coefficient P, the diffusion coefficient D, and the solubility coefficient S' can be represented by

$$P = P_0 \exp (-E_p/RT) \tag{2.38}$$

$$D = D_0 \exp (- E_d/RT) \tag{2.39}$$

The solubility constant can likewise be represented by

$$S' = S_0 \exp (-\Delta H/RT) \tag{2.40}$$

where E_p is the activation energy of permeation, E_d the activation energy of diffusion, and ΔH the heat of mixing. P_0, D_0 and S_0 are the preexponential factors [133,134].

The composition dependence of permeability in two phase systems compared the single-phase systems can be represented by the generalized curves shown in Figure 2.9. The single phase systems follow the behaviour expected of random copolymers.

For phase-separated polymer blends, the phase inversion is not a sharp transition, but rather occurs over a broad volume fraction range.

Only recently has the gas permeability of polymer-polymer miscible blends been experimentally investigated. Gas molecules are basically a probe by which the phase behaviour can be determined by its influence on the transport properties.

Gas permeability and diffusion constitute a rather unique method in that the "probe" is smaller than any conceivable level of phase separation. Shur and Ranby[58,71-74] have used gas permeation data to elucidate the structure of various poly vinyl chloride blends. Good agreement of this technique for characterizing blend phase behaviour was noted by comparison with other accepted techniques[3, p.301-303].

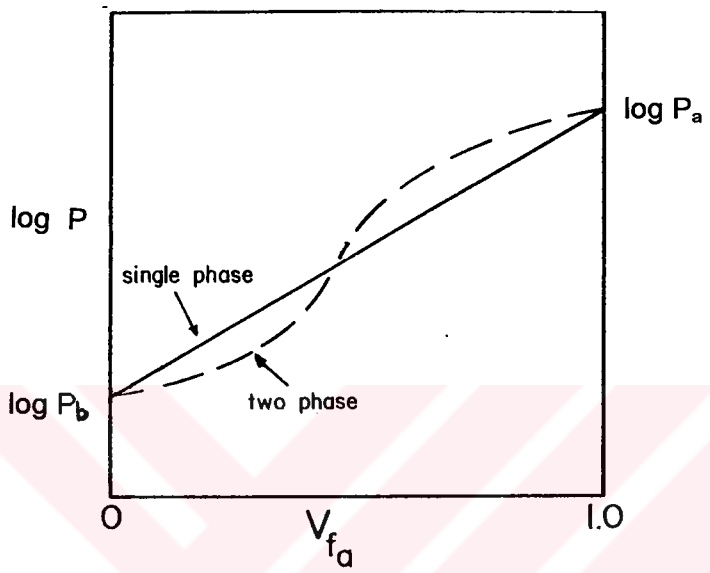


Figure 2.9 Generalized bahaviour for gaseous permeability in polymer blends; miscible versus phase separated

2.7.11 Crystallization Behaviour

In several of the reviews, the potential of achieving miscible polymer blends in which one or both of the components were crystalline was believed to be quite low due to the heat of fusion which would have to be overcome to achieve the necessary thermodynamic criteria for mixing. This generalization appears to be erroneous; the comprehensive survey of known miscible polymer blends listed many systems containing crystallizable components. In these blends, the crystalline component generally retained the ability to crystallize; however, miscibility was judged on the nature of the residual amorphous phase. The crystallization behaviour of these blends is quite important for a review of the properties of miscible polymer blends[3, p.306].

There is a great deal of interest in miscible(compatible) systems that contain at least one crystallizable component (crystalline/compatible blends). This is at least partially due to the fact that roughly one-half to two-thirds of all commercially significant polymers are crystalline or crystallizable. In these systems, the crystalline regions are phase separated from a miscible amorphous matrix. The most widely used technique for determining the magnitude of compatibility-inducing interactions in crystalline/compatible blends is melting point depression[18]. The depression in melting point of a semicrystalline polymer in a mixture is due to a decrease of the chemical potential of the amorphous (and miscible) phase of the sample which is composed of the two polymers. When this occurs, it has been shown that

$$1/T_m - 1/T_m^0 = - R V_i \chi \phi_2^2 / \Delta H_f V_2 \qquad (2.41)$$

where T_m and T_m^0 are the equilibrium melting points of the semicrystalline polymer in the blend and in the pure form, respectively; R is the gas constant; ΔH_f is the enthalpy of fusion of the polymer; V_i is the molar volume of component i; ϕ_2 is the volume fraction of polymer 2; and χ is the thermodynamic interaction parameter. The parameters of major interest in the preceding relationship are χ and ϕ. Notice that for χ's less than zero, polymer/polymer interactions result in an equilibrium melting point depression. Also note that T_m would be expected to a decrease as ϕ increases. Nishi and Wang speculate that for blend systems possessing χ's greater than zero, a melting point elevation should be observed.

Referring to equation (2.41) one can see that if the variation T_m with ϕ is known, and values for ΔH_f and T_m are available, a plot of $1/T_m - 1/T_m^0$ vs. ϕ_2^2 can be constructed that will yield a value of χ from the slope. It therefore appears that a relatively straightforward approach exists for determining the magnitude of interactions between components of crystalline/compatible blends. However, it is important to note that this approach has been developed from equilibrium conditions. Complications can arise if experimentally determined melting points are used in calculating χ[61,126,127,135].

2.7.12 Degradation Behaviour

Miscible polymer systems present the important possibility of permanently introducing substantial concentrations of chemically active substances into a polymer matrix without sacrificing physical or thermomechanical properties. The active substances could include agents designed to protect or encourage degradation, depending on the application. The thermally unstable commodity resin, PVC, has understandably received the most attention in this area. PVC is traditionally protected by very efficient, but low molecular weight, stabilizers, which may leach out under service.

The biodegradability of soluble polymer systems offers possibilities in application areas such as packaging, where fast degradation by the environment is desired[3, p 314-316].

CHAPTER 3

POLYMER ALLOYS AND BLENDS

3.1 HISTORICAL OUTLINE OF THE DEVELOPMENT OF POLYMER BLENDS

The contemporary reader of polymer blend literature may be under the impression that blending is a recent development. When asked to name the first polymer blend an audience usually casts about 70 % of its votes for "Noryl", 25 % for ABS, with the remaining 5 % for various blends.

This lack of historical perspective on the commercial development of polymer alloys and blends, is due to their rapid growth in importance during the 1980's. For example, in 1987, it was estimated that 60 to 70 % of polyolefins and 23 % of other polymers were sold as blends. Furthermore, while during the late 80's the annual growth rate of the plastics industry was 2 to 4 %, that of polymer alloys and blends was 9 to 11 % while the annual growth rate of engineering blends was 13 to 17 %. Clearly, the plastics industry is moving toward more complex systems. The future will bring a further increase of complexity in the form of multicomponent/multifunctional blends, foamed and reinforced polymer alloys and blends with more emphasis on enhanced optimization of material performance through processing[1].

3.2 POLY(VINYL CHLORIDE)

Poly(vinyl chloride), PVC is the oldest thermoplastic and, after polyethylene, still represents the most important of the general purpose plastics. It was first found and characterized more than 120 years ago, but due to its poor thermal stability, making processing difficult, it was not until about 1930 that people began producing commercial PVC products[136,p 97].

The economic and technical success of this material is due to the attractive price and the outstanding material properties. These can be varied across a wide spectrum by adding different additives. PVC is mainly used in products for the building industry, examples being plastics windows, roller blinds, pipes, floor coverings, wall coverings and roofing sheets. In addition, PVC is used in electrical engineering (cable insulations, plugs/connectors, etc.), in the automotive industry (roof lining, underbody protection, tarpaulins for trucks), in the manufacture of gardening equipment (hosepipes), children's toys (balls and other inflatable toys, dolls), records, shoe-soles and in many other products. About 15 % of production are used for packaging. This includes blister packaging, bottles (e.g. for cooking oil, sun-tan products, mineral water, etc.), packaging films and cups. In the medical field PVC products include blood bags, tubing and flow regulators for infusion and transfusion equipment[136-138].

PVC is produced by the polymerization of vinyl chloride. Three processes are available for this purpose: suspension, emulsion and mass polymerization. The resultant products differ in their uses and properties. In the suspension process the vinyl chloride and an initiator are finely dispersed in water by stirring. Product properties can be varied within a wide range. In the emulsion process the vinyl chloride is extremely finely dispersed in water with the aid of an emulsifier. Emulsion PVC is preferred for the manufacture of pastes. The mass process involves the polymerization of pure vinyl chloride and results in a very pure product [136,139].

3.2.1 Processing

Polyvinyl chloride is never processed in its virgin state. In every case a stabilizer has to be added to PVC to protect the plastic from decomposition by heat and light. The most important stabilizers are based on lead compounds. These are predominantly used in the manufacture of cable compounds and construction products. The use of cadmium compounds is restricted to window profiles, other profiles for outdoor use and roofing sheets. Probably cadmium stabilizers will be replaced within the next few years by stabilizers based on zinc and calcium. The low toxicity of selected tin stabilizers and calcium/zinc stabilizers allows them to be

used in the manufacture of food packaging, children's toys and medical devices[136,137].

PVC is processed at low temperatures around 180°C, placing low demands on the temperature stability of the pigments. For this reason cadmium pigments are now no longer used for colouring PVC. It is important that the colourants do not bleed. Apart from organic pigments, nickel and chrome titanium pigments, chrome yellow, molybdenum red, iron oxides and ultramarine blue are used. The most important white pigment is titanium dioxide[136,137].

Nowadays, one third of the PVC is processed with plasticizers to so-called flexible PVC. This includes cable compounds, plasticized films, coatings, floor coverings and other articles. By far the most important compound is dioctyl phthalate, or more exactly di-(2-ethylhexyl) phthalate (DOP). Esters of phosporic acid, of aliphatic dicarboxylic acids (adipic, sebacic, azelaic) and some speciality products are also used[137].

Impact modifiers are frequently added to rigid PVC. These are other plastics, e.g. ABS, which impart a certain toughness to rigid PVC[137,p 99] The polymeric additives used in PVC compositions fall into two broad functional groups: (i)processing aids and (ii)impact modifiers.

(i) Processing aids: The polymers used in this capacity improve the melt-processing characteristics of PVC compositions (rapidity of homogenisation and fusion) and the properties of the melt (melt strength, cohesion and elongation are increased; in many cases the melt modulus is reduced), but they also usually increase the melt viscosity (which is already high in uPVC compositions): some can also have an external lubricant effect (lubricating processing aids). At their usual levels of incorporation (1-6 phr) processing aids do not significantly affect the end-use properties of the composition.

The processing aids in commercial use may be broadly grouped under the following headings:

(a) acrylic polymers (acrylates and methacrylates);

(b) styrene copolymers (with acrylonitrile or certain methacrylates).

Both these general groups contain many proprietary products with varying applicability in different types of composition. Poly-α-methylstyrene and some ABS terpolymers are also used as processing aids[137,p 98].

(ii) Impact modifiers: The main function of these additives is to improve the toughness (resistance to impact at room and low temperatures) of uPVC compositions, in which they are usually incorporated in proportions of 5 to about 15 phr. Some types of impact modifier (e.g. (4), (5), and certain kinds of (7) below) are highly compatible with PVC and may be incorporated in high proportions , to act as plasticizers.

(1) acrylonitrile/butadiene/styreneterpolymer(ABS)
(2) methacrylate/butadiene/styrene terpolymers (MBS)
(3) modified acrylic polymers
(4) ethylene/vinyl acetate copolymers(EVA) and graft copolymers of vinyl chloride and EVA(EVA/VC)
(5) nitrile rubber (butadiene/acrylonitrile copolymers)
(6) polyurethane elastomers
(7) chlorinated polyethylene (various degrees of chlorination)

While the impact modifiers find their main application in uPVC compositions, some may be incorporated in semi-rigid and even flexible compounds, not primarily to contribute to toughness, but to improve melt strength in processing, emboss retention and thermoforming properties of sheet.

In some types of composition very high proportions of a polymeric modifier are included. Thus up to about 100 phr of particular processing aids, or modified ABS or MBS impact-modifier systems, may sometimes be used to improve the heat distortion properties of the material. Some flexible compositions may actually contain more of an ABS polymer than PVC resin, so that the latter may be regarded as a modifier for the former[137,p 99].

3.2.2 A Review Focusing On Commercial PVC Blends

The original idea of gaining extra performance by blending must be created to Thomas Hancock, who by mixing natural rubber with gutta percha obtained a mixture which was easily applied for waterproofing cloth.

Polyvinylchloride has been known in laboratories since 1872 but became commercial only in 1927 after the advantage of plasticization was discovered. However, development of acrylonitrile rubber (NBR), and in 1942 the discovery of its ability to permenantly plasticize PVC spurred rapid penetration of the market. The PVC/NBR blend was the first commercial thermoplastics blend in the modern sense of the world. In the same year, 1942, Dow Chemical Co. introduced Styralloy-22 (a precursor of interpenetrating polymer network materials, IPN), of polystyrene and polybutadiene. Thus the term "alloy" for the first time was used in reference to a polymeric mixture. In 1942 development of mechanical mixtures of NBR with poly(styrene-co-acrylonitrile), SAN, (known as ABS type A) was an important step in starting a flood of polymer alloys and blends. In fact the ABS type blends dominate the blend market; in 1986 they amounted to 74 % of all polymer alloys and blends (PAB) sales in Europe, 77 % in Japan and 69 % in North America. The dynamism of the market is such that annually about 80 new grades of ABS are introduced to the USA market alone[1,p 4-6].

The year 1960 was most important for modern engineering PAB's. During that year an addition of polystyrene (PS), to poly-2,6-dimethyl-1,4-phenyleneether (PPE), was found to allow processing of this new resin. Blends of PPE/PS are miscible. In 1964 Richardson Co. commercialized PPS blended with "crystal" PS. In 1965 General Electric Co. introduced a family of toughened PPE/PS under the name Noryl. Twenty years later the annual sales value of these blends exceeded one billion dollars. After expiry of the original patent several major polymer producers (e.g. BASF, Hüls, Borg-Warner, Asahi, Engineering Plastics Ltd., Mitsubishi) commenced sales of their own blends based on polyphenyleneether or its copolymers with PS and/or PS-copolymers. It must be stressed that the miscibility of PPE with PS opened a whole spectrum of possible modification of properties. It is sufficient for a copolymer to have a styrenic part in order to impart the desired properties to the mixture (e.g. toughening, flame resistance, solvent resistance). However, in spite of PPE/PS miscibility, no single phase blend is on the market.

Blends of ABS have been already mentioned. However due to the broad range of properties and commercial importance the blends of ABS with polyvinylchloride (PVC), marketed since 1969 by Borg Warner under the name of Cycovin, and those with polycarbonate (PC), sold under the name of Cycoloy deserve special mention.

In 1975 Du Pont de Nemours introduced new supertough polyamide (PA), Zytel-ST. The importance of this event extends beyond PA. The observation that addition of a small amount of finely dispersed polyolefin or rubber dramatically changes the fracture behavior of PA led to improvement of impact properties not only this but also other engineering resins: polycarbonate, polyesters, polyoxymethylene, etc.

While in the past blending relied mostly on mechanical incorporation of the ingredients newer technology introduces another degree of sophistication-reactive blending. During the last few years the importance of combined effects of chemistry, physics and engineering on performance of PAB's was particularly noticeable. Reactive blending of engineering polymers with maleated block copolymer provide a direct method of impact modification in 1987.

In 1979 the toughened blends of polycarbonate (PC), with thermoplastic polyesters, TPEs, were introduced by GEC-Europe under the name of Xenoy. Noryl-GTX is a blend of PPE with PA, introduced by General Electric Co. in 1983. By contrast with all other Noryls where PS acted as a PPE-soluble binder between PPE and an immiscible ingredient, here both PPE and PA (usually polyamide-6,6) are antagonistically immiscible[1,p 6-9].

Table 3.1 Commercial PVC Blends

Composition	Blend	Manufacturer	Properties and Uses
PVC blends	Oxyblend	Occidental Chem.	
PVC/AAS	Vifnen VN	Hitachi Chem.	electrical appliances
PVC/ASA	Geloy XP	General Electric	automotive
PVC/ABR	Shuvinite	Reichold Chem.	extrudable
PVC/ABS	Polyman 506	A.Schulman Inc.	housings, appliances
PVC/ABS	Abson	Abtec Chem.Co.	thermoformable sheets
PVC/ABS	Cycovin	Borg-Warner/Ube	flame retardancy
PVC/ABS	Ronfaloy V	DSM	business machines
PVC/ABS	Tufrex VB	Mitsubishi Monsanto	electronic housings
PVC/ABS	Kralastic	Uniroyal/Sumitomo	moldability
PVC/ABS, NBR, MBS or CPE	Benvic	Solvay	impact resistance
PVC/Acrylic	Acrylivin	Gen.Tire&Rubber Co.	thermoformable sheets
PVC/Acrylic	Kydex 100	Rohm&Haas Co.	
PVC/BR/ABS	Nitrilene	Rhein-Chemie	
PVC/BR/AN	Tylac	Standard Brands	
PVC/Elast.	Carloy	Cary Chem.Inc.	
PVC/EPDM	Oxytuf	Occidental Chem.	
PVC/EVA	Pantalast	Pantasote Inc.	building industry
PVC/EVA	Tenneco	Tenneco Polymers	coating, binding
PVC/NBR	Geon	B.F.Goodrich	
PVC/NBR	Denka LCS	Denki Kagaku	
PVC/Nitrile Rubber	Vynite	Alpha Chem.Plast.	coating, binding
PVC/PE	Ethavin	Vichem Corp.	thermoformable sheets
PVC/PMMA	Kydene	Rohm&Haas Co.	sheets
PVC/PMMA	Sunloid KD	Tsusunaka Plast.Ind.	
PVC/PMMA Copolymer	Viniproz	USSR	
PVC/PVAc	Bristrend	Polymer Inc.	linings
PVC/PVF	Koroseal	B.F.Goodrich	
PVC/TPU	Vyhene	Alpha Chem.Plast.	
PVC/TPU/NBR	Duralex	Dexter Plastics	impact resistance
PVC/TPU	Shutane	Reichold Chem.	
PVC/TPU	Uravin	Vichem Corp.	

3.3 COMPREHENSIVE SURVEY OF PVC BLEND SYSTEMS

Poly(vinyl chloride) represents one of the most rigorously investigated components of polymer blends. By virtue of the vast number of blends prepared, it is not surprising that PVC has found to be miscible with a number of structurally different polymers and copolymers. The capability of weak specific interactions is possible with PVC.

The following examples of blends containing PVC homopolymer have been given in the literature[3,p 217].

3.3.1 Blends of PVC with Polyesters

PVC is often present since it has been shown to be miscible with a large number of polymers[3,4], and particularly with a large number of polyesters including poly(caprolactone)PCL[8,51-62],poly(butyleneterephtalate)PBT[63], poly(valerolactone)[64,65], poly(1,4-butylene adipate)[66], and several others[3,4,67-75].

However, all polyesters are not miscible with PVC. Poly(β-propiolactone) and several others[78-80] are not. It has been suggested that the CH_2/COO ratio of the polyester must be equal or larger than 4 in order to have enough chain mobility to allow miscibility[78]. For all miscible polyester/PVC blends, it is now believed that there is a specific interaction between the carbonyl group of the polyester and the α-hydrogens of PVC[52-54,125,140] (hydrogen bonding interaction).

Poly(ε-caprolactone) was initially demonstrated by Koleske and Lundberg[56] to be miscible with PVC over the entire concentration range. In fact, the T_g-composition data were used to determine the T_g of amorphous poly-(ε-caprolactone) (PCL) by extrapolation of the amorphous blend data to 100% PCL. Crystallization kinetics of PCL in PCL-PVC blends were reported by Robeson[59] and were shown to reasonably agree with the kinetics predicted by the spherulitic growth rate equation. A unique method of determining the degree of crystalline content of PCL from data obtained on blends of PCL-PVC was reported. This method involved the determination of the glass transition shift from the amorphous state of the

PCL-PVC blends to the semicrystalline state. The degree of crystallinity of the blend could then be determined by a simple material balance. Olabisi[8] investigated the PCL-PVC blends using solvent probes in the inverse gas chromatography technique. The experimental data allowed for estimation of the interaction parameter for PCL and PVC which predicted miscibility based on its negative value. Detailed studies were reported for this blend, particularly concerned with the crystallization characteristics of PCL from PCL-PVC blends. Khambatta et al.[55] studied in detail the morphology of these blends using small-angle X-ray and light scattering. Hubbell and Cooper[51] investigated the segmental orientation of the components of the PVC-PCL blends using dynamic differential infrared dichroism. They reported that PCL gives miscible blends with PVC in all proportions, and PCL is a very effective plasticizer for PVC. Painter, Coleman and Zarian [11,12,54,80] reported that a hydrogen bonding type of interaction in compatible PCL-PVC blends. Small-angle X-ray scattering was used to characterize the morphologies of PCL-PVC blends by Russell and Stein[55,62]. SAXS results gave insight into the miscibility of the two polymers.

The use of PCL-b-PDMS copolymers as surface modifying additives in polymer blends were also investigated. When these copolymers were blended at low levels (0.25 - 10.0 % by weight) with various commercial resins such as PVC, PMMA, and PET, the resulting systems displayed silicone-like, hydrophobic surface properties, as determined by critical surface tension measurements or water contact angles[100].

Poly(butylene terephthalate) has a melting point (220°C) in excess of the stability limit of PVC ; thus, common melt mixing techniques cannot be employed. However, Robeson[63] observed that N-methyl pyrrolidone used as a mutual solvent at 150°C could be successfully used to prepare PBT-PVC blends. After extensive mixing, coagulation, and proper drying, rapid molding at 220°C followed by quenching yielded transparent blends exhibiting single, sharp glass transition temperatures. Crystallization of PBT occured when blends were raised above the respective T_g's; however, the amorphous phase still exhibited a single T_g higher than the more amorphous quenched samples. The increase in T_g was attributed to an increase in the PVC content of the amorphous phase and restriction of the segmental motion of the amorphous phase due to crystallization of one of the constituents.

Blends of PVC with ethylene/vinyl acetate copolymers (EVA) have been most widely studied[3,67-71]. Miscibility appears optimum at vinyl acetate contents of 65-70%, although values as low as 45% VA have been experimentally observed to have limited miscibility[70]. Miscibility has also been inferred from diffusion data of gas molecules, which can be used as probes to assess the level of molecular mixing[71]. Nuclear magnetic resonance (nmr) data on blends based on a copolymer of 45% VA content indicated partial miscibility with the level very dependent on sample preparation conditions[69]. Marcincin et al.[70] studied EVA (45% VA)-PVC and chlorinated EVA-PVC blends. While definite phase separation was observed with the EVA-PVC blends, chlorination of up to 38% based on EVA weight yielded blends with PVC having single T_g's.

Polyester oligomers in the range of 2000 to 4000 M_n, offering improved permenance in plasticized PVC over the standard low molecular weight plasticizers, are commonly utilized. These structures are lower in molecular weight than the range designated for this survey. Many of these structures may indeed be miscible with PVC at higher molecular weight. These polyester oligomers (OH terminated) have been extended to high molecular weight by reaction with diisocyanates. Typical polyesters cited included butanediol, hexanediol, or ethylene glycol as the dihydroxy reactant and adipic acid, sebacic acid, azelaic acid, or succinic acid as the dicarboxylic acid reactant. Two elastomeric block copolymers that have been reported as permanent plasticizers for PVC are the poly(butylene terephthalate)-poly(tetrahydrofuran) $(AB)_n$ block copolymer[141] and polyester (i.e., PCL) based thermoplastic polyurethanes[81,82].

3.3.2 Blends of PVC with Polyurethanes

Blends of PVC with various types of polyurethanes (PU) have gained considerable technological value. A survey of pertinent literature indicated that a combination of these polymers in bulk or as laminates, offers advantages in terms of increased flexibility, tensile, impact, and fire-retardent properties[82].

Many studies have been done on the compatibility between polylactone-urethanes (PLCU) and polyether-urethanes (PEU)[83,84] with the conclusion of good compatibility between PLCU and PVC, and partial compatibility under a certain circumstance between PEU and PVC[82]. Some studies have been done on the

compatibility between PVC and polyester-urethanes (PESU)[85], The crystallinity of these polyurethanes (PUs) and the compatibility of blends of PUs with PVC were studied by several characterization techniques by Zhu[86]. The results indicated that polybutyleneadipate urethane/PVC (PBAU/PVC) and polyhexyleneadipate urethane/PVC (PHAU/PVC) were compatible systems, but polyethyleneadipate urethane/PVC (PEAU/PVC) was incompatible.

The miscibility of thermoplastic elastomers (TPUs) with PVC was studied by Kim [87]. PVC blends with TPUs, prepared from diisocyanate, hydroxy-terminated poly(butylene adipate) (PBA) as the soft segment, and dimethylolpropionic acid as the chain extender carrying a latent anionic site for neutralization by triethylamine, showed a single T_g. When hydroxy-terminated poly(propylene glycol) was used as the soft segment instead of hydroxy-terminated PBA, PVC/TPU blends showed two separate T_g's of PVC and TPU[87].

3.3.3 Blends of PVC with Polyacrylates and Polymethacrylates

Mixtures of a series of polymethacrylates and polyacrylates with PVC were studied by several authors[39-50]. It has been found that all polymethacrylates up to poly(n-hexyl methacrylate), and poly(n-propyl acrylate) and poly(n-butyl acrylate) are compatible with PVC. Higher chain polyacrylates are incompatible[40,41]. For example, the three following binary systems, PVC/poly(n-propyl methacrylate)(PVC/PPMA), PVC/poly(n-butyl methacrylate)(PVC/PBMA) and PVC/poly(n-amyl methacrylate)(PVC/PAMA), are miscible, since only one T_g is observed at any composition[41]. In contrast, blends involving two methacrylates are expected to be immiscible. Perrin and Prud'homme indicated that ternary PVC/PPMA/PAMA and PVC/PBMA/PAMA blends are miscible by adding PVC[22].

The first study on PVC and PMMA was done by Schurer et al.[49], who concluded that PMMA/PVC is miscible only in blends having PVC contents greater than 60 % w/w. Jager et al.[88], showed that the lower critical solution temperature (LCST) behaviour causes partial phase separation of PMMA/PVC blends above a certain temperature. McKeown[40] stated that PMMA and PVC are miscible in all compositions when methyl ethyl ketone is the casting solvent. Other factors that influence the miscibility, such as tacticity and molecular weight, can be equally as important for this system, as demostrated recently[49]. The PMMA and PVC blend

is a well-known system. This system makes a hydrogen-bonding type of specific interaction [45]. Lee and Lai[42] studied the compatibility of PVC with polymethacrylates by using viscometric method. The results showed that the compatible ranges for PVC-poly(glycidylmethacrylate)[poly(GMA)] and PVC-poly(hydroxyethylmethacrylate) [poly(HEMA)] blend systems are located, respectively, at greater than 76 and 90 % PVC. They also studied mechanical properties of PVC blens and corresponding graft copolymers[43]. The mechanical properties for polymer blends are obviously affected by the compatibility of the polymer pairs. The PVC-poly(GMA) blends have better mechanical properties than the corresponding graft copolymers. The mechanical properties for PVC-poly(HEMA) blends are worse than those for the PVC-g-HEMA graft copolymers.

3.3.4 Blends of PVC with Polyolefins

Chlorinated Polyethylene (CPE) is a commonly used impact modifier of PVC. The morphology of an immiscible polymer blend has a significant effect on the impact behaviour of the material. Based on compounding conditions, Siegmann and Hiltner[89] reported that at concentrations less than 13 wt% CPE PVC was in the continuous phase, while the CPE was in the noncontinuous phase. The CPE particles ranged between 100 and 400 nm in size. Increasing the CPE concentration above 13 wt% reversed the phase distribution. A significant increase in impact properties was also observed for CPE levels above 13 v/wt %. Scanning electron microscopy (SEM) was used to image the surface structure of these blends, and both transmission electron microscopy (TEM) and scanning-transmission electron microscopy (S-TEM) were used to image the morphological boundaries of the blends by Chen and Collier[90].

3.3.5 Blends of PVC With Various Copolymers

PVC and various types of copolymer blends were studied[67-70,91-99]. Mixtures of PVC involving styrene/acrylonitrile copolymers (SAN) have considerable technological importance. For example, SAN is an effective additive for raising the heat distortion temperature of PVC. ABS plastics are blended with PVC, and latex rubbers with grafted SAN shells are used as impact modifiers for PVC[91]. In each of these, the issue of miscibility of PVC with SAN copolymers is an important one. It

is, of course, well-known that PVC is not miscible with polystyrene[92] or with polyacrylonitrile[93]. Shur and Ranby[74] conclude that the SAN phase (containing 27% AN) of an ABS plastic forms a miscible blend with PVC based on the observation of a single composition-dependent glass transition temperature. Deanin and Moshar[94] and Breuer et al.[95] also conclude that the SAN of ABS has "high compatibility" with PVC. On the other hand, Pavan et al.[96] and Congdon et al.[97,p 255] conclude immiscibility based on the observation of two T_gs for similar blends.

Wang and Cooper[98] reported that two PVC-poly(butadiene-co-acrylonitrile) (BAN) blends which exhibit differences in blend compatibility. The BAN31/PVC (BAN containing 31% acrylonitrile) system is considered to be nearly compatible as evidenced by T_g shifts, stress-strain results, orientation characteristics, and TEM micrographs. Similar experiments indicate that the BAN44/PVC system is incompatible, and contains a mixed phase of BAN44-PVC and a pure BAN44 phase.

Clas and Eisenberg[99] studied blends of PVC with Ethyl Acrylate 4-Vinyl Pyridine (PEA-4-VP) copolymers of different 4-VP contents (2-14 mol %). These were found to be partially miscible as evidenced by the presence of a single, though broad, tangent δ peak obtained from torsion pendulum experiments. Hydrogen bonding or dipole-dipole interactions were the most likely in this system.

3.3.6 Ternary Blends of PVC

Most studies of ternary A/B/C systems reported in the literature[21-36] deal with the addition of a miscible polymer A to an immiscible B/C pair, the A/B and A/C pairs being miscible or at least partially miscible. For example, it was reported in section 3.4.3, PVC was used to solubilize totally immiscible system of poly(n-propyl methacrylate) and poly(n-amyl methacrylate)[22].

Wang and Chen[25] reported mixtures of two compatible polymers, PVC and poly(acrylonitrile-co-butadiene) containing 40 percent acrylonitrile, can be compatible with poly(vinylidene chloride-co-vinyl chloride), which is incompatible and partially compatible respectively with these two polymers. Replacing the rubber by poly(acrylonitrile-co-butadiene) containing 30 percent acrylonitrile, shows that

these threepolymers, in which each pair is incompatible or at most partially compatible, also form compatible ternary blends.

Huarng and White[26] investigated that the phase equilibrium of the ternary system PVC/SAN(77/23)/PMMA using various characterization techniques. PVC is immiscible in the SAN copolymer. PVC has miscibility with PMMA. Polymers with acrylonitrile are also often miscible with esters. Miscibility of PMMA and SAN is thus not unexpected. It would appear that PMMA is a good choice of a polymer to add to PVC/SAN blends to induce miscibility[26]. Another paper[142] studied by Huarng is binary and ternary phase equilibrium in the system PCL/PVC(77/23)/SAN. PCL/PVC and PCL/SAN are largely miscible systems but PVC/SAN is immiscible. The ternary system shows considerable miscibility.

Lee and Chen[27] studied a series of tricomponent blends of PVC/CPE/Ethylene propylene diene terpolymer (EPDM). CPE with ethylene segments similar to EPDM and chlorinated sequences similar to PVC, serves as a compatibilizer, as well as a high temperature impact modifier; while EPDM is chosen as the low temperature impact modifier.

A ternary blend consisting of chlorinated polyethylene (CPE), PVC and epoxidized natural rubber (ENR) was investigated to define the miscibility regime by Koklas [20]. In this ternary blend where ENR plays the role of the compatibilizer, it was established that different amounts are required to cause miscibility for different ratios of CPE/PVC; the highest at equal concentrations of the chlorinated components. Depending on the PVC/CPE ratio and the amount of compatibilizer, a wide spectrum of mechanical properties was obtained.

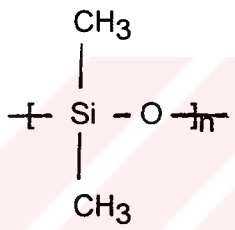
3.4 POLYSILOXANES

In the silicone-containing polymers, silicone atoms contribute the inorganic character and are present either alone in the backbone (silanes) or with atoms of oxygen (siloxanes), carbon (sialkylenes and siarylenes), or nitrogen (silazanes).

Of these, the siloxanes or silicone polymers have been studied the most and are also of the greatest commercial importance[143,p 47-68]. Polysiloxanes can be

prepared by four major types of polymer forming reactions, including: (1) hydrolysis of chlorosilanes; (2) equilibration of lower siloxanes; (3) ring opening polymerization reactions and (4) special condensation polymerization reactions. Of these four major types of reactions, the first and the last are step growth polymerization processes, equilibration is a step growth redistribution process and the ring opening polymerization is a chain growth polymerization reaction. In principle, equilibration reactions are perhaps the most characteristic reactions in the polysiloxane forming processes, because, with the notable exception of certain types of anionic ring opening polymerizations, they occur to some extent in all of the above mentioned process[144].

The most important siloxane polymer is poly(dimethylsiloxane) (PDMS),



PDMS is also one of the most flexible chain molecules known, both in the dynamic sense and in the equilibrium sense[145]. Dynamic flexibility refers to a molecule's ability to change spatial arrangements by rotations around its skeletal bonds. The more flexible a chain in this sense, the more it can be cooled before the chains lose their flexibility and mobility and the polymer becomes glassy. Thus, chains with high dynamic flexibility generally have very low glass transition temperatures (T_gs). Because exposing a polymer to a temperature below its T_g generally causes it to become brittle, low values of T_g can be very advantageous particularly in the case of fluids and elastomers[143].

The T_g of PDMS -125°C, is the lowest recorded for any polymer. One of the most exceptional properties of siloxane polymers is their excellent elasticity at unusually low temperatures. The structural features of polysiloxanes which are responsible for their highly pronounced elasticity are generally as follows: (1) the unusual flexibility of the Si-O-Si bond angles; (2) the large difference in sizes of the alternating silicone and oxygen atoms; (3) the relatively free rotation of the organic

substitutents around the C-Si bond and the shielding of the main chain backbone by these pendant groups; (4) the regularly coiled helical structures of polymer segments at lower temperatures, and (5) the relatively large free volume between neighboring chain segments.

All these factors contribute to the weak secondary van der Waals attractive forces between the neighboring polymer chains, which account for their macroscopic properties including:
(1) the ease with which these polymers undergo viscous flow at low shear stress as reflected by the low values of their activation energies; (2) their Newtonian flow behaviour with constant viscosity-temperature coefficients; (3) their very low glass transition temperatures; (4) their high rates of crystallization on stretching (for symmetrically substituted polymers) even at very low temperatures; and (5) their high solubilities in nonpolar solvents, such as aliphatic and aromatic hydrocarbons[144].

The unusually high thermal and thermo-oxidative stability of the polysiloxanes is another important property of this family of polymers. While most polymers containing carbon-carbon single bond main chain units begin to degrade at temperatures above 250°C, rigorously, purified polysiloxanes are stable under high vacuum or in an inert atmosphere to at least 350-400°C[144].

Siloxane polymers have much higher permeability to gases than most other elastomeric materials. Therefore, these polymers have long been of interest for gas separation membranes, the goal being to vary the basic siloxane structure to improve selectivity without decreasing permeability. Soft contact lenses prepared from PDMS provide a final example[143].

Polysiloxanes are also materials of broad applicability in a variety of industrial areas because of their well-known surface-modifying properties. As a result of their large molar volumes, low cohesive-energy densities, and high chain flexibility, polysiloxanes have exceptionally low surface tension, surface energies, and solubility parameters[103,146,147]. The extremely non-polar nature of the polysiloxane structure together with the low level of intermolecular attractions cause them to be both thermodynamically and mechanically incompatible with virtually all commercial polymers. Their experimental solubility parameters range

from ≈ 14.9 - 15.6 $(J/cm^3)^{1/2}$ whereas most other polymers fall within ≈15.8 - 18.8 $(J/cm^3)^{1/2}$ for polyolefins to ≈26-28 $(J/cm^3)^{1/2}$ for the more polar polyamides[148,149].

The same chemical characteristics render the dimethylsiloxanes insoluble in many solvents normally used for polymerizations[105]. Therefore, PDMS has in practice only little use for surface modification by blending, since it tends to be rejected from the matrix. An additional reason for utilizing PDMS in engineering-material blends is its elastomeric nature and low glass-transition temperature (-125°C). This enables PDMS to be used as a bulk modifier of brittle base polymers in a manner similar to rubber toughening; use of polyorganosiloxanes as toughening modifiers for epoxy resins has recently been studied[150].

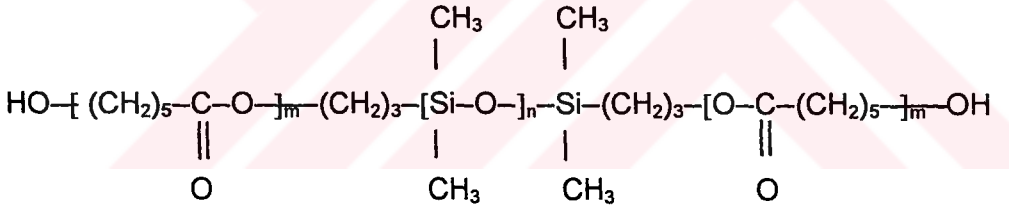
An effective way to increase the compatibility of such blends is to form copolymers of siloxanes with carbon-based polymers[103]. A triblock polycaprolactone-poly(dimethylsiloxane)-polycaprolactone (PCL-PDMS-PCL), Tegomer is a good example for this purpose[101]. The choice of the triblock PDMS copolymer with PCL ends seems very appropriate for optimization of the advantages of each component. The surface-modifying and toughening characteristics of PDMS are combined with the compatibilizing effects of PCL to provide major mechanical and interfacial improvements to a variety of blends with other polymer matrices[100,102,103].

CHAPTER 4

EXPERIMENTAL WORK

4.1 MATERIALS AND CHEMICALS

Polycaprolactone-Poly(dimethylsiloxane)-Polycaprolactone (PCL-PDMS-PCL) triblock copolymer was supplied by Th.Goldschmidt A.G. of Germany, under the name Tegomer (Tegomer H-Si 6440). The molecular weight, (M_n) of Tegomer is 6500±600 $gmol^{-1}$ with PCL end blocks, M_n 2000 $gmol^{-1}$. Tegomer has the following molecular structure:



n/m = 30/18

Poly(vinyl chloride), PVC is a commercial product of Fluka A.G. (M_r ~48000$gmol^{-1}$). K value is 55-57.

2-ethylhexyl acrylate (EHA) ($H_2C=CHCO_2CH_2CH(C_2H_5)(CH_2)_3CH_3$) was a product of Rohm & Haas Co. It was freed from inhibitor by washing 5 %(w/v) NaOH solution and distilled water. It was dried with Na_2SO_4 and freshly distilled under reduced pressure before use.

Azobisisobutyronitrile (AIBN) was a product of Fluka and was recrystallized from ethanol. It was used as initiator in the polymerization of EHA.

Tetrahydrofuran (THF), used as solvent in blend preparation, was a product of Merck A.G.

4.2 EXPERIMENTAL SET-UP AND EQUIPMENT

The experimental set-up and equipment used for this work consisted of teflon-coated aluminium moulds, an analytical balance, a vacuum oven and a vacuum pump, a vacuum distillation apparatus, a desiccator, an electronic digital caliper and other auxiliary equipments such as aluminium dishes, beakers, pyrex tubes, round bottom flasks, pipettes, graduated cylinders. The equipment used for the characterization tests were Gel Permeation Chromatography (GPC), Fourier Transform Infrared (FTIR), Differential Scanning Calorimeter (DSC), Dynamic Mechanical Thermal Analyser (DMTA), Tensilon Tester, Ubbelohde-type viscometer, Contact Angle, Gas Permeability testing appliance, Sartorious type density measurement apparatus and Scanning Electron Microscope (SEM).

4.2.1 Teflon-Coated Aluminium Moulds

Teflon-coated aluminium moulds with interior dimensions 5.2x5.2x1.6 cm^3 and 11.4x11.4x0.27 cm^3 were used. Aluminium moulds were supplied by Fischer Scientific Co.

4.2.2 Analytical Balance

An analytical balance of Mettler, AT 200, was used in the experiments. It featured a bright VFD display to four decimal places. Its weighing capacity was 205 g.

4.2.3 Vacuum Oven and Vacuum Pump

A vacuum oven was used for the drying of the polymer films at room temperature or higher temperatures. It was an EV 018 type of oven from Nüve and operated from ambient to 90°C within +0.1°C. There were a temperature control system on the oven. A vacuum pump (N 026 type vacuum pump from Germany) was connected to the vacuum oven.

4.2.4 Vacuum Distillation Apparatus

Vacuum distillation was used in the purification of monomeric 2-ethylhexyl acrylate.Tthe diagram of vacuum distillation apparatus is shown in Figure 4.1.

4.2.5 Desiccator

A glass desiccator was used to provide low humidity when THF was slowly evaporated under ambient conditions.

4.2.6 Nitrogen, Oxygen and Carbondioxide Gas Supplies

Nitrogen, oxygen and carbondioxide gases were supplied from Boss A.Ş., Gebze.

4.2.7 Electronic Digital Caliper

Electronic Digital Caliper was used to measure the thickness of the polymer films. The device has a measuring range between 0-150 mm with an accuracy of + 0.02mm.

4.2.8 Gel Permeation Chromatography (GPC)

Gel permeation chromatographs were obtained on a Waters Instruments (Waters 510 Pump-Waters 410 Refractometer). Styragel HT6E and HR1 columns were used. Tetrahydrofuran served as eluent at 25°C. The flow rate was 1 ml/min.

4.2.9 Fourier Transform Infrared Spectrophotometer (FTIR)

The infrared spectra of polymers and polymeric blends were obtained using a Nicolet 510 P FTIR spectrophotometer, at room temperature.

4.2.10 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry (DSC) measurements were conducted in a Schimadzu DSC-41 Model apparatus at a heating rate 10°C/min.

A : manostat pressure regulator
B : vacuum pump
C : cold trap
D : sample collector
E : condenser
F : thermometer
G : distillation flask
H : heating mantle
I : heater

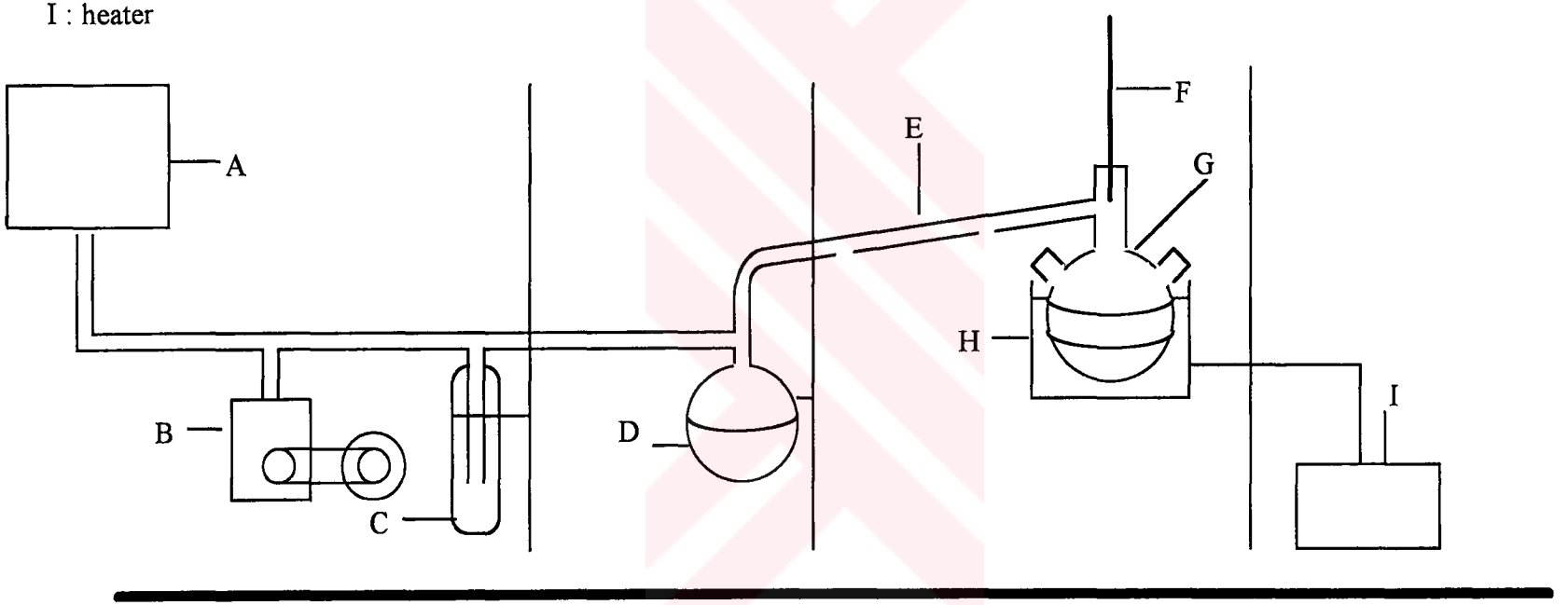


Figure 4.1. Vacuum distillation apparatus

4.2.11 Dynamic Mechanical Thermal Analyser (DMTA)

A polymer Laboratories DMTA was used. measurements were made at a frequency of 1 Hz. The rate of heating was 5°Cmin^{-1}.

4.2.12 Tensilon Tester

The tensile strength and elongation measurements were performed at room temperature with a Tensilon, Toyo Measuring Instruments Co.Ltd. (UTM II) tester using a crosshead speed of 10 mmmin^{-1}.

4.2.13 Scanning Electron Microscopy (SEM)

Micrographs were obtained using a JEOL-JXA 840 A scanning electron microscope.

4.2.14 Viscometry

The instrument was a Cannon 75M 710 Model Ubbelohde type glass viscosimeter which has a time resolution of ± 0.001 s. Figure 4.2 gives a picture of Ubbelohde type viscosimeter. A cylindirical glass bath filled with deionized water was used as constant temperature bath. A Polyscience Model 71 type heater-circulator capable of thermostatic temperature control was immersed into this bath. Temperature of bath was measured by glass mercury thermometer. The viscometric measurements were carried out at constant temperature of 25±0.01°C.

4.2.15 Contact Angle Measurements

Contact angle measurements were conducted on a Kernco Model G-III Goniometer at room temperature.

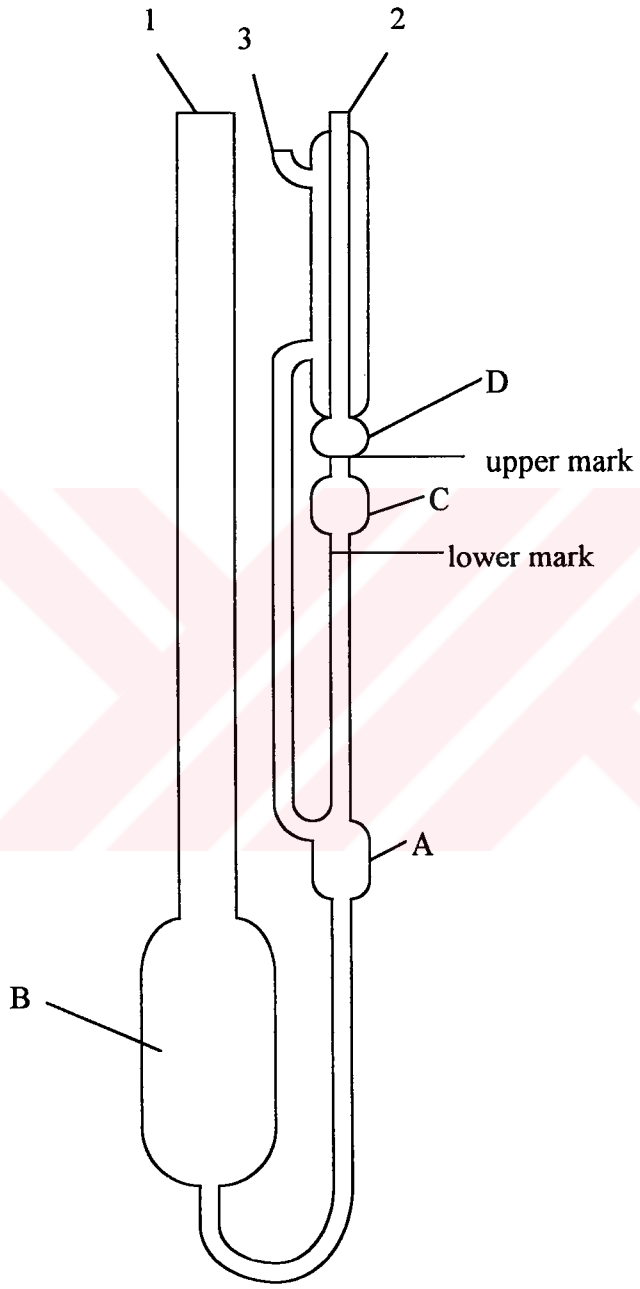


Figure 4.2. Ubbelohde type viscometer. 1: Charge inlet; 2: Opening to air; 3: Close / Open tube; A : Drain bulb; B : Reservoir; C : Measure bulb; D : Initial head bulb.

4.2.16 Gas Permeability Testing Appliance

The measurements of O_2, CO_2 and N_2 permeability were made on thin films of the blends (thickness about 0.03 mm) at 25°C with a gas permeability testing appliance (GDP/E Brugger, Munich).

4.2.17 Density Measurements

The density measurements were performed using a pycnometer at 20°C.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Synthesis of Poly(2-ethylhexyl acrylate) (PEHA)

2-ethylhexyl acrylate monomer containing 1 (w/w %) AIBN initiator was introduced into pyrex reaction tube and was degassed on vacuum line. The tightly capped tube was put in a constant temperature bath at 60°C for 15 h. The reaction mixture was poured into a large amount of methanol to precipitate. It was collected by filtration and dried under vacuum. Yield was 80 %. $[\eta]$=1.6048, THF, 25°C.

4.3.2 Preparation of Polymer Blends

In this study, three types of blends were prepared;
(1) Binary PVC/Tegomer blends (1-10 wt % of Tegomer addition in binary blend)
(2) Binary PVC/PEHA blends (1-10 wt % of PEHA addition in binary blend)
(3) Ternary PVC/PEHA/Tegomer blends (small amounts (1-10 wt %) of Tegomer were added into the PVC/PEHA mixtures in the ratios 99/1, 95/5, and 90/10)

All three types of blends were prepared using the same method.
Polymer blends were prepared by solvent casting from THF with a total polymer concentration 3 % (w/v). Solutions were poured into teflon-coated aluminium moulds, and THF was slowly evaporated under ambient conditions in a vacuum desiccator to provide low humidity. The resulting films were dried to a constant weight in a vacuum oven for 3 weeks at 50°C. The absence of THF was confirmed

by the absence of an IR absorption band at 1065 cm^{-1}. The films were kept in a desiccator at room temperature until being used for further investigations.

4.4 CHARACTERIZATION METHODS

4.4.1 Specific Interactions

The existence of specific molecular interactions in polymer blends is shown by using FTIR spectroscopy. FTIR spectroscopy, with its inherent sensitivity and computational facilities, offers considerable potential for studying the compatibility of polymer blends. Studies of specific interactions are almost invariably performed on solutions of low molecular weight liquids and thin films of polymers. Band peak-shifts are determined by comparing spectra of pure components, and the blend.

For specific interaction measurements of binary and ternary blends, a Nicolet 510 P FTIR spectrophotometer were used at room temperature[112].

4.4.2 Glass Transition Temperatures

The transition behaviour of the binary and ternary blends was investigated by differential scanning calorimetry (DSC). DSC measurements were conducted in a Schimadzu DSC-41 model apparatus at a heating rate of 10°C/min. In most cases, 5 to 20 mg sample weight was satisfactory. The reference material was α-Al_2O_3, known to be unaffected by repeated heating. Nitrogen gas supply was used for blanketing the sample. Samples were tested in aluminium pans.

After obtaining a uniform thermal history, reproducible scans were recorded and glass transition temperature was taken at the onset of the corresponding heat-capacity jump. The melting temperature was reported at the minimum of the endothermic peak. Determination of transition temperatures of polymers by DSC is given in the ASTM Standard Test Method (D-3418-82). Glass transition temperature (T_g) and melting temperature (T_m) are shown in Figure 4.3 and 4.4, respectively. The determination of calculated T_g values of blends according to Fox equation was shown in Appendix A.

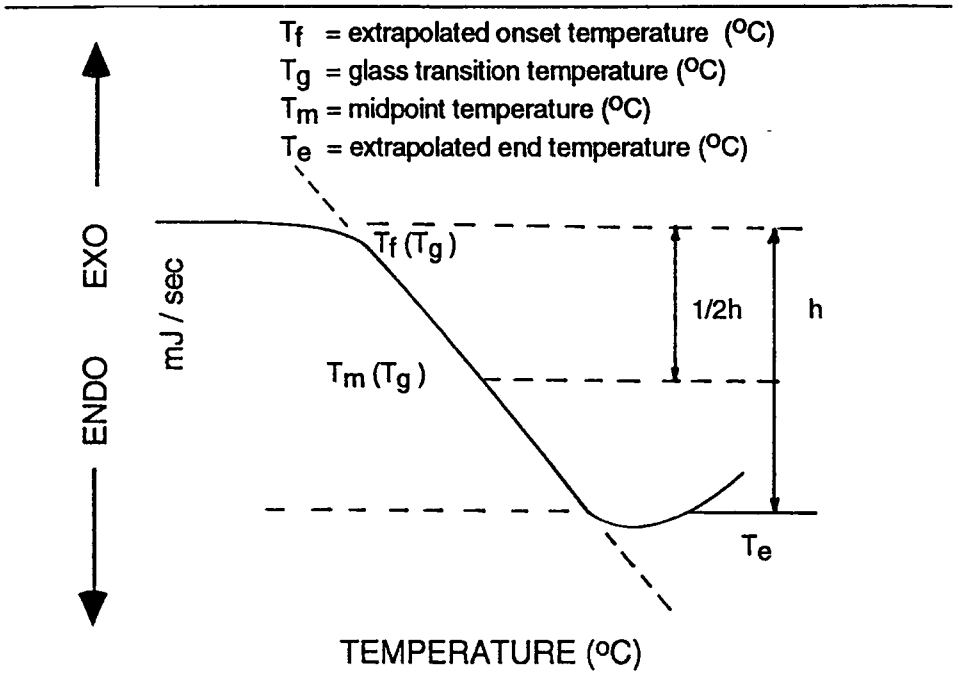


Table 4.3 Glass transition of a polymer

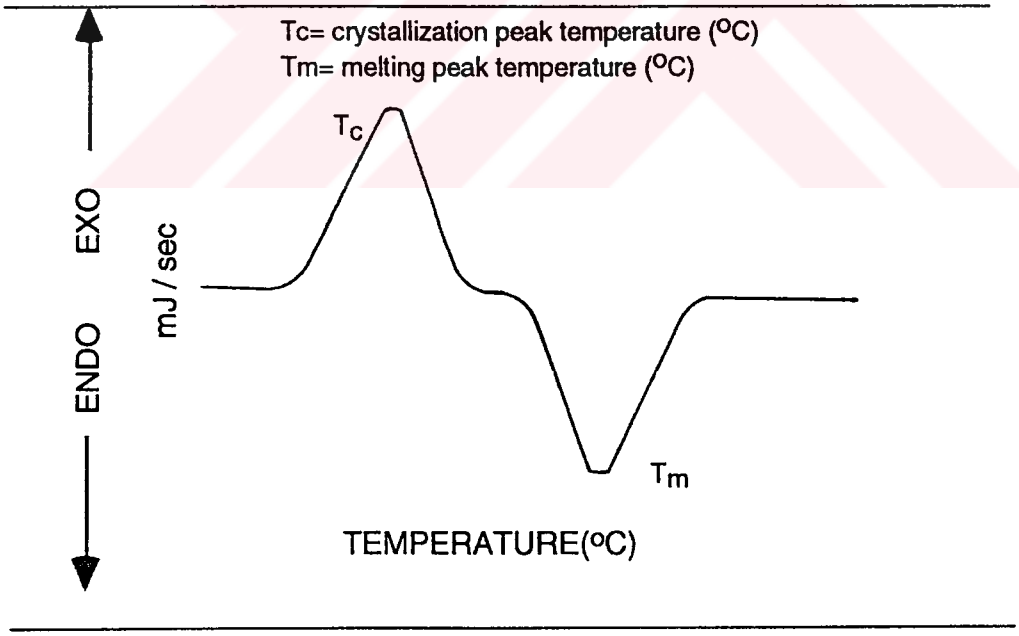


Table 4.4 T_c and T_m temperatures of a polymer

4.4.3 Viscoelastic Properties

The dynamic mechanical method assesses the structure and properties of solids and visco-elastic liquids via their dynamic moduli and damping. The method has great sensitivity in detecting changes in internal molecular mobility and in probing phase structure and morphology. Secondary relaxations in the glassy state can be easily studied as well as the glass transition (T_g) relaxation process[151].

The storage modulus, E' (or G' in shear) is defined as

$$E' = \frac{\text{amplitude in phase stress component}}{\text{strain amplitude}} \qquad (4.1)$$

The loss modulus, E'' (or G'') is defined as

$$E'' = \frac{\text{amplitude of out of phase stress component}}{\text{strain amplitude}} \qquad (4.2)$$

The storage modulus is the elastic response and corresponds to completely recoverable energy whereas the loss modulus is the viscous response corresponding to energy lost through internal motion.

The tangent of loss angle, tan δ, is dimensionless and is equal to the ratio of energy lost (dissipated as heat) to energy stored per cycle

$$\tan\delta = \frac{\text{loss modulus}}{\text{storage modulus}} = \frac{E''}{E'} \qquad (4.3)$$

For dynamic mechanical analysis, a Polymer Laboratories Dynamic Mechanical Thermal Analyser was used at a frequency of 1 Hz.

The tan δ-temperature dispersion and the dynamic storage modulus, E', and the dynamic loss modulus, E'', versus temperature plots for the pure homopolymer PVC and one of the blend containing 10 % Tegomer in PVC. DMTA was used in tensile mode for the measurements. The temperature range was 20°C to 100°C.

4.4.4 Stress-Strain Tests

Probably the most widely used mechanical test is the stress-strain test. Stress-stress measurements are generally made in tension by stretching the specimen at a uniform rate and simultaneously measuring the force on the specimen. The test is continued until the specimen breaks[126].

Mechanical properties of the homopolymer PVC and the binary and ternary polymer blends were also studied. The tensile strength and elongation measurements were performed on a Tensilon (UTM II) tester at room temperature with a crosshead speed of 10 mm/min. Young's modulus (E), ultimate tensile strength (σ) and elongation at break (ε) were determined.

4.4.5 Morphology

In polymer science, the term morphology generally refers to form and organization on a size scale above the atomic arrangement but smaller than the size and shape of the whole sample. Examples of polymer morphology include the size and shape of fillers and additives and the size, distrubition and association of the structural units within the manostructure. Microscopy is the study of the fine structure and the morphology of objects with the use of optical, transmission electron or scanning electron microscopes[152].

For the investigation of the morphology of the samples, scanning electron microscope (SEM) was used. The samples were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 A°.

Micrographs were obtained using a JEOL JXA-840 A scanning electron microscope. Secondary electron images (SEI) of homopolymers (PVC and PEHA) and the binary (PVC/Tegomer and PVC/PEHA) and ternary (PVC/PEHA/Tegomer) blends were obtained. Fracture surface morphology at high resolution was investigated.

4.4.6 Viscosity Measurements

To investigate the compatibility of polymer blends, some viscosity measurements were performed. Basically the dilute solution viscometry hinges on the classical Huggins equation [130] that expresses the specific viscosity (η_{sp}) of the polymer as a function of the concentration C, when one of the components is alone in the solution

$$\eta_{sp}/C = [\eta] + bC \tag{4.4}$$

where b is the interaction term and the slope in the η_{sp}/C vs. C plot. The theoretical consideration starts from the derivation by Krigbaum and Wall[131]. The specific viscosity η_{spm} of a mixed polymer solution can be expressed as follows:

$$\eta_{spm} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \tag{4.5}$$

where $[\eta_1]$ is the intrinsic viscosity of component 1 alone in the solution with common solvent, C_1 is the concentration of component 1 in mixed polymer solution, and b_{12} is the interaction coefficient for the mixture of components 1 and 2. The subscript 2 refers to component 2. The coefficient b_{11} is related to the Huggins constant k, when component 1 is in the solution alone. The relationship between b_{11} and k is written as

$$b_{11} = k_1[\eta_1]^2 \tag{4.6}$$

The interaction coefficient between the two polymers, b_{12} can be theoretically calculated as follows:

$$b_{12}^* = (b_{11} + b_{22})/2 \tag{4.7}$$

The experimental b_{12} can be obtained from Equation 4.5 by substituting into the equation the concentration of components 1 and 2 in the mixture (C_1) and (C_2) and the intrinsic viscosity of pure components $[\eta_1]$ and $[\eta_2]$, the value of b_{11} and b_{22} determined from Equation 4.6 and the specific viscosity of the mixture (η_{spm}) at the corresponding total mixture concentration as determined from the experiment.

The compatibility of polymer mixtures can be characterized by a parameter Δb.

$$\Delta b = b_{12} - b_{12}^{*} \qquad (4.8)$$

Negative values of Δb are found for solutions of systems with incompatible polymers, while positive values refer to the attractive interactions and compatibility[128-131,76,77].

We have used the above equations to characterize the compatibility of binary PVC/Tegomer and binary PVC/PEHA blends and ternary PVC/PEHA/Tegomer blends.

Intrinsic viscosities $[\eta]$ of homopolymers and blend solutions in THF at 25°C have been measured using Ubbelohde type viscometer. The viscometer was immersed in a constant temperature bath controlled for $\pm$ 0.01°C.

The determination of the viscosimetric interaction coefficients, b_{12} and compatibility parameters, Δb of binary and ternary blends were given in Appendix B.

4.4.7 Surface Properties

Surface properties of polymers play critical roles in many applications. For these applications, in order to obtain optimum performance in the final system, it is necessary to have balanced bulk/surface properties in the polymeric materials employed.

One of the easier way of achieving the desired surface and bulk properties in a polymer system is by blending the base resin with a small amount of a surface active copolymer. The change in the surface properties were monitored by the changes in the critical surface tensions and water contact angles of the films prepared from the blends[100].

Contact angle measurements of the polymer blend (PVC/Tegomer)films prepared by casting from 3 % (w/v) THF solutions were conducted on a Kernco Model G-III Goniometer. Contact angles were measured at room temperature using distilled, deionized water.

4.4.8 Gas Permeability

Permeability may apply to any form or shape of a material, but the property is most important and most conveniently studied in the passage of matter through a thin film or membrane.

The permeability coefficient (P) is generally the proportionality constant between the flow of penetrant per unit area of membrane per unit time and the driving force per unit thickness of membrane[139,p 794].

The permeation of gases for O_2, CO_2 and N_2 were made on thin films (thickness were about 0.03 mm) of the blends at 25°C with a gas permeability meter (GDP/E Brugger, Munich). Electrical connection of the permeability meter is 220 V alternating current power consumption around 30 watts and measurement range is approximately 1 ml/(m^2.d.bar) up to 30000 ml/(m^2.d.bar). Measurement time depends on the permeability of the sample. Sample diameter must be 110 mm.

Samples to be tested have at least one smooth side which can be well sealed and this side is always face the lower part of the permeation cell. On one side of the sample, a pressure of the desired measuring gas equalling the atmospheric pressure prevails constantly, while the very small measurement volume (approx. 0.5 ml) is evacuated at the beginning of the measurement on the other side of the sample. After detachment of the vacuum pump, the actual measurement begins. This is accomplished by measuring with an electronic pressure sensor the pressure rise in the measuring volume resulting from the measuring gas diffusing through the film. This pressure rise results from the pressure difference, which becomes even smaller, according to an exponential function and it is electronically logarithmically plotted. This produces a linear relationship of the output voltage of the appliance to time, i.e. the curve traced by the plotter is a straight line, from whose slope the gas permeability can be calculated by multiplying with an appliance factor[153].

Gas permeability is determined by using following equation:

$$q = 3.41 \times 10^7 \times V / N \times T \qquad ml/m^2.d.bar \qquad (4.9)$$

where q is the gas permeability in ml/(m^2.d.bar); ml under normal conditions:1013 mbar, 273 K. V is the measurement volume, N is the slope of the straight line in s/scale division and T is room temperature in K.

Permeation constant (P) is also calculated by following equation.

$$P = 1.16x10^{-9} x\ q\ x\ l' \text{ ml/(cm.s.bar)} \quad (4.10)$$

where $1.16x10^{-9}$ is the multiplication factor to obtain P in ml/cm.s.bar and l' is the film thickness in cm.

Gas permeability(q) and permeation constant(P) values of homopolymer PVC and PVC/Tegomer blends were given in Appendix C. Also, the calculation of activation energies of permeation (E_p) was shown in Appendix C.

4.4.9 Density Determination

Density can be regarded as a measure for the free volume between the molecules of the polymer structure[133]. The Archimedean principle is applied for determining the density of a polymer and a polymer blend. A pycnometer was used for determining the density of polymer films.

The experimental and calculated density data of homopolymers and the binary PVC/Tegomer blends and calculations were given in Appendix D.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 SPECIFIC INTERACTIONS OF BLENDS

5.1.1 Binary PVC/Tegomer Blends

Using FTIR spectroscopy, we have been able to show the existence of specific molecular interactions in PVC/Tegomer miscible blends. Figure 5.1 and 5.2 show the FTIR spectrum of Tegomer and PVC/Tegomer (90/10) blend. The specific interactions determined by FTIR showed significant amounts of shifting in carbonyl band for PVC/Tegomer system, as seen in Figure 5.3. The carbonyl absorption (-C=O-) bands were observed at 1724.5 and 1730 cm^{-1} for triblock copolymer (a) and the blend (b) respectively. Approximately a 6 cm^{-1} shift in carbonyl absorption band was observed (Table 5.1). In miscible blends a shift of the carbonyl band is observed in FTIR spectroscopy while it is not seen in immiscible blends[52]. Similar results for this type of shift were reported in earlier studies for PVC/PCL blends [52-54]. It was mentioned that the band at 1737 cm^{-1} is associated with the amorphous phase, and the band at 1724 cm^{-1} is associated with crystalline phase of PCL. At PVC concentration in excess of 2/1 molar ratio PVC/PCL, it was indicated that the blends are essentially amorphous and their miscibility in amorphous state results from a specific interaction between two polymers[54].

In our work, the carbonyl band of the Tegomer also showed shifting to a higher frequency (1730 cm^{-1}) to form a miscible blend with PVC. It is known that when the chlorinated polymer has α-hydrogens (e.g.PVC) extensive association will occur with the polyester, with the interaction presumably being dominated by hydrogen bonding between the carbonyl group and the α-hydrogens[52-54,124,125]. It is suggested that the miscibility behaviour of PVC/Tegomer blend is due to a

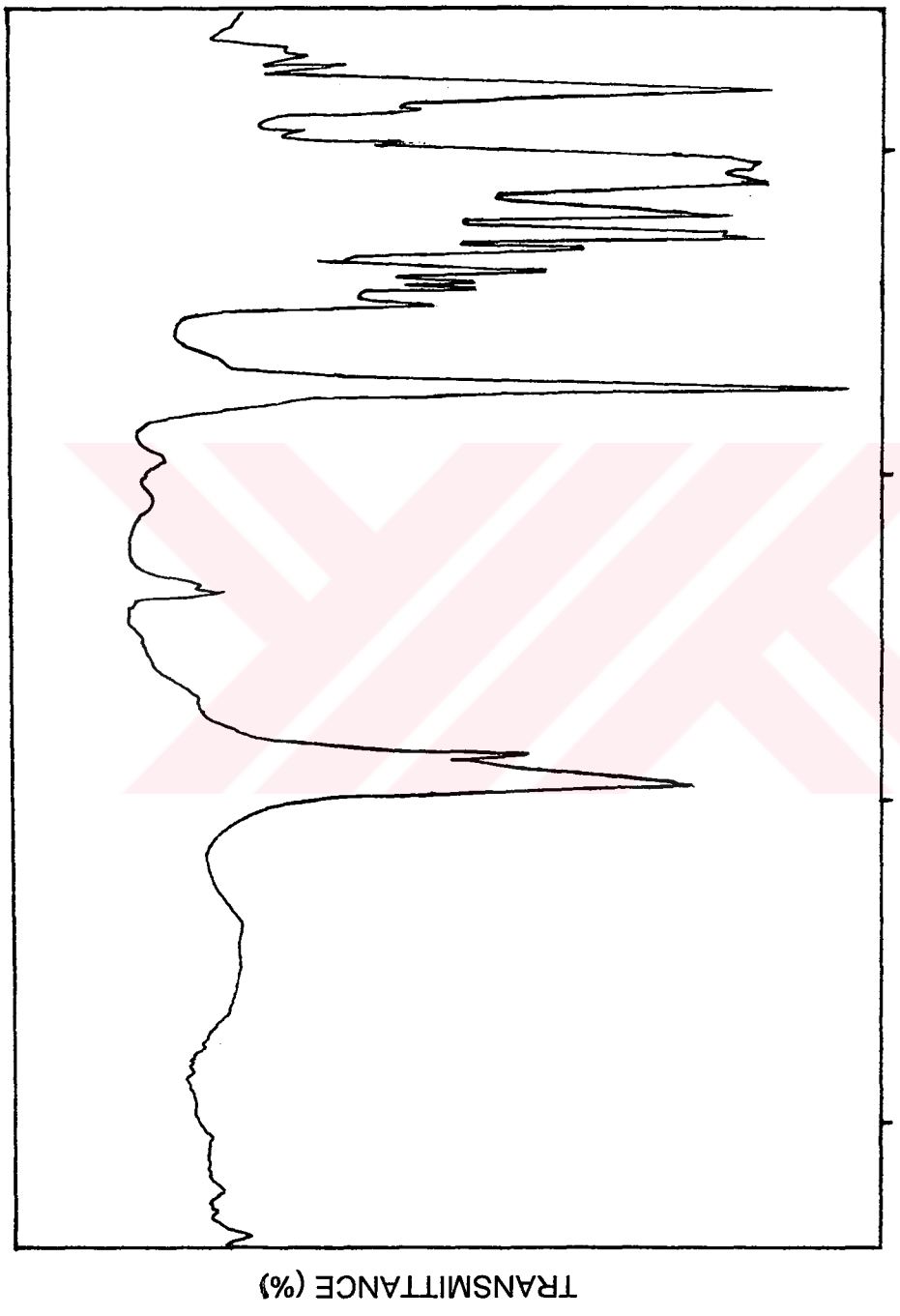


Figure 5.1 FTIR spectrum of Tegomer

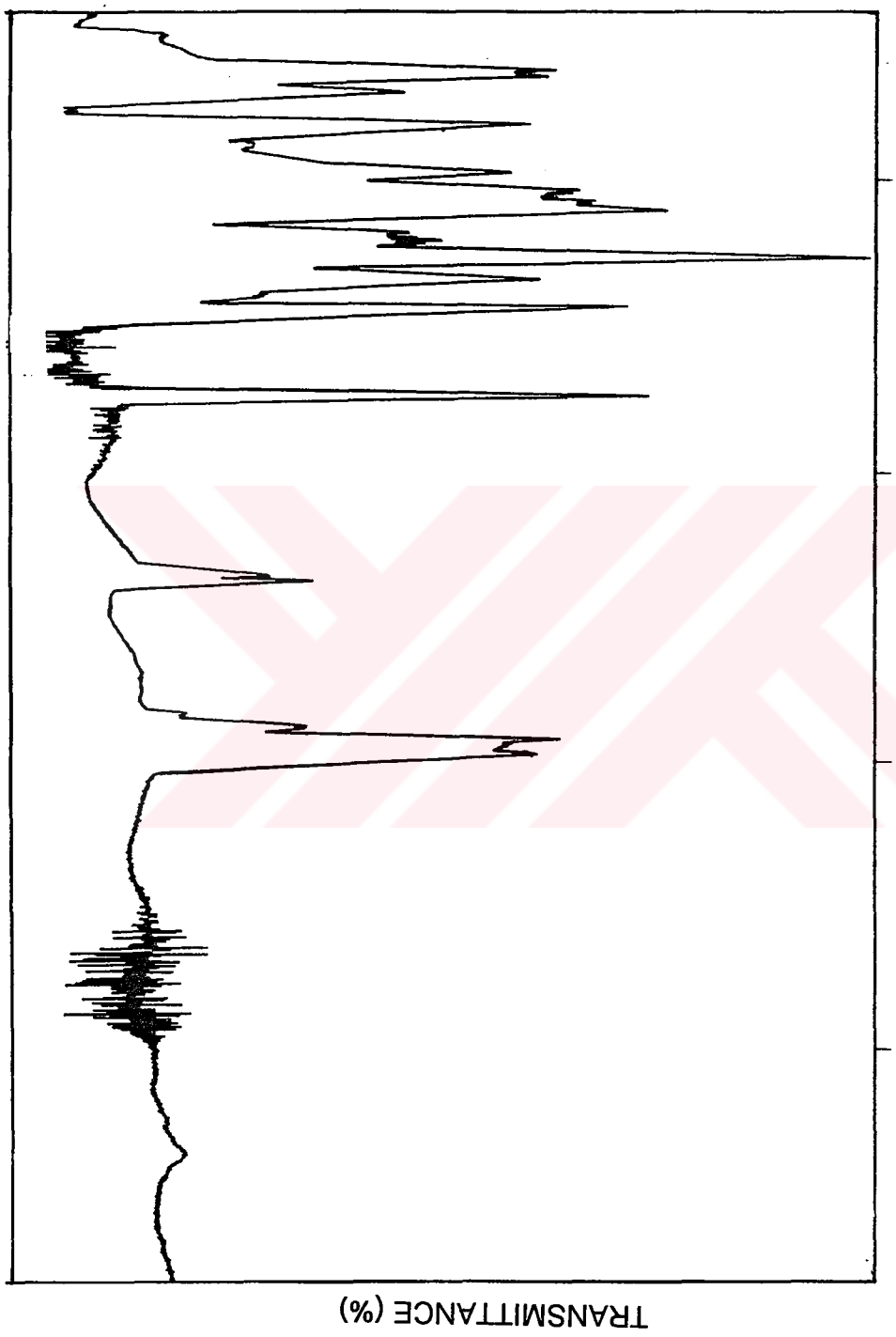


Figure 5.2 FTIR spectrum of PVC/Tegomer (90/10) blend

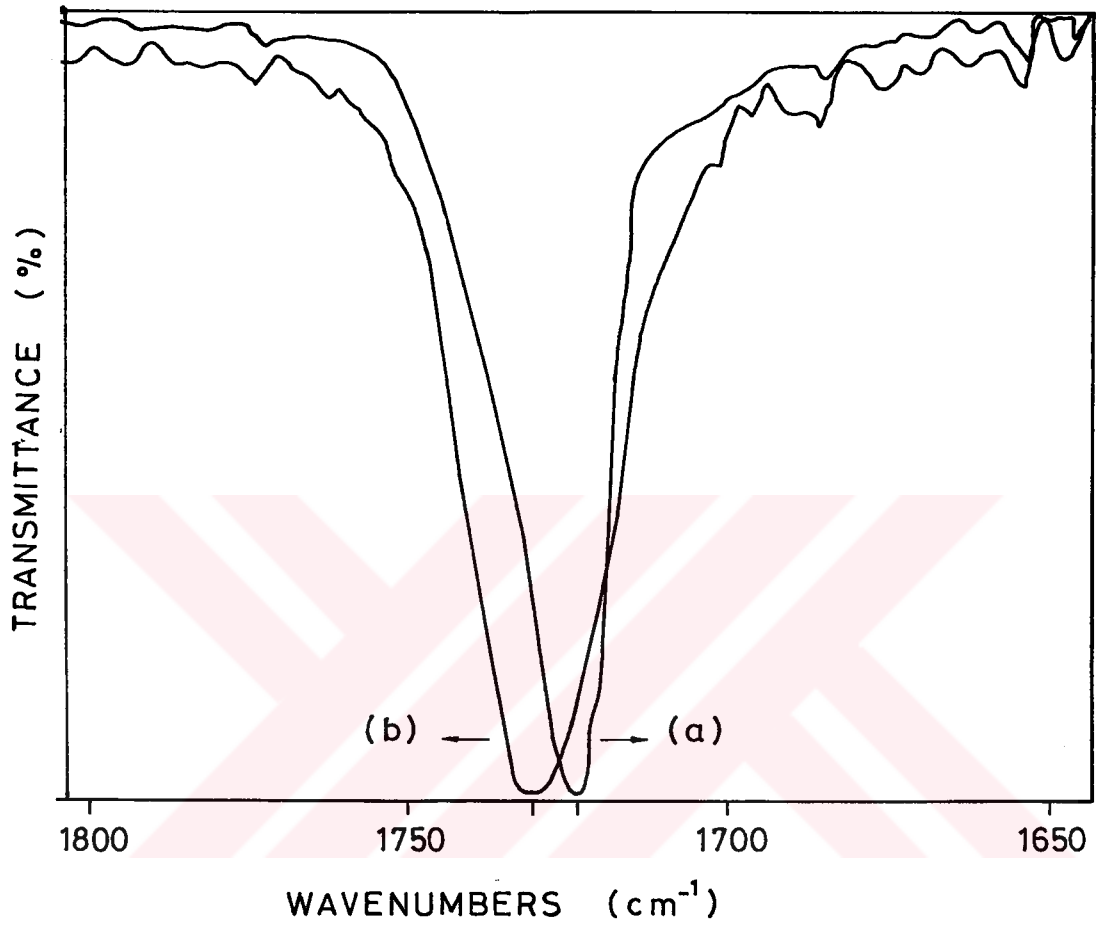


Figure 5.3 The shift of carbonyl (-C=O-) band
(a) Tegomer (b) PVC/Tegomer (90/10) blend

hydrogen bonding interaction, C=O....H-C, between the α-hydrogen of PVC and the carbonyl groups of the Tegomer

Table5.1 C=O and C-H band positions of Tegomer and PVC/Tegomer blend

Sample	Frequency (cm^{-1})	
	C=O	C-H
Tegomer	1724.5	2959
PVC/Tegomer blend (90/10)	1730	2963

It is also observed that the C-H stretching frequency shifts progressively to a higher frequency with increasing Tegomer content in the blend.

The other characteristic peaks of the PDMS component of the copolymer were observed at 1260 cm^{-1} and 800 cm^{-1} for Si-CH_3 deformation, at 1026 cm^{-1} for Si-O-Si asymmetric stretching vibration (Figure 5.1).

5.1.2 Binary PVC/PEHA Blends

Figure 5.4 shows the FTIR spectrum of the poly-2 ethylhexyl acrylate (PEHA). The carbonyl (C=O) band is the characteristic peak of PEHA homopolymer (1738 cm^{-1}). The carbonyl absorptions of samples were observed at 1738 cm^{-1} for the binary blends of PVC/PEHA at all compositions we have worked (0/100, 99/1, 95/5, 90/10). No specific interaction can be seen in these immiscible binary blends of PVC/PEHA.

5.1.3 Ternary PVC/PEHA/Tegomer Blends

The specific interactions determined by FTIR showed significant amount of shifting in carbonyl band for PVC/PEHA/Tegomer system, as seen in Table 5.2 and Figure 5.5

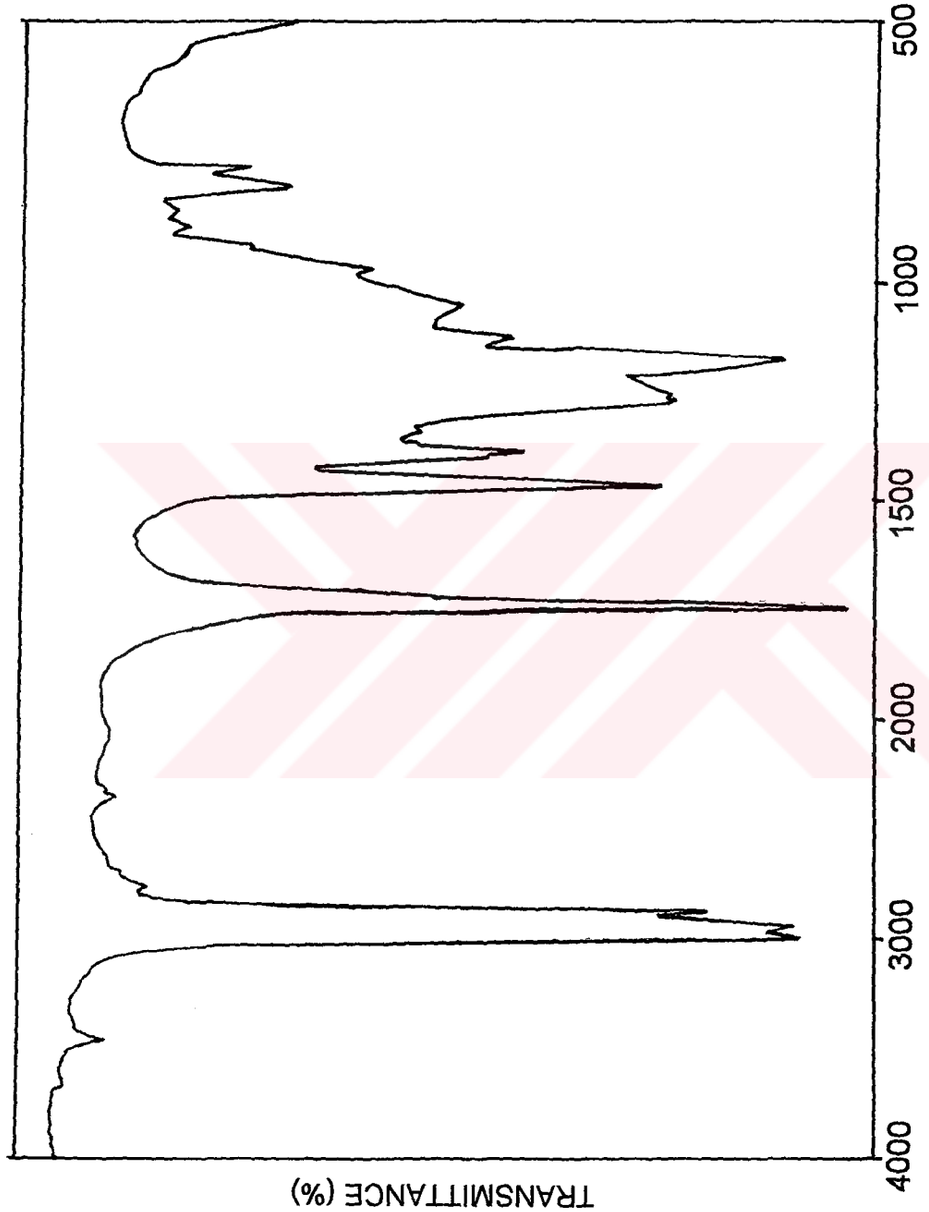


Figure 5.4 FTIR spectrum of PEHA

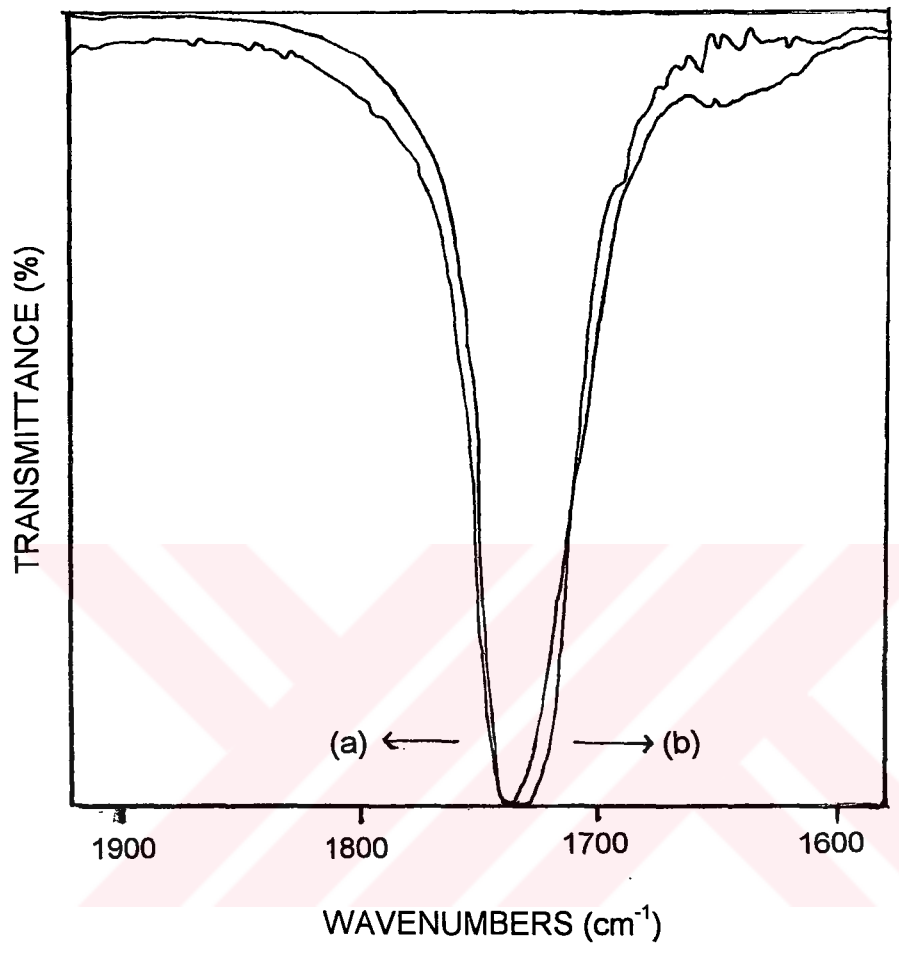


Figure 5.5 The shift of carbonyl (-C=O-) band
(a) PEHA (b) PVC/PEHA/Tegomer (85.5/4.50/10)

The carbonyl absorption band appears at lower frequencies for ternary blends of PVC/PEHA/Tegomer (at 1730 cm^{-1} for 89.1/0.90/10 and 1728 cm^{-1} for 85.5/4.50/10 compositions) (Table 5.2). Shifts to lower frequencies and line broadening can be indicative of hydrogen-bonding interactions in the blends[39,101].

Table 5.2 Carbonyl band positions for homopolymer and polymer blends

Sample	Frequency, cm^{-1}
	C=O
Tegomer	1724.5
PEHA	1738
PVC/PEHA/Tegomer (89.1/0.90/10)	1730
PVC/PEHA/Tegomer (85.5/4.50/10)	1728

5.2 TRANSITION BEHAVIOUR OF BLENDS

5.2.1 Binary PVC/Tegomer Blends

The most commonly used method for establishing miscibility in polymer blends is the determination of the glass transition. We used both DSC and DMTA to determine the T_gs of the blends.

5.2.1.1 Differential Scanning Calorimetry (DSC) Measurements

A concise arrangement of DSC thermograms of PVC, Tegomer and the blends is shown in Figure 5.6 . The glass transition of pure PVC was observed at 79°C (Figure 5.6a). PVC/Tegomer blends exhibit single T_gs which change with blend composition (Figure 5.6b-g). The T_gs of the blends at the range of composition we worked (1-10 %) decreased with the amount of triblock copolymer in the blend. The T_g seen for 90/10 blend was 35°C, the lowest T_g observed for PVC/Tegomer

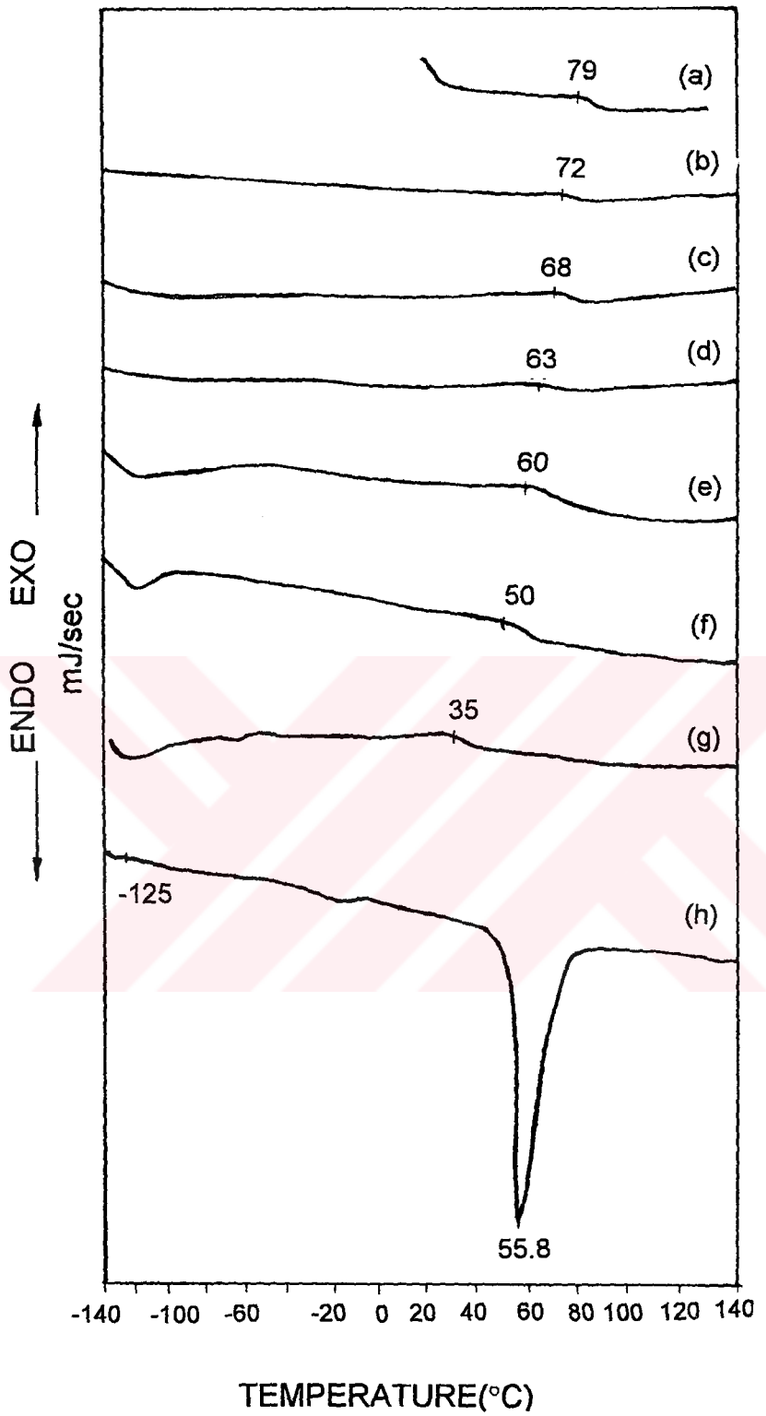


Figure 5.6 DSC thermograms for PVC/Tegomer blends of different compositions: (a) pure PVC; (b) 1% Tegomer; (c) 2% Tegomer; (d) 4% Tegomer; (e) 6% Tegomer; (f) 8% Tegomer; (g) 10% Tegomer; (h) pure Tegomer

system. DSC analysis of Tegomer clearly indicated the formation of two phase morphology with siloxane glass transition temperature around -125°C and polycaprolactone melting points around +55°C, as shown in Figure 5.6h. These transitions could not be observed in the DSC thermograms of the blends, probably due to small amounts of copolymer addition (1-10 wt %).

The DSC data obtained for each sample are also shown in Figure 5.7 in a plot of glass transition temperature versus copolymer composition. According to T_g criterion[3], since these blends show single T_gs, it can be said that there is extensive interaction between the segments of the two polymers and they are then miscible. This result is confirmed by a decrease in T_g with the addition of copolymer to PVC as shown in Figure 5.7.

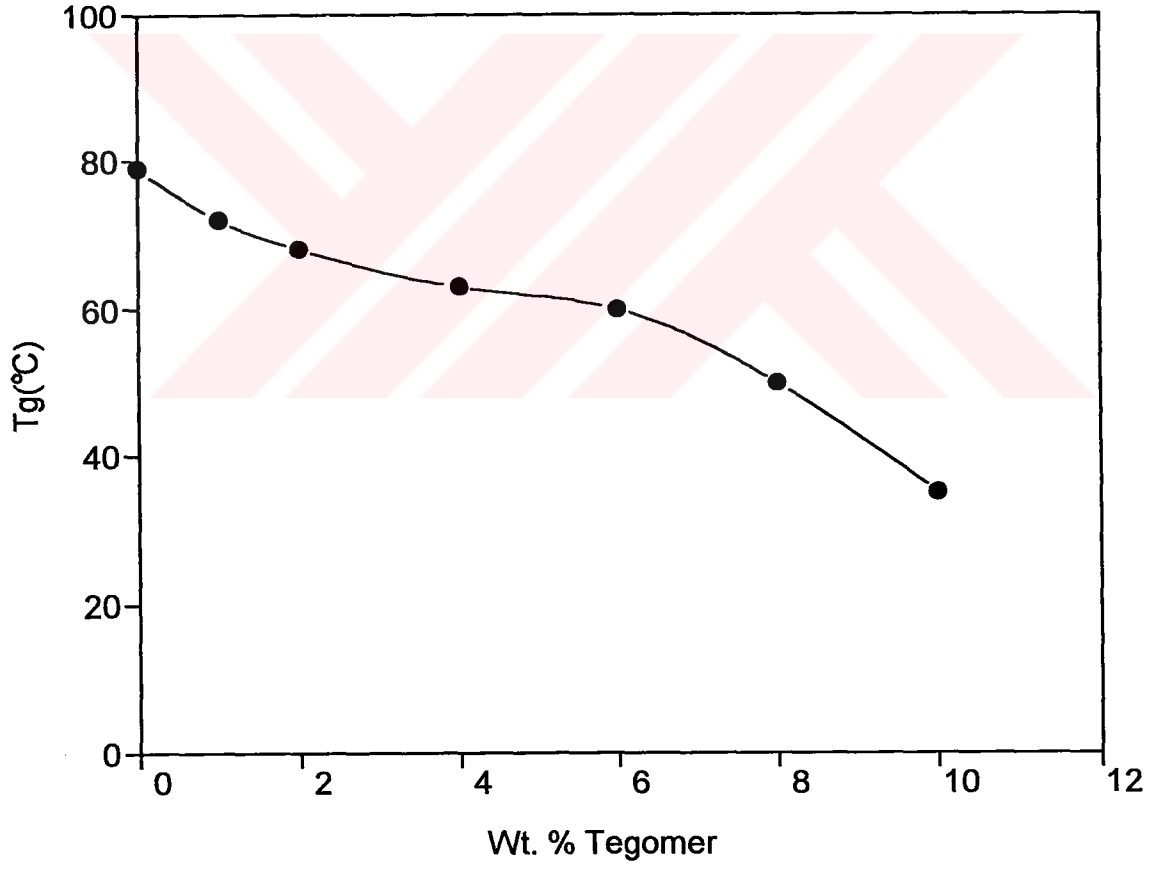


Figure 5.7 T_g as a function of Tegomer content in PVC/Tegomer blends

5.2.1.2 Dynamic Mechanical Thermal Analysis(DMTA) Measurements

Figure 5.8 shows the dynamic storage modulus (E') and the dynamic loss modulus (E'') versus temperature plot for PVC homopolymer and PVC/Tegomer (90/10) blend. The glass transition (T_g) of PVC that corresponds to a sharp decrease in E' (Figure 5.8a) is observed at 50°C whereas the T_g of 90/10 blend is at 37°C. The DMTA spectrum of the blend is consistent with the single T_g behaviour observed in the DSC results. The dynamic mechanical testing results of pure PVC were compared with previous studies[45,51,87,151]. At this temperature range (20-100°C), the peaks of E' and E'' seem to move to lower temperatures upon blending, as was previously reported for PCL/PVC[44]. The value of E' (at 20°C) for PVC is relatively higher (1.65 GPa) than blend (1.20 GPa) at the same temperature. This decrease in E' in the blend (90/10) may be attributed to the plasticizing effect of triblock copolymer on PVC. PVC/Tegomer blend (90/10) exhibits a single peak in E'' vs temperature curve, however the peak seems to be broader than that of the pure PVC homopolymer.

5.2.2 Binary PVC/PEHA Blends

Table 5.3 shows the DSC results of binary PVC/PEHA blends. The glass transition temperatures of PVC and PEHA homopolymers were observed at 79 and -30°C, respectively. PVC/PEHA blends exhibit only one T_g at around 67°C. The binary blends of PVC/PEHA are supposed to be immiscible[40] therefore classical observation of two glass transition temperatures (T_g) for the homopolymers is expected. However, the low transition temperature which corresponds to PEHA component could not be seen in PVC/PEHA blends, probably due to the small amounts of PEHA addition (1-10 wt %).

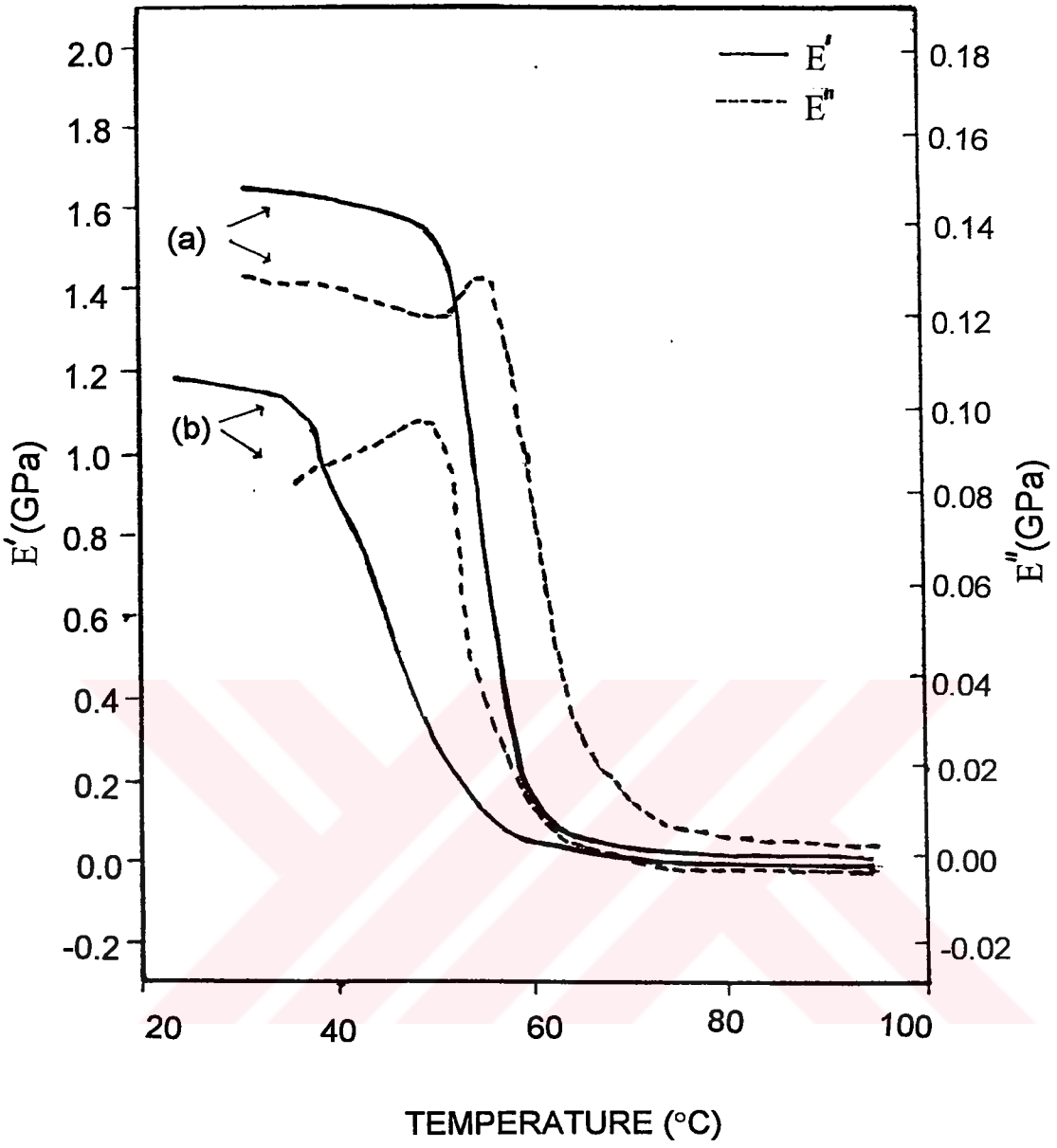


Figure 5.8 Plots of the dynamic storage modulus (E') and dynamic loss modulus (E'') vs temperature at 1 Hz for pure PVC(a) and for PVC/Tegomer (90/10) blend(b)

Table 5.3 Glass transition temperatures of binary PVC/PEHA blends of various compositions

Composition, wt %		T_g (°C)
PVC	PEHA	
100	0	79
99	1	67
95	5	67
92	8	67
90	10	67
0	100	-30

5.2.3 Ternary PVC/PEHA/Tegomer Blends

Glass transition temperatures were measured for a variety of compositions of the ternary PVC/PEHA/Tegomer blends containing PVC/PEHA ratios of 99/1, 95/5, 90/10. The experimental and calculated T_g values are listed in Table 5.4. T_g values of ternary systems are predicted according to Fox Equation[23,154].

$$1 / T_g = w_1 / T_{g1} + w_2 / T_{g2} + w_3 / T_{g3} \qquad (5.1)$$

where w_1, w_2 and w_3 are the weight fractions of the blend components: PVC, PEHA and Tegomer, respectively. PVC/Tegomer mixtures led to the conclusion that this binary system is miscible at the range of composition we worked (1-10 wt % Tegomer)[101]. We have investigated the effect of Tegomer in the immiscible binary blends PVC/PEHA. All ternary blends seem to be miscible systems because a single T_g was observed experimentally at the compositions given in Table 5.4.

In ternary blends with PVC/PEHA ratio, 99/1, the experimental T_gs are considerably lower than those predicted by Fox equation (Equation 5.1). T_g values for ternary blend systems were also calculated without taking into account the presence of the minor component (PEHA in this case) in the mixture. The calculated T_gs by using Equation 5.1 for ternary blends of PVC/PEHA (99/1) with varying Tegomer composition (1-8 wt %) are close to the T_g values calculated without taking into account the presence of minor component (PEHA). Because of this prediction, it is

Table 5.4 Glass transition temperatures of ternary PVC/PEHA/Tegomer blends of various compositions

Composition, wt %			T_g(°C)		
PVC	PEHA	Tegomer	exp.	calc. ternary[a)]	calc. binary[b)]
99	1	0	67	----	----
98.01	0.99	1	45	75	76
94.05	0.95	5	45	63	64
91.08	0.92	8	40	61	55
95	5	0	67	----	----
94.05	4.95	1	67	67	74
90.25	4.75	5	62	56	64
89.30	4.70	6	58	54	61
87.4	4.60	8	54	48	55
85.5	4.50	10	53	43	49
90	10	0	67	----	----
89.1	9.9	1	68	58	64
85.5	9.5	5	62	48	64
81	9	10	62	36	48

[a)] Calculated T_gs by Equation (5.1)
[b)]Calculated T_gs without taking into account the presence of the minor component in ternary blends ($1/T_g=w_1/T_{g1}+w_2/T_{g2}$)

which PVC/PEHA ratios are 95/5 and 90/10. In these systems PEHA addition leads to an increase in the experimental values of T_g.

Comparisons of experimental and predicted T_gs for ternary blends of PVC/PEHA/Tegomer in which PVC/PEHA ratio was 90/10, show that minor component, Tegomer in this case, does not affect the results in great extent. Consequently, we cannot ascertain by DSC if immiscible regions are involved in the blends, since all ternary blends show single T_g behaviour. The T_g transitions of PEHA and Tegomer components; -30°C and -125°C (for PDMS)[101], respectively could not observed in the DSC thermograms of the blends, probably due to the small amounts of PEHA and copolymer addition (1-10%). However, this single T_g shifts to higher temperatures (towards the T_g of pure PVC) with the increase in concentration of immiscible component, PEHA. The data presented in Table 5.4 exhibit the changes in T_g of ternary blends depending on the composition clearly.

5.3 MECHANICAL PROPERTIES OF BLENDS

5.3.1 Binary PVC/Tegomer Blends

Typical stress-strain behaviour for homopolymer (PVC), triblock copolymer (Tegomer) and the selected blends in the range of 1-10 % Tegomer content, are shown in Figure 5.9. The stress-strain results are summarized in Table 5.5. The data are averages of three to four runs for ultimate strength(σ), Young's modulus(E), and elongation at break(ε).

It can be seen, in Figure 5.9 and Table 5.5 that, the blends show an increase in flexibility with respect to the PVC homopolymer. E and σ drop as the copolymer concentration in the blend increases. The highest amount of Tegomer in the blend is 10 %. The ultimate strength at break and Young's modulus of the blend (90/10) show a decrease by a factor of 2 compared to homopolymer PVC, however its elongation at break (ε) is 472 % exhibiting a dramatic increase (by a factor 59) with respect to PVC (ε=8 %).

The tensile properties of these blends indicate that Tegomer is an effective plasticizer for PVC. A similar behaviour is observed for PCL/PVC blends[51].

The modulus and ultimate strength drop rapidly at the composition range 0-60 wt % PVC. The ability to elongate rises quickly with higher concentrations of PCL up to about 50 % PVC. However, when the tensile properties of PCL/PVC[51] and PVC/Tegomer blends are compared, the dramatic effect of small amounts of siloxane addition on the ability of elongation of the blends can be clearly seen. The lowest PCL concentration used in PCL/PVC blend is 25 %, and it exhibits an elongation value of 148 %. However, in our system, PVC/Tegomer blend, the elongation at break is 472 % with only 10 % copolymer addition to PVC.

5.3.2 Binary PVC/PEHA Blends

The stress-strain results of binary PVC/PEHA blends are summarized in Table 5.6 and Figure 5.10 The data are the averages of three to four runs for ultimate tensile strength (σ), Young's modulus (E) and the elongation at break (ε).

It is noteworthy that the binary blends of PVC/PEHA show an increase in flexibility with respect to PVC homopolymer as can be seen easily in Table 5.6. Although tensile strength somewhat decreases with the addition of PEHA, the elongation at break increases remarkably. PVC/PEHA blend (95/5) seems to have optimum properties at the composition range we have worked. Only 5 % of PEHA suffices to increase elongation at break (ε) to almost 100 %. However, it is not easy to explain this synergism on the mechanical properties of binary blends, since no molecular interactions or segment associations[20] between PVC and PEHA components could be observed by other techniques.

Table 5.5 Tensile Properties of PVC/Tegomer Blends

Composition of the blends		Ultimate Elongation	Ultimate tensile strength	Young's Modulus (MPa)
PVC	**Tegomer**	ε (%)	σ (MPa)	$Ex10^{-2}$
100	0	8	28	6.1
99	1	18	16	4.6
98	2	55	15	3.1
96	4	82	14	2.8
94	6	95	13	3.9
92	8	207	17	3.5
90	10	472	14	3.6

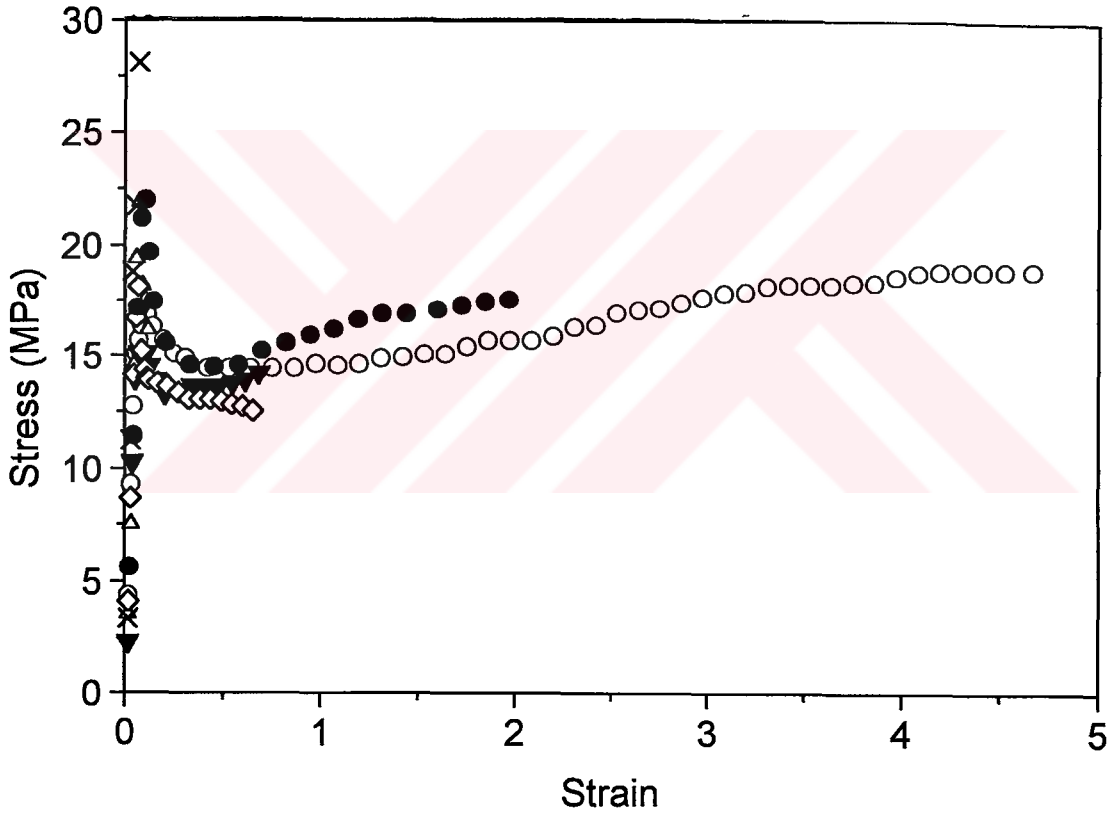


Figure 5.9 Stress-strain curves for PVC/Tegomer blends: (x) pure PVC; (Δ) 1% Tegomer; (▼) 4% Tegomer; (◊) 6% Tegomer; (●) 8% Tegomer; (o) 10% Tegomer

Table 5.6 Tensile properties of binary PVC/PEHA blends

Composition, wt % PVC	PEHA	Ultimate elongation (ε, %)	Ultimate tensile strength (σ, MPa)	Young's modulus ($Ex10^{-2}$ MPa)
100	0	8	28	6.1
99	1	55	20	4.0
98	2	73	20	8.1
95	5	97	25	7.3
94	6	119	22	5.3
92	8	72	20	5.2
90	10	56	16	3.9

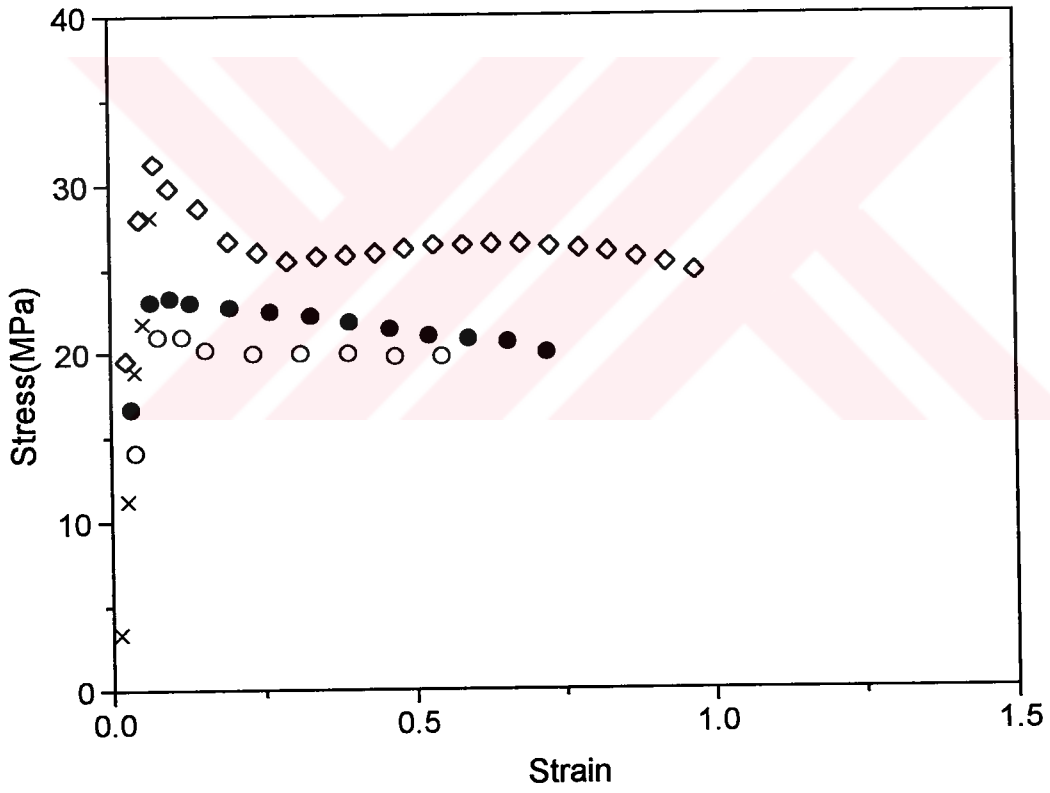


Figure 5.10 Stress-strain curves for PVC/PEHA blends: (x) pure PVC; (o) 1% PEHA; (◊) 5% PEHA; (●) 8% PEHA

5.3.3 Ternary PVC/PEHA/Tegomer Blends

The effect of the addition of Tegomer into PVC/PEHA systems (99/1 and 95/5 ratio) at varying compositions can be clearly seen in Figure 5.10, 5.11 and 5.12. Ultimate elongation at break (ε) increases with the increasing amount of Tegomer in ternary blends. For example, for the ternary blend of PVC/PEHA/Tegomer (91.08 / 0.92 / 8) an increase in ε value (by a factor 4) with respect to PVC/PEHA (99/1) binary blend was observed(Tables 5.6 and 5.7). However σ and E values of the above ternary blend decrease slightly (by a factor of 1.3) compared to binary blends of PVC/PEHA(99/1).

Table 5.7 Tensile properties of ternary PVC/PEHA/Tegomer blends of various compositions

Composition of the ternary blends, wt %			Ultimate elongation (ε, %)	Ultimate tensile strength (σ, MPa)	Young's modulus ($Ex10^{-2}$ MPa)
PVC	**PEHA**	**Tegomer**			
99.00	0.00	1	18	16	4.6
98.01	0.99	1	90	19	3.5
94.05	0.95	5	169	21	4.1
91.08	0.92	8	230	16	2.8
95.00	0.00	5	95	13	3.5
94.05	4.95	1	101	14	5.1
93.10	4.90	2	342	17	3.6
90.25	4.75	5	381	16	4.2
89.30	4.70	6	142	13	3.2
87.40	4.60	8	113	14	5.4
85.50	4.50	10	183	16	3.3

We had similar observation in stress-strain behaviour for the ternary blends of PVC/PEHA/Tegomer in which PVC/PEHA ratio was 95/5. In this case, the synergetic effect of Tegomer addition on elongation can be easily seen in the stress-strain curve of ternary blend PVC/PEHA/Tegomer (90.25 / 4.75 / 5) (Figure 5.12). Tensile strength and Young's modulus of these ternary blends are lower

than that of binary PVC/PEHA blend (95/5). However, they have superior mechanical properties compared to binary PVC/Tegomer blends (95/5) studied previously[101]. The ultimate elongation of ternary blend PVC/PEHA/Tegomer (90.25 / 4.75 / 5) increased approximately by a factor 4 with respect to binary blends of PVC/PEHA (95/5) and PVC/Tegomer (95/5).

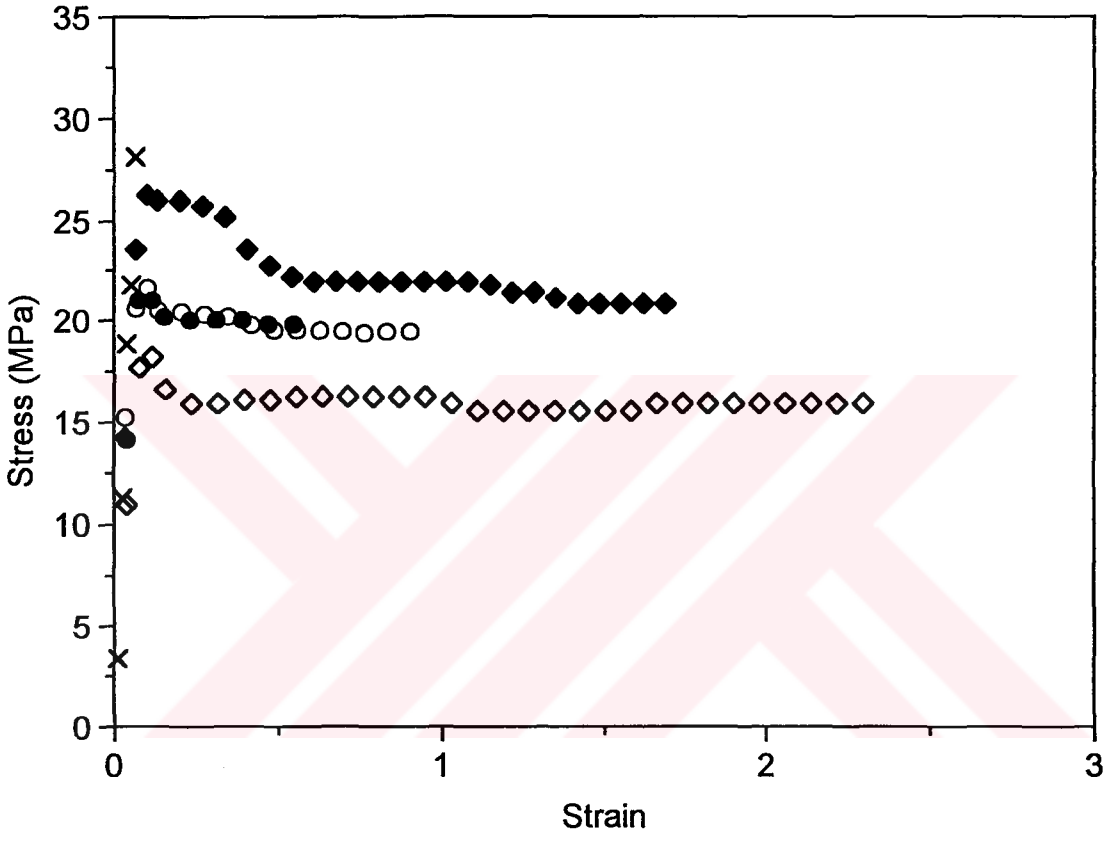


Figure 5.11 Stress-strain curves for homopolymer(x) PVC; (●) binary PVC/PEHA (99/1) blend; (o) ternary PVC/PEHA/Tegomer (98.01/0.99/1) blend; (♦) ternary PVC/PEHA/Tegomer (94.05/0.95/5) blend and (◊) ternary PVC/PEHA/Tegomer (91.08/0.92/8) blend

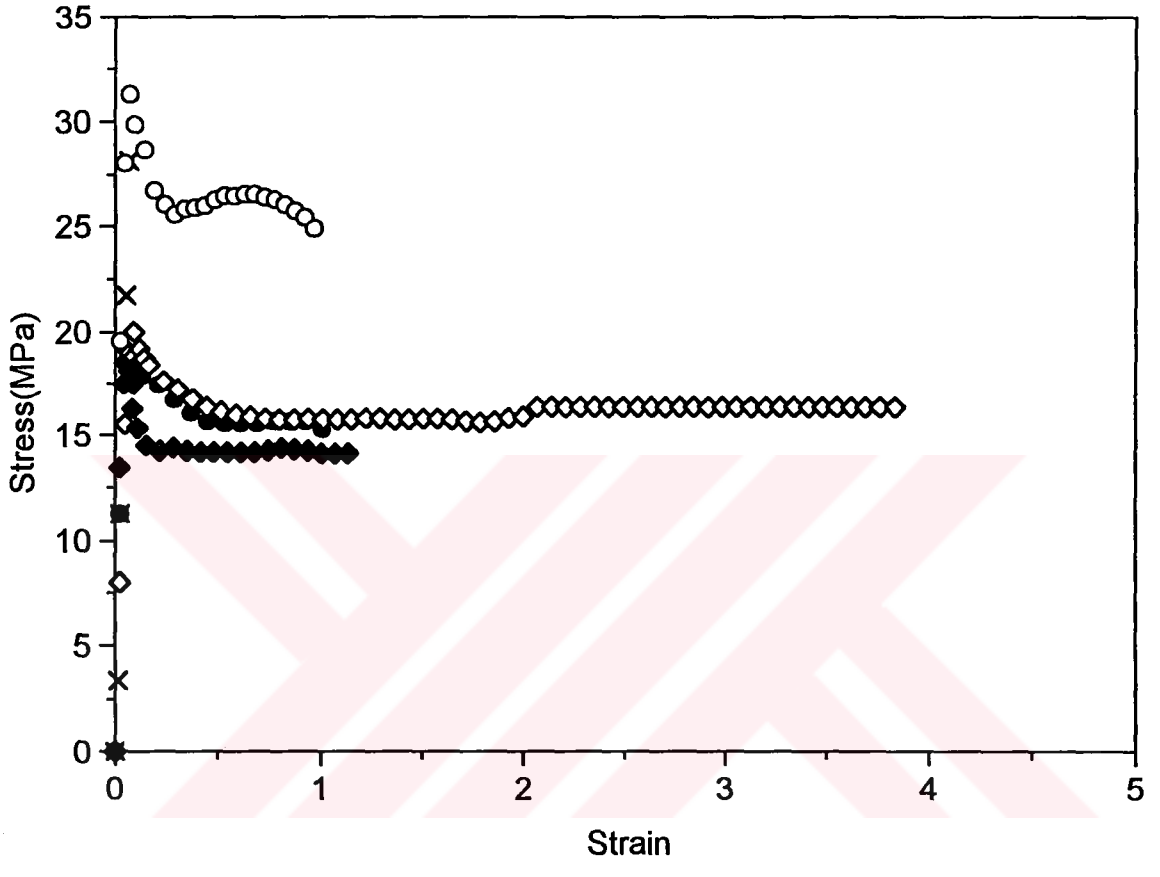


Figure 5.12 Stress-strain curves for homopolymer(x) PVC; (o) binary PVC/PEHA (95/5) blend; (●) ternary PVC/PEHA/Tegomer (94.05/4.95/1) blend; (◊) ternary PVC/PEHA/Tegomer (90.25/4.75/5) blend and (♦) ternary PVC/PEHA/Tegomer (87.4/4.60/8) blend

5.4 MORPHOLOGY STUDIES OF BLENDS

5.4.1 Binary PVC/Tegomer Blends

Figure 5.13(a-f) show the SEM images of PVC homopolymer and 90/10 PVC/Tegomer blend.. Secondary electron images (SEI) were applied in SEMs.

Figure 5.13(a-c) show the fractured surface of the homopolymer, PVC, at different magnifications (X1200, X3000, and X20000). SEI of PVC at X1200 magnification shows a brittle fracture that is consistent with mechanical properties of pure PVC polymer. At higher magnifications, a spherical structure was observed in the fractured surface of PVC. White spheres with varying sizes (500-1250 A°) form parallel lines which can be easily detected in Figure 5.13(b) and 5.13(c).

It is known that various levels of morphology exist in suspension PVC powder[155]. Powder particles known as grains are irregular in shape and are about 100-150 μm in diameter. Each grain consists of many microparticles which are about 1-2 μm in diameter. These microparticles are made up of still smaller structures, submicroparticles[90,155-157]. We observed these submicroparticles as white spheres in our study, and the similar morphology of PVC is illustrated in various papers. The parallel lines of these particles seen in the micrograph of PVC have similar characteristics with PVC samples reported very recently[155-159].

The fractured surface morphology of PVC/Tegomer blend (90/10) is shown in Figures 5.13(d-f). Figure 5.13(d) shows an even and relatively smooth fractured surface of blend 90/10. This is in contrast to the uneven and rough surface of freeze-fractured PVC, as shown in Figure 5.13(a). The spherical morphology found in this blend is identical to that of pure PVC. However, the particles that are deformed into dense monolayers (parallel lines) seen in pure PVC do not seem to appear in the 90/10 blend case. No two-phase morphology could be observed in these high resolution SEMs and blended PVC has genuinely different morphology, although triblock copolymer component is not observed.

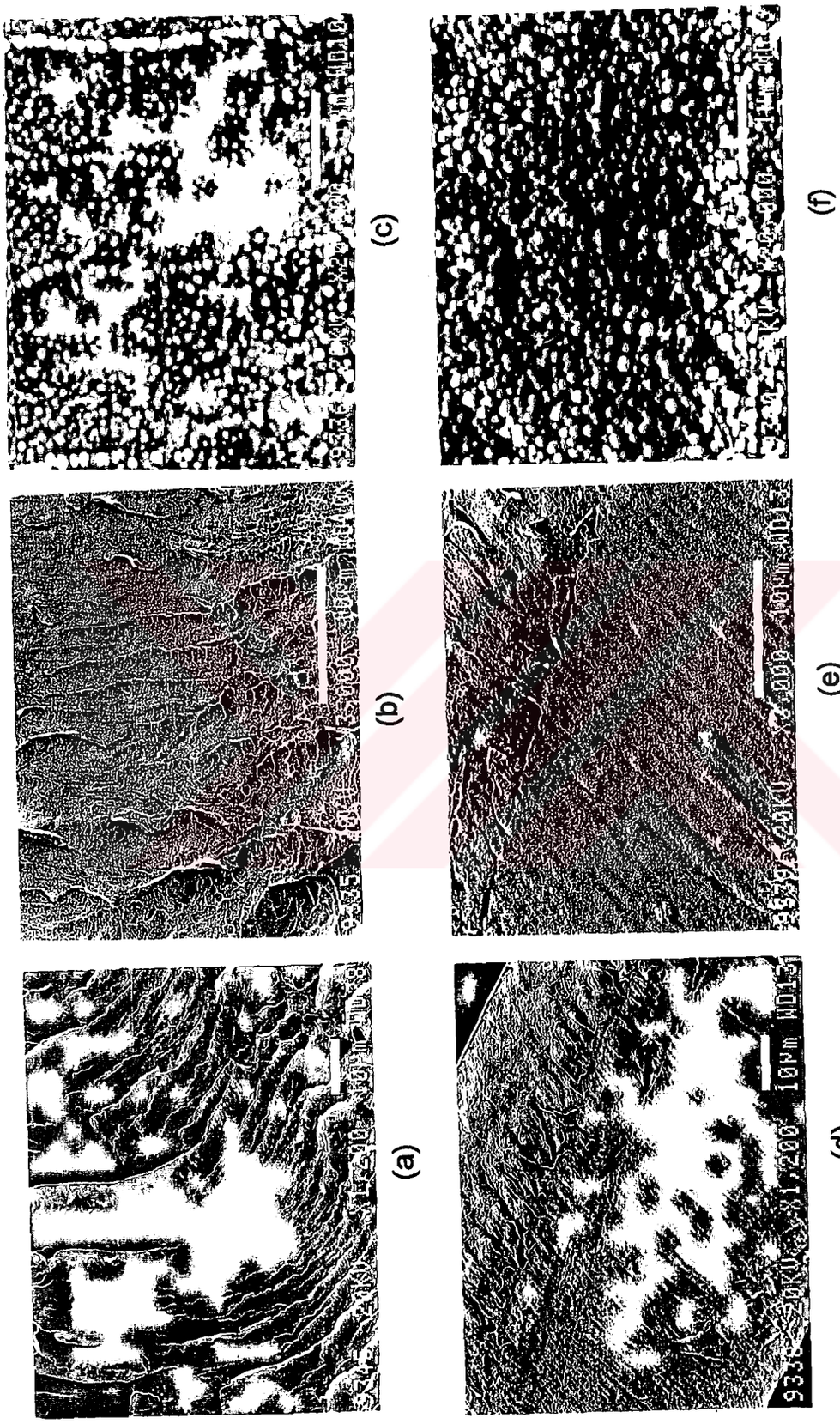


Figure 5.13 SEM micrographs of homopolymer PVC (a-c) and PVC/Tegomer (90/10) blend (d-f)

5.4.2 Binary PVC/PEHA Blends

Figure 5.14 (a-d) shows the SEM images obtained for the PVC homopolymer, binary blends of PVC/PEHA (99/1). Figures 5.14 a and 5.14 b show the fractured surface of the homopolymer PVC, at two different magnifications (X1200 and 20000). SEM image of PVC at X1200 magnification shows a brittle fracture that is consistent with mechanical properties of pure PVC polymer. The typical white spherical structure was observed at high magnification (X20000). These white submicroparticles (1000-2200 A°) were also emphasized in Section 5.4.1.

The fractured surface morphology of PVC/PEHA binary blends (99/1) is shown in Figures 5.14 c and 5.14 d. PEHA component seems to have an effect on the blend morphology because of the holes appeared on the surface. Also, the average size of the white spherical particles decreased to about 900 A°.

In PVC/PEHA binary blends domain size (the size of voids) may be dependent on the PEHA content as can be seen in Figures 5.15 (a-c). With an addition of 5 wt% PEHA into PVC, the voids seem to increase in size.

5.4.3 Ternary PVC/PEHA/Tegomer Blends

The morphology of binary PVC/PEHA blends was reported in previos section. Figure 5.14 (e,f) and 5.15 (d-f) show the SEM images for the ternary PVC/PEHA/Tegomer (98.01/0.99/1) and PVC/PEHA/Tegomer (90.25/4.75/5), respectively.

The average size of the white spherical particles of PVC decreased to about 900 A° with the addition of PEHA to PVC/PEHA (99/1) blend as mentioned previously. The similar surface structure was also observed for the PVC/PEHA (99/1) blends compatibilized by triblock copolymer, Tegomer (Figures 5.14 e,f). The addition of Tegomer (1 wt%) did not cause a decrease in the size of porous regions as can be seen in Figure 5.14 e however at X20000 magnification, the spherical particles seem to deform into dense monolayers (parallel lines in Figure 5.14 f).

In PVC/PEHA binary blends domain size may be dependent on the PEHA content. With the addition of 5 wt % PEHA into PVC, the voids seem to increase in size. On the other hand, these holes where particles were pulled out during fracture were

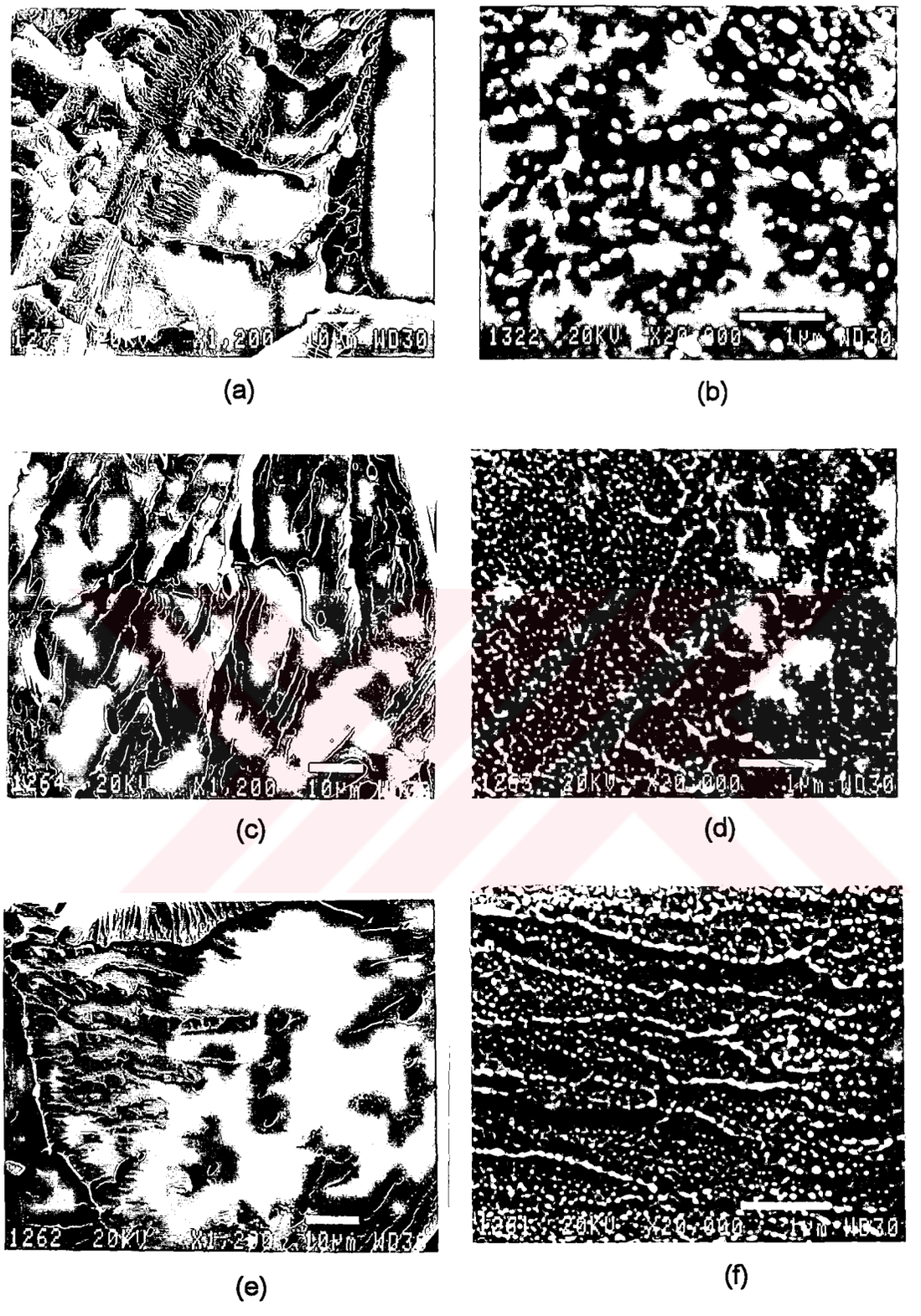


Figure 5.14 SEM micrographs of homopolymer PVC (a,b); binary PVC/PEHA (99/1) blend (c,d) and ternary PVC/PEHA/Tegomer (98.01/0.99/1) blend (e,f)

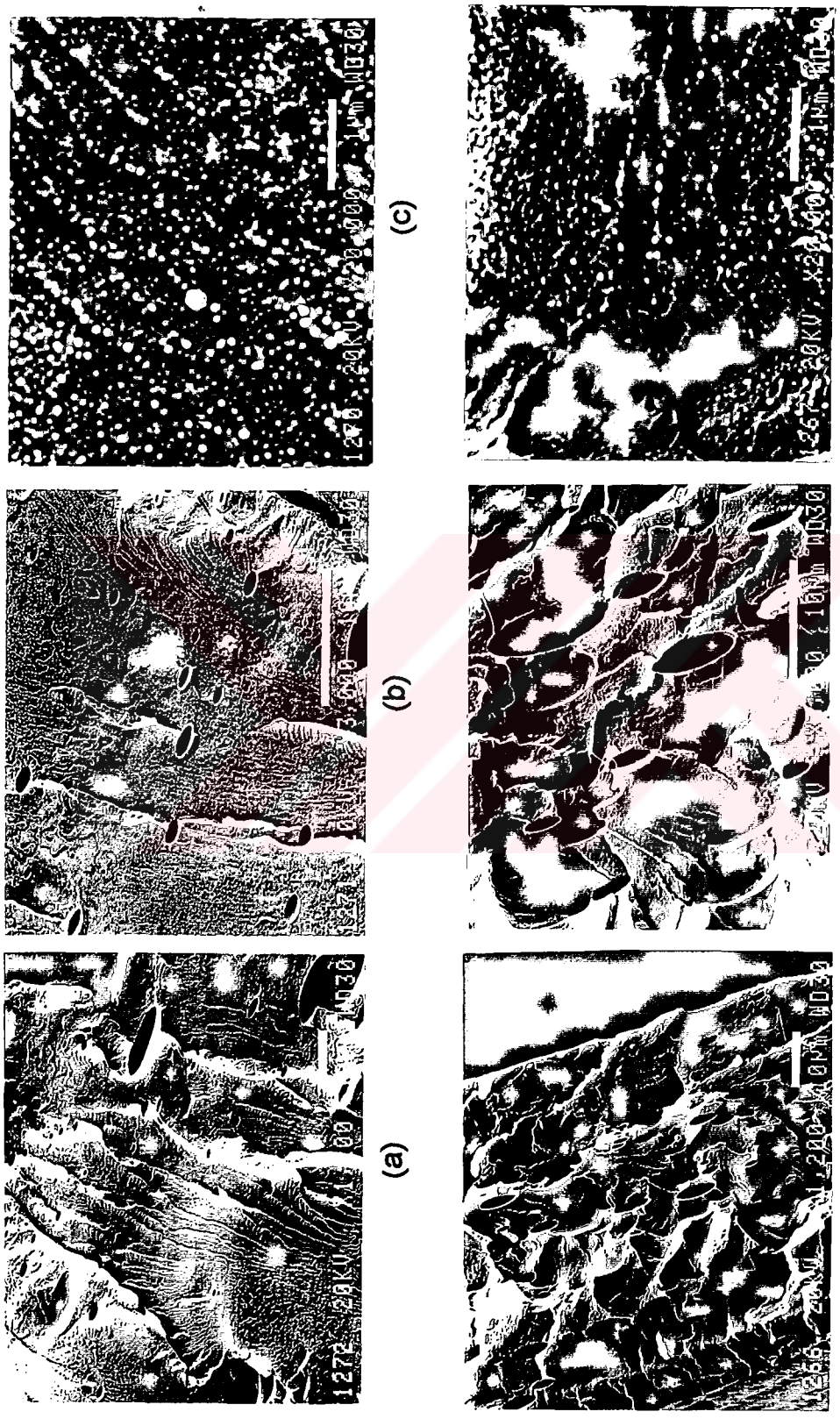


Figure 5.15 SEM micrographs of binary PVC/PEHA (95/5) blend (a-c) and ternary PVC/PEHA/Tegomer (90.25/4.75/5) blend(d-f)

changed in size also when we add 5 wt % Tegomer into the PVC/PEHA blend system. In Figures 5.15 d and 5.15 e, the Tegomer addition seems to be effective on the surface morphology of the blend since the number and also the size of the voids increased. Although we expected that copolymer addition as a compatibilizer may reduce the interfacial tension in the binary blend causing a decrease in the domain size of the dispersed phase as reported earlier for a similar system[19], SEM micrographs of ternary blends PVC/PEHA/Tegomer (98.01/0.99/1 and 90.25/4.75/5) did not exhibit such a morphology. Consequently, we can not claim that ternary blends of PVC/PEHA/Tegomer are one phase systems although at X20000 magnifications, all SEM micrograps of binary and ternary blends exhibit similar morphologies with pure PVC homopolymer (Figures 5.14 (d,f) and 5.15 (c,f)) and no two-phase morphologies could be detected at this magnification.

5.5 VISCOSITY MEASUREMENTS OF BLENDS

The reduced viscosity measurement is adopted and attempted to elucidate the compatibility of the polymer blends. The compatibility of the polymer blend mixtures is characterized by the parameter Δb, from the Krigbaum and Wall theory[131] as reported earlier in Section 4.4.6.

5.5.1 Binary PVC/Tegomer Blends

Specific viscosities (η_{spm}) of all blends were determined in THF at 25°C. Figure 5.16 shows the intrinsic viscosity values vs. C for PVC and Tegomer. The graphs are linear and the points are fitted to the straight line very well. The intercept of the line with y-axis gives the intrinsic viscosities, $[\eta]$ of the corresponding polymer solutions.

Intrinsic viscosity and b values of the polymers (PVC and Tegomer) and the binary PVC/Tegomer blends were shown in Table 5.8.

Δb values were calculated by using Equation 4.5 in Section 4.4.6. The values of Δb for PVC/Tegomer blends are positive at all mixture compositions. Positive values of

Δb refer to the attractive interactions and compatibility. The change in Δb values with Tegomer content in binary PVC/Tegomer blends were presented in Figure 5.17.

5.5.2 Binary PVC/PEHA Blends

The intrinsic viscosity values vs. C for PEHA are also shown in Figure 5.16. The graphs are also linear and the points are fitted to the straight line. Intrinsic viscosity and b values of the homopolymer, PEHA and the binary PVC/PEHA blends were shown in Table 5.9.

The Δb values are negative at all compositions that we have worked. Negative Δb values refer to the incompatibility.

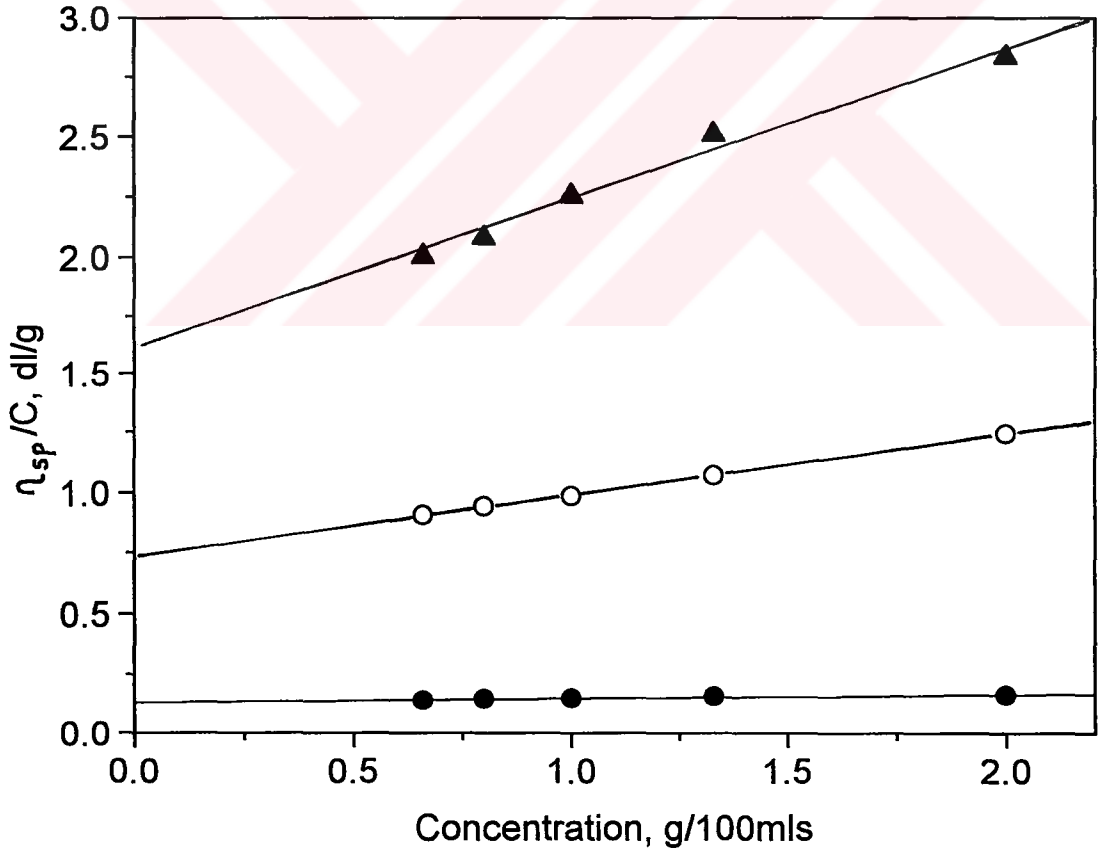


Figure 5.16 η_{sp}/C vs C graph of homopolymers
(▲) PEHA ; (o) PVC; (●) Tegomer

Table 5.8 Intrinsic viscosities and b values of the homopolymers and binary blends of PVC/Tegomer in THF at 25°C.

Sample		[η] (dl/g)	$b^{(a)}$	$b_{12}^{(b)}$	$\Delta b^{(c)} = b_{12} - b_{12}^{*}$
PVC		0.739	0.252	-----	-----
Tegomer		0.1336	0.016	-----	-----
PVC	Tegomer				
99	1	0.776	0.240	0.305	0.196
95	5	0.809	0.190	0.310	0.180
90	10	0.864	0.151	0.453	0.320

(a) slope of η_{spm}/C vs C plot
(b) b_{12} is the interaction coefficient calculated from Eq.4.5
(c) $b^{*}_{12} = (b_{11} + b_{22}) / 2$

5.5.3 Ternary PVC/PEHA/Tegomer Blends

For ternary blends of PVC/PEHA/Tegomer, we have treated PVC/PEHA system as the component 1 and Tegomer as the component 2 in Equation (4.5) in Section 4.4.6. And b_{12}^{*} was calculated from the arithmetical mean of b_{11} and b_{22} in Equation (4.7) in Section 4.4.6. b_{11} and b_{22} were assumed to be experimentally determined values (slopes of η_{sp}/C vs. C graph) for PVC/PEHA system and Tegomer, respectively.

Δb values were calculated and the change in values with Tegomer content in ternary blends was presented in Figure 5.17. The intrinsic viscosity and b values of the ternary blends (PVC/PEHA/Tegomer) were shown in Table 5.9. It is interesting to note that although binary blends of PVC/PEHA give negative values for Δb, ternary blends seem to have positive values, indicating compatibility (Table 5.9). However at some compositions, especially in ternary blends with PEHA concentration 5 and 10 wt %, Δb values are strongly dependent on the Tegomer content (Figure 5.17).

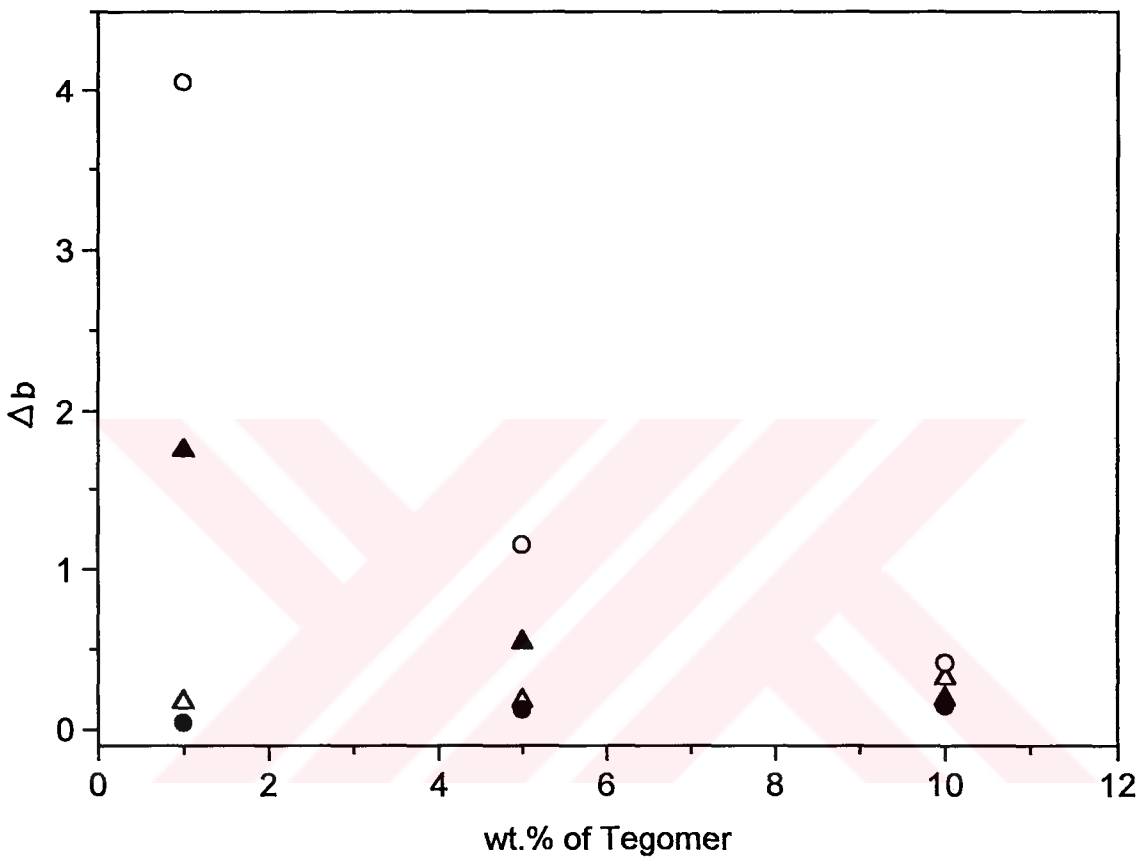


Figure 5.17 Δb vs weight % of Tegomer for binary PVC/Tegomer blend (Δ) ; ternary PVC/PEHA/Tegomer blend with PVC/PEHA ratio: 99/1 (●); ternary PVC/PEHA/Tegomer blend with PVC/PEHA ratio:95/5 (▲); ternary PVC/PEHA/Tegomer blend with PVC/PEHA ratio:90/10 (o)

Table 5.9 Intrinsic viscosities and *b* values of the homopolymer, PEHA and blends in THF at 25°C

Sample			[η] (dl/g)	b [a)]	b_{12} [b)]	Δb [c)]=b_{12}-b_{12}^*
PEHA			1.6048	0.631	---	--- --- ---
PVC	PEHA	Tegomer				
99	1	0	0.778	0.234	0.208	-0.233
98.01	0.99	1	0.620	0.316	0.171	0.046
94.05	0.95	5	0.566	0.328	0.248	0.123
89.1	0.90	10	0.579	0.302	0.269	0.144
95	5	0	0.807	0.217	-0.038	-0.480
94.05	4.95	1	0.696	0.304	1.878	1.755
90.25	4.75	5	0.677	0.305	0.659	0.543
85.5	4.50	10	0.606	0.300	0.308	0.192
90	10	0	0.797	0.226	-0.009	-0.451
89.1	9.9	1	0.776	0.305	4.180	4.059
85.5	9.5	5	0.789	0.303	1.274	1.152
81.0	9.0	10	0.674	0.298	0.536	0.415

[a)] slope of η_{spm}/C vs C plot
[b)] b_{12} is the interaction coefficient calculated from Eq.4.5
[c)] $b_{12}^* = (b_{11} + b_{22})/2$

It is also found in this study that Δb values change with total concentration of the mixture[42,75-77,128]. We have used 2 g/dL as the highest concentration in these viscosity measurements and in the calculation of b_{12} by using Equation 4.5 in Section 4.4.6.. η_{spm} value at this concentration was used.

5.5.4 Discussion About Viscosity Measurements of Binary and Ternary Blends

The intrinsic viscosities of blends of PVC/Tegomer, PVC/PEHA and PVC/PEHA/Tegomer have been studied in THF as a function of blend composition. In order to predict the compatibility of polymer pairs in solution, the interaction parameter term, Δb, obtained from the Krigbaum and Wall theory[131], and the difference in the intrinsic viscosities of the polymer mixtures were used.

The value of Δb for binary PVC/Tegomer blends are positive, indicating attractive interaction between the component polymers. For binary PVC/PEHA blends, Δb values are negative for all compositions, which is an indication of repulsive interaction between components. Negative Δb values refer to the incompatibility. Ternary PVC/PEHA/Tegomer blends have positive Δb values, indicating compatibility although binary blends of PVC/PEHA give negative values for Δb (Table 5.9). However at some compositions, especially in ternary blends with PEHA concentration 5 and 10 wt %, Δb values are strongly dependent on the Tegomer content (Figure 5.17).

5.6 SURFACE PROPERTIES OF BINARY PVC/TEGOMER BLENDS

The surface properties of the blends were investigated by contact angle measurements. Contact angles were measured at room temperature for the water droplet. The results were reproducible at ±2°C in most cases and were given in Table 5.10.

We observed the substantial increase in water contact angles even at very low percentages of Tegomer content. Usually a contact angle of 90° or more indicates silicone-like surfaces[100]. As a control, we measured the contact angle of poly(dimethyl siloxane) homo network which was prepared in a previous work and it was found to be 105°[160]. It is known that siloxane containing copolymers migrate to the air polymer interface due to their low critical surface energy[104,161].

The increase in the water contact angles indicates that the surface accumulation of siloxane segments is not negligible in the blend, and the surface properties of PVC can be modified with the addition of small amounts of Tegomer.

Table 5.10 Water contact angle measurements of PVC/Tegomer blends

Tegomer content in the PVC/Tegomer blend, (wt %)	Contact angle (°)
PVC	80
PCL[a]	85
PDMS[b]	105
Tegomer[a]	88
1	90
2	92
4	94
6	94
8	90
10	91

[a] Films were prepared by melting at 60°C
[b] Poly(dimethylsiloxane) network[160]

5.7 GAS PERMEATION AND DENSITY MEASUREMENTS OF BINARY PVC/TEGOMER BLENDS

The transport behaviour of CO_2, O_2 and N_2 in films of PVC/Tegomer blends has been studied at various temperatures (5-50°C). The results of permeability measurements for CO_2, O_2 and N_2 through the films of homopolymer PVC and PVC/Tegomer (90/10) blends at these temperature ranges are presented in Figure 5.18 and 5.19. The permeability coefficient (P) values of CO_2, O_2 and N_2 increases with temperature. Permeation rates follows Arrhenius relationship with temperature, $P = P_0 \exp(-E_p/RT)$[134]. Activation energies of permeation (E_p) were also calculated for homopolymer PVC and PVC/Tegomer blends. Figure 5.20 shows the increased E_p values through blends with increasing Tegomer content.

The permeability coefficient (P) values of CO_2, O_2 and N_2 tend to increase also with the triblock copolymer content. Figure 5.21 shows the results of permeability measurements through the films of PVC/Tegomer blend at 20°C. From the observed relationship between logarithm of permeability coefficient and copolymer content, we could say that there is no indication of phase inversion for these blends at these compositions. According to the earlier works in the literature, Arrhenius

plots of log P versus blend composition for incompatible blends have to be to S-shaped and this is interpreted as being the result of a phase inversion[58,71-74].

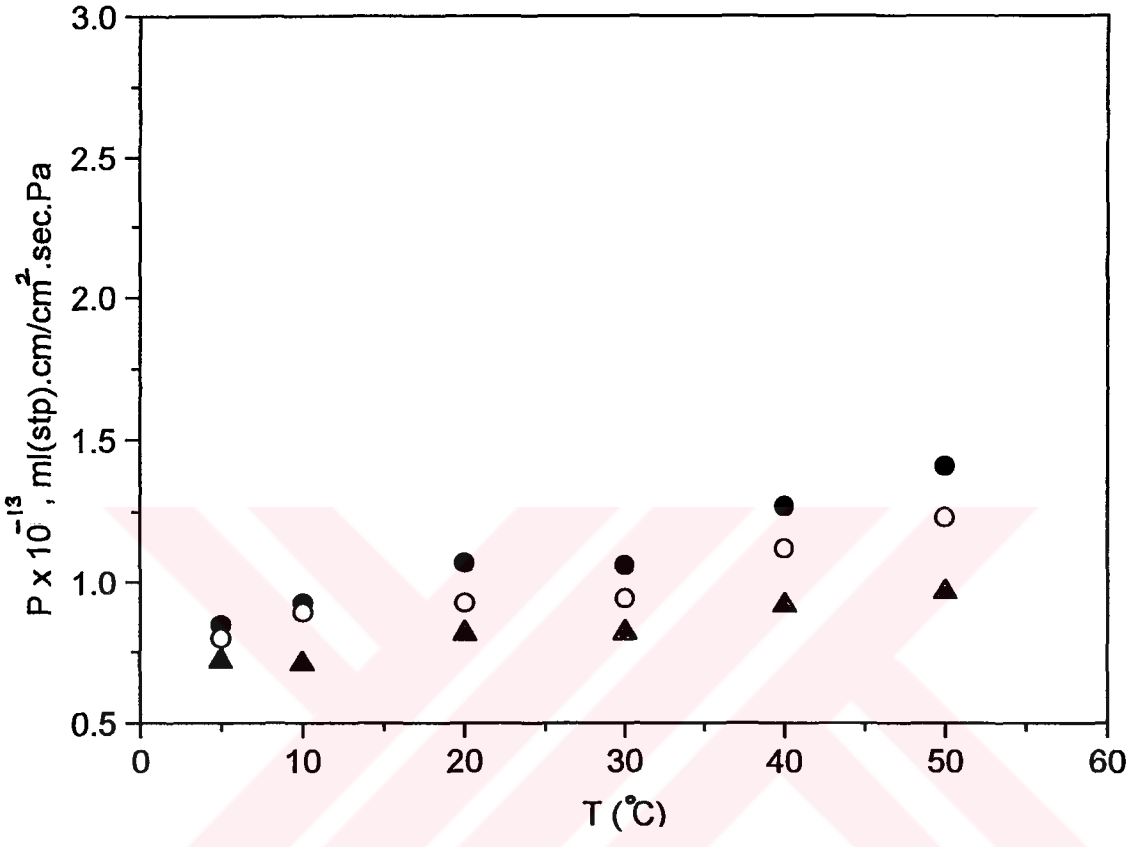


Figure 5.18 Permeability coefficient of (●) CO_2, (o) O_2 and (▲) N_2 vs temperature for PVC homopolymer

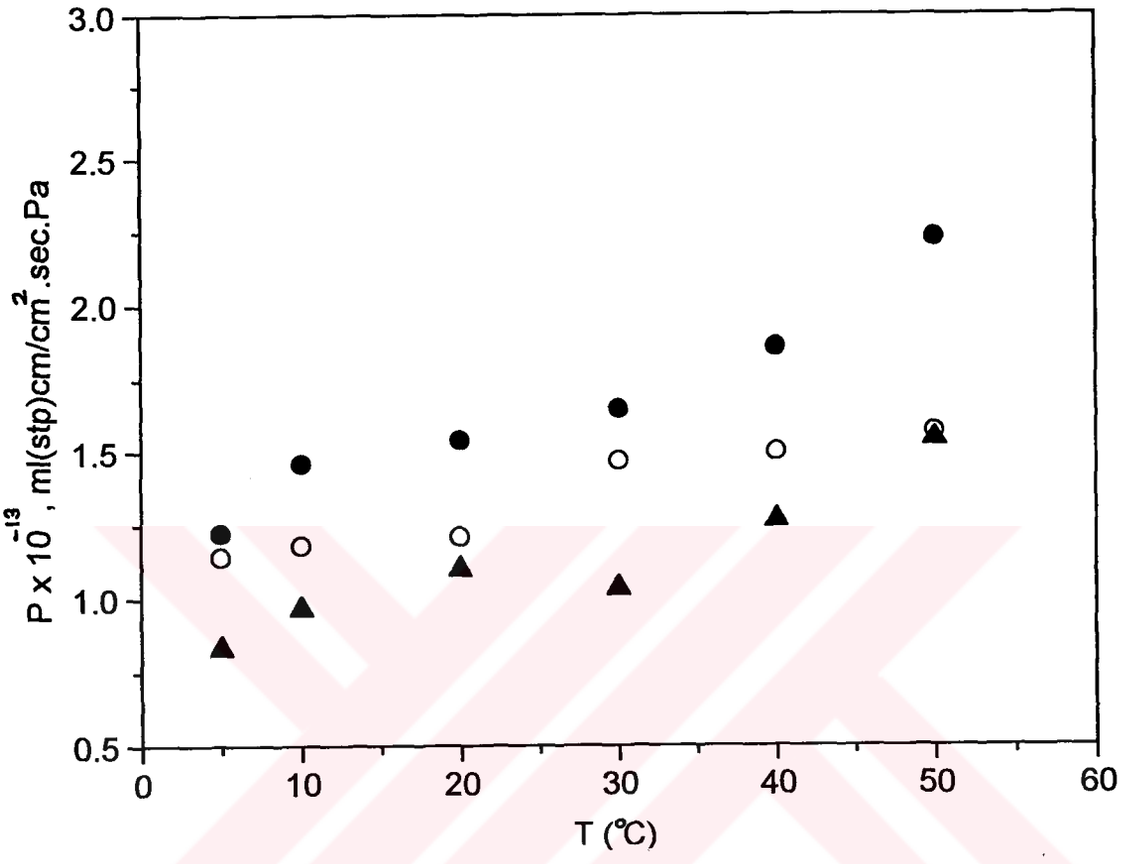


Figure 5.19 Permeability coefficient of (●) CO_2, (o) O_2 and (▲) N_2 vs temperature for PVC/Tegomer (90/10) blend

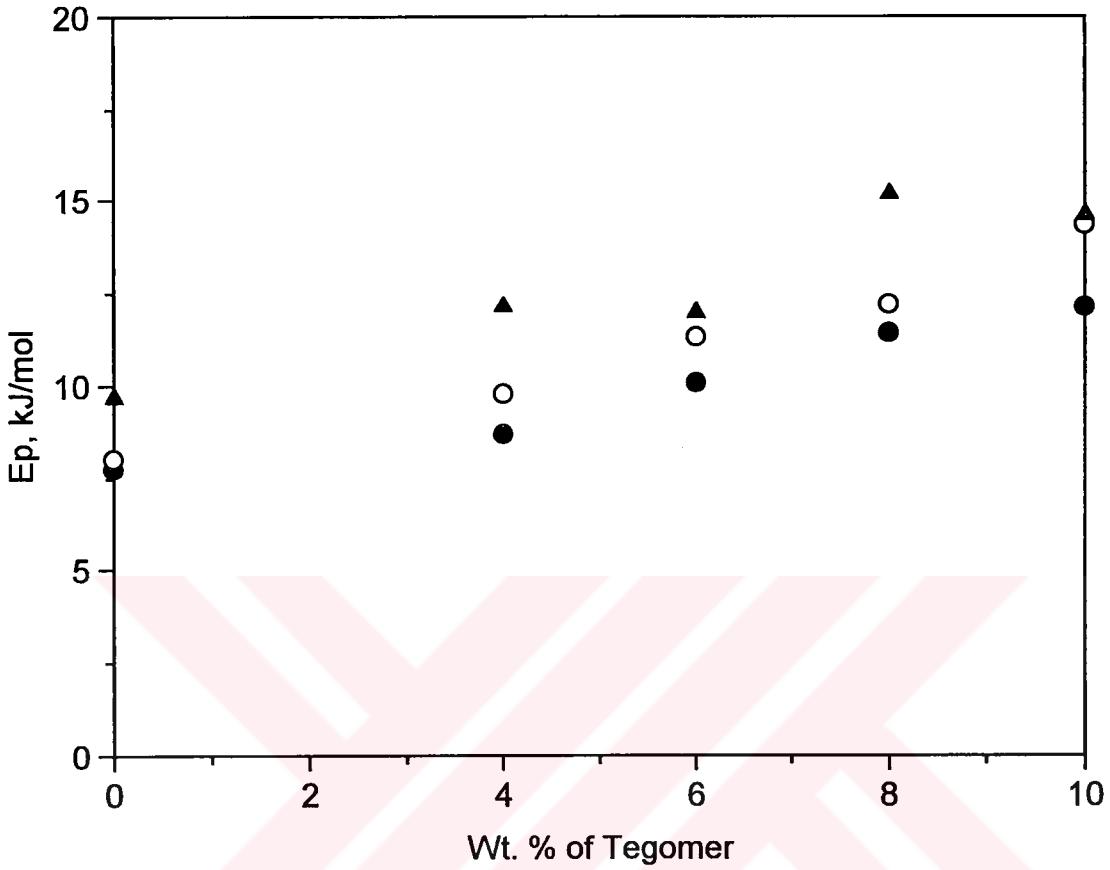


Figure 5.20 Activation energy of permeation for (●) CO_2, (o) O_2 and (▲) N_2 vs polymer blend composition

It is known that plasticization increases the molecular mobility of polymer chains[139]. Therefore, we expect that gas permeation would be easier through polymers having increased chain mobility. Blends of PVC/Tegomer have higher permeability coefficients than pure PVC homopolymer and the increase in gas permeation is relatively greater when we compared the values with PCL/PVC blends reported earlier[58]. This might be due to the effect of PDMS segments in the copolymer. PDMS is the most commonly cited material[134] with its high gas permeability, owing to the flexibility of the Si-O-Si bonds which impart segmental mobility to polysiloxane chains[143]. Hence, Tegomer (triblock PCL-PDMS-PCL copolymer) with PCL seems very appropriate for optimization of gas permeation properties of PVC homopolymer, since it enhances mobility in PVC and increases permeability more effectively than pure PCL.

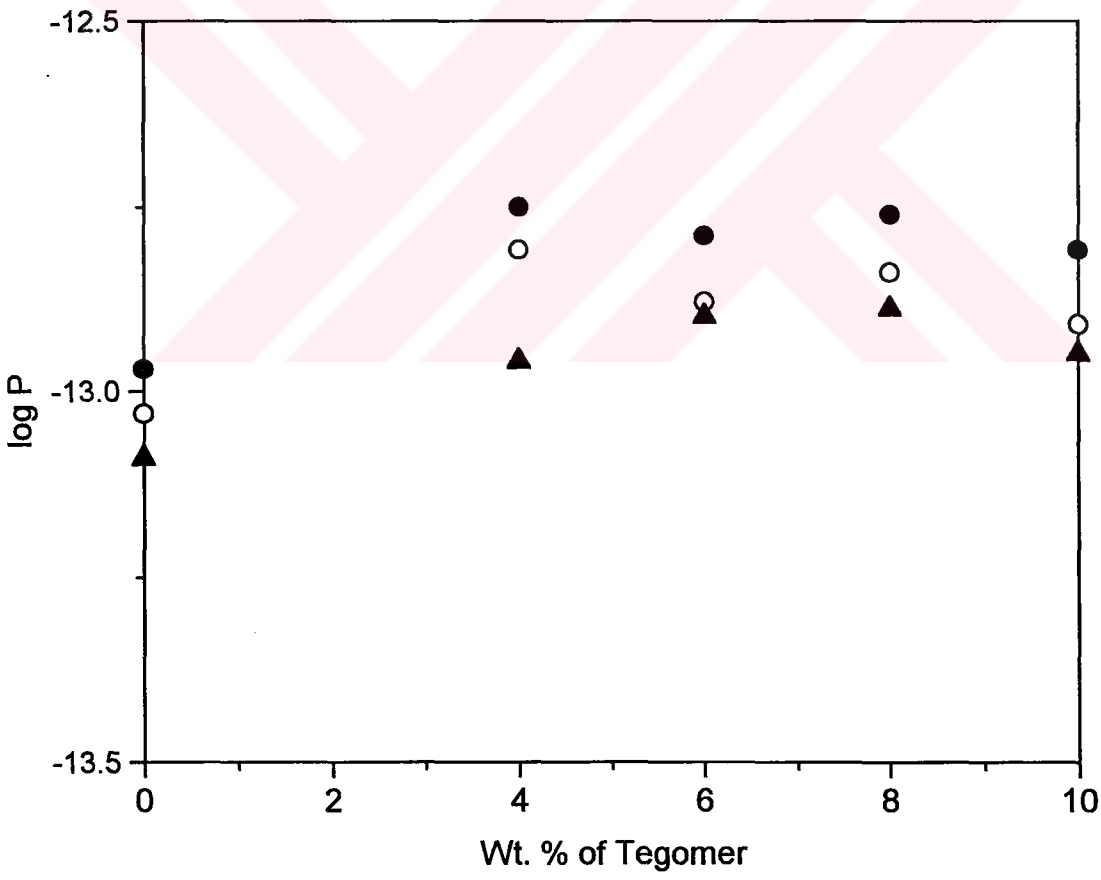


Figure 5.21 Permeability coefficients of (●) CO_2, (o) O_2, (▲) N_2 vs Tegomer composition for PVC/Tegomer blends at 20°C.

P, in a strict sense, is not only a function of the chemical structure of the polymer. The P varies also with the morphology of the polymer and depends on many physical factors such as density, crystallinity, and orientation[133].

Density can be regarded as a measure for the free volume between the molecules of the polymer structure. The experimental density values of PVC/Tegomer blends (1-10%) were compared with the calculated values, assuming volume additivity of the two components. As can be seen in Figure 5.22, experimental densities of the blends are higher than calculated ones. The results of the density measurements suggest that the polymer chains become close packed in the blends and this indicates the molecular interaction and the compatibility of two components, Tegomer and PVC.

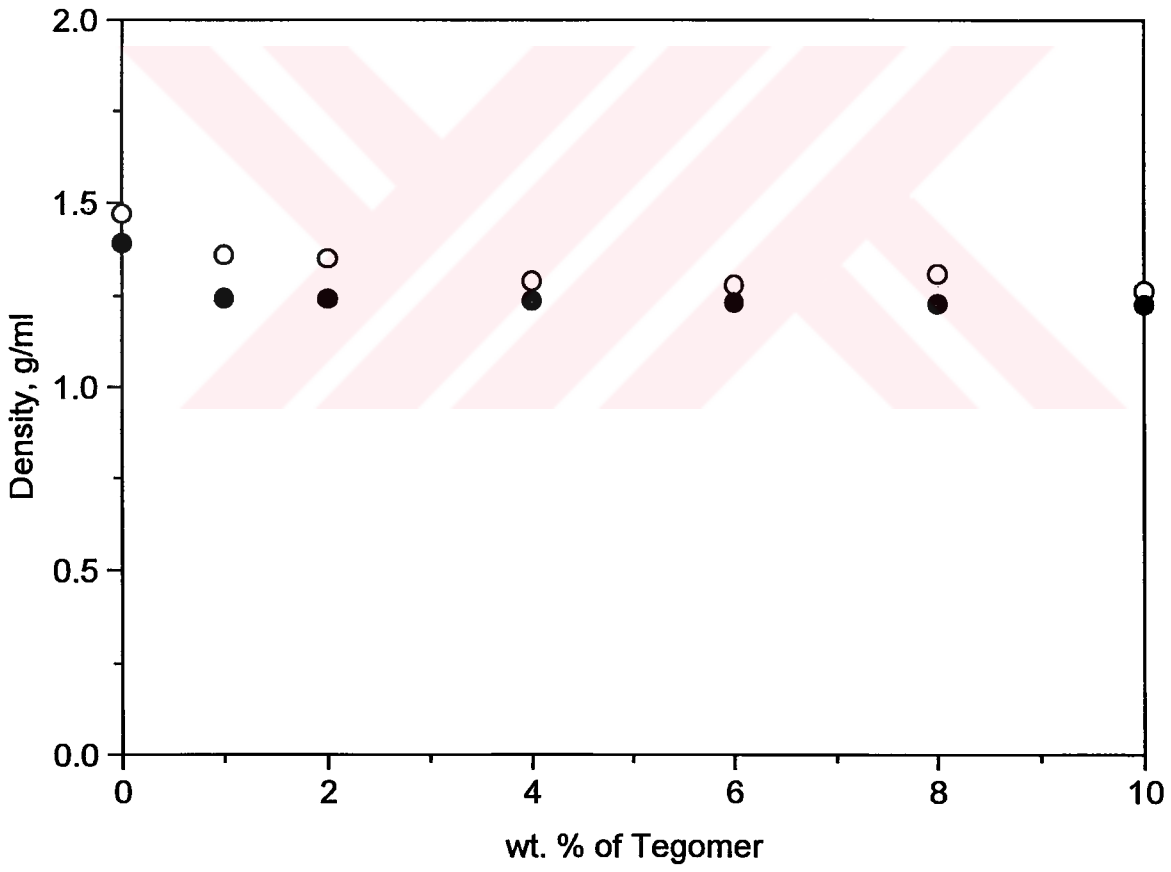


Figure 5.22 Experimental and calculated densities of PVC/Tegomer blends vs Tegomer composition (o) experimental (●) calculated

In conclusion, we can say that permeation rates of CO_2, O_2 and N_2 measured at different temperatures (5-50°C) showed linearity in Arrhenius plot of permeability vs. Tegomer content in the blends. This indicates that PVC/Tegomer blends form a compatible system. Permeation rates follow Arrhenius relationship with temperature. Therefore, the permeability coefficient (P) values increases with temperature. The activation energy of permeation of PVC/Tegomer blends increases with increasing Tegomer content in the blend. It is known that plasticization increases the molecular mobility of polymer chains. Incorporation of Tegomer softens the PVC film and make it more flexible, hence it is suitable for packaging.

CONCLUSIONS AND RECOMMENDATIONS

The conclusion that can be drawn from the experimental findings of this work can be summarized as follows:

Poly(viny chloride) blends were prepared by solvent casting method. The miscibility, thermal, mechanical, morphological, viscosimetric and surface properties of poly(vinyl chloride)/Tegomer, poly(vinyl chloride)/poly(2-ethylhexyl acrylate), and poly(vinyl chloride)/poly(2-ethylhexyl acrylate)/Tegomer blends were investigated bu using several techniques.

The results of DSC, DMTA and FTIR analysis showed that the binary PVC/Tegomer blends are miscible for the composition range of 1-10 wt % Tegomer content. FTIR analysis of blends reveal the existence of specific interactions via hydrogen bonding between the α-hydrogen of PVC and the carbonyl group of PCL in the triblock copolymer (Tegomer). No specific interaction can be seen in blends of PVC/PEHA. The carbonyl absorption band appears at lower frequencies for ternary blends of PVC/PEHA/Tegomer. Shifts to lower frequencies and line broadening can be indicative of hydrogen bonding interactions in the ternary blends.

PVC/Tegomer blend system exhibited a single glass transition(T_g)according to DSC and DMTA results. Binary blends of PVC/PEHA are found to be immiscible according to DSC and viscosity measurements. Ternary blends of PVC/PEHA/Tegomer exhibited also a single T_g behaviour and viscosity measurements indicate some compatibility.

Stress-strain results showed that Tegomer is a very effective plasticizer for PVC, and it has a synergetic effect on the properties of PVC. Even at very low percentages of copolymer content, the stress-strain behaviour of the blends changes dramatically. The extent of mechanical properties was found to be dependent on the amount of the triblock copolymer content. Elongation at break (ε)

of the blend with 10 % Tegomer content exhibits a sharp increase (ε = 472 %) with respect to homopolymer (ε = 8 %). Binary blends of PVC/PEHA show an increase in flexibility with respect to PVC homopolymer. Although tensile strength somewhat decreases with the addition of PEHA, the elongation at break increases remarkably. Tegomer addition makes a synergetic effect on the miscibility and the properties of binary PVC/PEHA blends. Even at very low percentages of copolymer content, the stress-strain behaviour of the blends changes dramatically. The elongation at break of the ternary blend PVC/PEHA/Tegomer (90.25/4.75/5) exhibits a sharp increase with respect to binary blends of PVC/PEHA (95/5), and PVC/Tegomer (95/5). The stress-strain results showed that the ε value of ternary PVC/PEHA/Tegomer (90.25/4.75/5) blend is 381 %. For PVC/PEHA (95/5), ε is 97 %. For PVC/Tegomer (95/5), ε is 95 %.

SEM micrographs of pure PVC and PVC/Tegomer blends show slightly different fractured surfaces, however no two-phase morphology could be observed. In SEM micrographs of binary PVC/PEHA and ternary PVC/PEHA/Tegomer blends, especially PEHA component seems to cause voids on the surface during fracture. However, at higher magnification of SEM images, there is no two-phase morphology.

The surface properties of PVC/Tegomer blends were investigated by contact angle measurements. Contact angle measurements showed that the addition of small amounts of Tegomer may change surface properties of pure PVC homopolymer dramatically. The increase in the water contact angles indicates that the surface accumulation of siloxane segments is not negligible in the blend, and the surface properties of PVC can be modified with the addition of small amounts of Tegomer.

The CO_2, O_2 and N_2 permeability of PVC/Tegomer blend system was determined and a considerable increase in permeability of the blends was observed with respect to homopolymer PVC. The permeability coefficient (P) values of CO_2, O_2 and N_2 increases with temperature. Permeation rates follow Arrhenius ralationship with temperature. It is known that plasticization increases the molecular mobility of polymer chains. Incorporation of Tegomer softens the PVC film and make it more flexible, hence it is suitable for packaging. PVC/Tegomer blends provide an

improvement in physical properties of PVC homopolymer particularly low temperature flexibility at a cost of relatively higher permeability to gases.

The present investigations concerns the preparation of poly(vinyl chloride) based blends. The aim was to improve the physical and mechanical properties of PVC homopolymer and to modify the surface properties of PVC with siloxane containing copolymers. It was observed that Tegomer is a very effective plasticizer for PVC, and it has a synergetic effect on the properties of PVC. Tegomer addition also makes a synergetic effect on the miscibility of binary PVC/PEHA blends. Even at very low percentages of copolymer content, the mechanical properties of the blends changes dramatically. Pure PVC and the blends showed slightly different fractured surfaces, however no two phase morphology could be observed. The surface properties of PVC were modified with the addition of small amounts of Tegomer. For future studies, experiments may be performed to obtain new polymer blend systems which have superior and desirable properties.

REFERENCES

[1] UTRACKI, L.A., Polymer Alloy and Blends:Thermodynamics and Rheology, Hanser Publishers, New York, (1989)

[2] MARTUSCELLI, E., PALUMBU, R. and KRYSZEWSKI, M., Polymer Blends, Plenum Press, New York, (1980)

[3] OLABISI, O., ROBESON, L.M. and SHAW, M.T., Polymer-Polymer Miscibility, Academic Press, New York, (1979)

[4] PAUL, D.R. and NEWMAN, S., Polymer Blends, Academic Press, London, (1978)

[5] SÖLC, K., Polymer Compatibility and Incompatibility, Principles and Practices, Vol 2, (1980)

[6] FRIED, J.R., Polymer Science and Technology, Prentice Hall Inc., New Jersey, (1995)

[7] SEMERAK, S.W. and FRANK, C.W., Excimer Fluorescence as a Molecular Probe of Blend Miscibility: Comparison with Differential Scanning Calorimetry, Advances in Chemistry Series, Vol 203, pp. 757, (1983)

[8] OLABISI, O., Polymer Compatibility by Gas-Liquid Chromatography, Macromolecules, Vol 8, pp. 316, (1975)

[9] BARLOW, J.W. and PAUL, D.R., The Importance of Enthalpic Interactions in Polymeric Systems, Polymer Engineering Science, Vol 27, pp.1482, (1987)

[10] CANGELOSI, F. and SHAW, M.T., Hydrogen Bonding in Polymer Systems, Polymer Engineering and Science, Vol 23, pp. 669, (1983)

[11] PAINTER, P.C., PARK, Y. and COLEMAN, M.M., Hydrogen Bonding in Polymer Blends, Macromolecules, Vol 21, pp. 66, (1988)

[12] COLEMAN, M.M., SERMAN, C.J., BHAGWAGAR, D.E. and PAINTER, P.C., A Practical Guide to Polymer Miscibility, Polymer Reviews, Vol 31, pp. 1187, (1990)

[13] EKLIND, M., SCHHANTZ, S., MAURER, F.H.J., JANNASCH, P. and WESSLEN, B., Characterization of the Interphase in PPO/PMMA Blends Compatibilized by P(S-g-EO), Macromolecules, Vol 29, pp. 984, (1996)

[14] HEUSCHEN, J., VION, J.M., JEROME, R. and TEYSSIE, Ph., Polycaprolactone Based Block Copolymers: 4 Interfacial Activity in Poly(Vinyl Chloride) Containing Polyblends, Polymer, Vol 31, pp. 1473, (1990)

[15] BRAUN, D., FISCHER, M. and HELLMANN, G.P., Block-graft Copolymers as Compatibilizers in Polymer Blends, Polymer, Vol 37(17), pp. 3871, (1996)

[16] GHODGAONKAR, P. and SUNDARARAJ, U., Effect of Compatibilization in Immiscible Polymer Blends, Polymer Materials Science and Engineering, Vol 75, pp. 439, (1996)

[17] CHUNG, T.C. and RHUBRIGHT, D., Polypropylene-graft-Polycaprolactone: Synthesis and Applications in Polymer Blends, Macromolecules, Vol 27, pp. 1313, (1994)

[18] FENG, H., TIAN, J. and YE, C., Compatibilization Effect of Graft Copolymer on Immiscible Polymer Blends: II. LLDPE/PS/LLDPE-g-PS Systems, Journal of Applied Polymer Science, Vol 61, pp. 2265, (1996)

[19] JANNASCH, P., GUNNARSSON, O. and WESSLEN, B., Compatibilizing Effects of Poly(syrene-graft-ethylene oxide) in Blends of Polystyrene and Butyl Acrylate Polymers, Journal of Applied Polymer Science, Vol 59, pp. 619, (1996)

[20] KOKLAS, S.N., SOTIROPOULOU, D.D., KALLITSIS, J.K. and KALFOGLOU, N.K., Compatibilization of Chlorinated Polyethylene/Poly(vinyl chloride) Blends with Epoxidized Natural Rubber, Vol 32(1), pp. 66, (1991)

[21] AJJI, A. and UTRACKI, L.A., Interphase and Compatibilization of Polymer Blends, Polymer Engineering Science, Vol 36(12), pp. 1574, (1996)

[22] PERRIN, P. and PRUDHOMME, R.E., Miscibility Behavior of Ternary Polymethacrylate-Based Blends, Acta Polymer, Vol 44, pp. 307, (1993)

[23] AMEDURI, B. and PRUDHOMME, R.E., Miscibility Behavior of Ternary Poly(caprolactone)/Poly(vinyl chloride)/Chlorinated Poly(vinyl chloride) Blends, Polymer, Vol 29, pp. 1052, (1988)

[24] XI, X., XIANDE, M. and KEQIANG, C., A Study on Poly(vinyl chloride) Blends with Chlorinated Polyethylene and Polyethylene, Polymer Engineering Science, Vol 27(6), pp. 391, (1987)

[25] WANG, Y. and CHEN, S., Polymer Compatibility: Ternary Blends of Poly(vinyledene chloride-co-vinyl chloride), Poly(vinyl chloride) and Poly(acrylonitrile-co-butadiene), Polymer Engineering Science, Vol 21, pp. 47, (1981)

[26] HUARNG, J.C., MIN, K. and WHITE, J.L., Miscibility and Morphology of the

Poly(vinyl chloride)/Styrene-Acrylonitrile Copolymer/Poly(methyl methacrylate) Ternary Blend System, Polymer Engineering Science, Vol 28, pp. 1085, (1988)

[27] LEE, Y. and CHEN, C., Properties of PVC/CPE/EPDM Polyblends, Journal of Applied Polymer Science, Vol 33, pp. 1231, (1987)

[28] JO, W.H., KWON, I.H. and KWON, Y.K., Phase Behavior of Ternary Polymer Blends of Poly(styrene-co-acrylic acid), Poly(ethylene oxide) and Poly(methyl methacrylate), Macromolecules, Vol 24, pp. 4708, (1991)

[29] LANDRY, C.J.T., YANG, H. and MACHELL, J.S., Miscibility and Mechanical Properties of a Ternary Polymer Blend: Polystyrene/Polycarbonate/Tetramethyl polycarbonate, Polymer, Vol 32, pp. 44, (1991)

[30] REMIRO, P.M. and NAZABAL, J., Phase Behavior of Ternary PBT-PC/Phenoxy Blends, Journal of Applied Polymer Science, Vol 42, pp. 1475, (1991)

[31] VANNESTE, M., GROENINCKX, G. and REYNAERS, H., Miscibility, Crystallization and Melting Behavior and Semicrystalline Morphology of Ternary Blends of Poly(ε-caprolactone), Poly(hydroxy ether of bisphenol A) and Poly(styrene-co-acrylonitrile), Polymer, Vol 38, pp. 4407, (1997)

[32] EGUIAZABAL, J.I., IRUIN, J.J., CORTAZAR, M. and GUZMAN, G.M., Ternary Polymer Mixtures: Polyacrylate/Phenoxy/Poly(butylene terephthalate), Journal of Applied Polymer Science, Vol 32, pp. 5945, (1986)

[33] GUO, H., GVUZDIC, N.V. and MEIER, D.J., Phase Morphology and Compatibilization of Multicomponent Polymer Blends, Polymer Materials Science and Engineering, Vol 75, pp. 444, (1996)

[34] POMPOSO, J.A., CALAHORRA, E., EGUIAZABAL, J.I. and CORTAZAR, M., Miscibility Behavior of Ternary Poly(methyl methacrylate)/Poly(ethyl methacrylate)/ Poly(p-vinylphenol) Blends, Macromolecules, Vol 26, pp. 2104, (1993)

[35] POMPOSO, J.A., CALAHORRA, E. and CORTAZAR, M., Hydrogen Bonding in Polymer Systems Involving Poly(p-vinylphenol) 2. Ternary Blends with Poly(ethyl methacrylate) and Poly(methyl methacrylate), Macromolecules, Vol 27, pp. 252, (1994)

[36] JANNASCH, P. and WESSLEN, B., Poly(styrene-graft-ethylene oxide) as a Compatibilizer in Polystyrene/Polyamide Blends, Journal of Applied Polymer Science, Vol 58, pp. 753, (1995)

[37] FLORES, R., PEREZ, J., CASSAGNAU, P., MICHEL, A. and CAVAILLE, J.Y., Dynamic Mechanical Behavior of Poly(vinyl chloride)/Poly(methyl

methacrylate) Polymer Blends, Journal of Applied Polymer Science, Vol 60, pp. 1439, (1996)

[38] SCHMIDT, J.J., GARDELLA, J.A.JR. and SALVATI, L.JR., Surface Studies of Polymer Blends 2. ESCA and IR Study of Poly(methyl methacrylate)/Poly(vinyl chloride) Homopolymer Blends, Macromolecules, Vol 22, pp. 4489, (1989)

[39] PARMER, J.F., DICKINSON, L.C., CHIEN, J.C. and PORTER, R.S., Miscibility of Poly(methacrylate)/Poly(vinyl chloride) Blends, Macromolecules, Vol 22, pp. 1078, (1989)

[40] WALSCH, D.J. and McKEOWN, J.G., Compatibility of Polyacrylates and Polymethacrylates with Poly(vinyl chloride) 1. Compatibility and Temperature Variation, Polymer, Vol 21, pp. 1330, (1980)

[41] TREMBLAY, C. and PRUDHOMME, R.E., Miscible Blends of Amorphous Polymers, Journal of Polymer Science Polymer Physics Edition, Vol 22, pp. 1857, (1984)

[42] LEE, W. and LAI, C., Investigation of the Compatibility for PVC Blend by Reduced Viscometric Method, Journal of Applied Polymer Science, Vol 66, pp. 761, (1997)

[43] LEE, W. and LAI, C., Mechanical Properties of Poly(vinyl chloride) Blends and Corresponding Graft Copolymers, Journal of Applied Polymer Science, Vol 67, pp. 307, (1998)

[44] SATU, T., TSUJITA, Y., TAKIZAWA, A. and KINOSHITA, T., Miscibility and Volume Changes of Mixing in the Poly(vinyl chloride)/Poly(methy methacrylate) Blend System, Macromolecules, Vol 24, pp. 158, (1991)

[45] FLORES, R., PEREZ, J., CASSAGNAU, P., MICHEL, A. and CAVAILLE, J.Y., Dynamic Mechanical Behavior of Poly(vinyl chloride)/Poly(methyl methacrylate) Polymer Blends, Journal of Applied Polymer Science, Vol 60, pp. 1439, (1996)

[46] ZHAO, Y. and PRUDHOMME, R.E., A Nonradiative Energy Transfer Fluorescence Study: Blends of Poly(vinyl chloride) and Poly(methyl methacrylate) of Different Tacticities and Molecular Weights, Macromolecules, Vol 23, pp. 713, (1990)

[47] WLOCHOWICZ, A. and JANICKI, J., The Supermolecular Structure of Poly(vinyl chloride) and Poly(methyl methacrylate) Blends, Journal of Applied Polymer Science, Vol 38, pp. 1469, (1989)

[48] SHEN, S. and TORKELSON, J.M., Miscibility and Phase Separation in Poly(vinyl chloride)/Poly(methyl methacrylate) Blends: Study of Thermodynamics by Thermal Analysis, Macromolecules, Vol 25, pp. 721, (1992)

[49] SCHURER, J.W., DEBOER, A. and CHALLA, G., Influence of Tacticity of Poly(methyl methacrylate) on the Compatibility with Poly(vinyl chloride), Polymer, Vol 16, pp. 201, (1975)

[50] ALBERT, B., JEROME, R., TEYSSIE, P., SMYTH, G., BOYLE, N.G. and McBRIERTY, V.J., Investigation of Compatibility in Syndiotactic Poly(methyl methacrylate)/ Poly(vinyl chloride) Blends, Macromolecules, Vol 18, pp. 388, (1985)

[51] HUBBELL, D.S. and COOPER, S.L., The Physical Properties and Morphology of Poly(ε-caprolactone) Polymer Blends, Journal of Applied Polymer Science, Vol 21, pp. 3035, (1977)

[52] PRUDHOMME, R.E., Miscibility Phenomena in Polyester/Chlorinated Polymer Blends, Polymer Engineering Science, Vol 22, pp. 90, (1982)

[53] VARNELL, D.F, MOSKALA, E.J., PAINTER, M.C. and COLEMAN, M.M., On the Application of Fourier Transform Infrared Spectroscopy to the Elucidation of Specific Interactions in Miscible Polyester/Poly(vinyl chloride) Blends, Polymer Engineering Science, Vol 23, pp. 658, (1983)

[54] COLEMAN, M.M. and ZARIAN, J., Fourier Transform Infrared Studies of Polymer Blends II. Poly(ε-caprolactone)/Poly(vinyl chloride) System, Journal of Polymer Science Part B, Vol 17, pp. 837, (1979)

[55] KHAMBATTA, F.B., WARNER, F., RUSSELL, T. and STEIN, R.S., Small Angle X-Ray and Light Scattering Studies of the Morphology of Blends of Poly(ε-caprolactone) with Poly(vinyl chloride), Journal of Polymer Science Part B, Vol 14, pp. 1391, (1976)

[56] KOLESKE, J.V. and LUNDBERG, R.D., Lactone Polymers 1. Glass Transition Temperature of Poly(ε-caprolactone) by means of Compatible Polymer Mixtures, Journal of Polymer Science Part A-2, Vol 7, pp. 795, (1969)

[57] AUBIN, M., BUSSIERES, D., DUCHESNE, D. and PRUDHOMME, R.E., Miscibility of Polylactone/Chlorinated Polymer Blends and Polymer Compatibility and Incompatibility, MMI Press Symposium Series, Michigan, Vol 2, pp. 223, (1980)

[58] SHUR, Y.J. and RANBY, B., Gas Permeation of Polymer Blends III. Poly(vinyl chloride)(PVC)/Acrylonitrile-butadiene-styrene (ABS) terpolymer, Journal of Macromolecular Science and Physics, Vol B14, pp. 565, (1977)

[59] ROBESON, L.M., Crystallization Kinetics of Poly(ε-caprolactone) from Poly(ε-caprolactone)/Poly(vinyl chloride) Solutions, Journal of Applied Polymer Science, Vol 17, pp. 3607, (1973)

[60] AUBIN, M., BEDARD, Y., MORRISSETTE, M.F. and PRUDHOMME, R.E., Miscible Blends Prepared from Two Crystalline Polymers, Vol 21, pp.

233, (1983)

[61] ZHANG, H. and PRUDHOMME, R.E., Determination of Thermodynamic Polymer-Polymer Interaction Parameter of Miscible Blends Prepared from Two Crystalline Polymers, Journal of Polymer Science Polymer Physics Edition, Vol 24, pp. 723, (1987)

[62] RUSSELL, T.P. and STEIN, R.S., An Investigation of the Compatibility and Morphology, Journal of Polymer Science Polymer Physics Edition, Vol 21, pp. 999, (1983)

[63] ROBESON, L.M., Miscible Blends of Poly(vinyl chloride) and Poly(butylene terephthalate), Journal of Polymer Science Polymer Letters Edition, Vol 16, pp. 261, (1978)

[64] AUBIN, M. and PRUDHOMME, R.E., Preparation and Properties of Poly(valerolactone), Polymer, Vol 22, pp. 1223, (1981)

[65] AUBIN, M. and PRUDHOMME, R.E., Studies of Polylactone-Poly(vinyl chloride), Polylactone- Poly(vinyl fluoride), Polylactone-Poly(vinyledene fluoride), Journal of Polymer Science Polymer Physics Edition, Vol 19, pp. 1245, (1981)

[66] ZISKA, J.J., BARLOW, J.W. and PAUL, D.R., Miscibility in PVC-Polyester Blends, Polymer, Vol 22, pp. 918, (1981)

[67] RANBY, B., Two Component Polymer Systems: Physical Properties as Related to Compatibility and Interaction, Journal of Polymer Science, Vol 51, pp. 89, (1975)

[68] SVANSON, S. and ELMQVIS, C., Phase Relations in Poly(vinyl chloride)/Ethylene-vinyl acetate Copolymer Blends with Low Contents of the EVA Copolymer, Journal of Applied Polymer Science, Vol 21, pp. 943, (1977)

[69] ELMQVIST, C. and SVANSON, S., NMR Investigation of Phase Relations in PVC [Poly(vinyl chloride)]-EVA (Ethylene-vinyl acetate) Copolymer Blends with Impact Strength, European Polymer Journal, Vol 11, pp. 789, (1975)

[70] MARCINCIN, K., ROMANOV, A. and PULLACK, V., Study of Dynamic Mechanical Properties of Poly(vinyl chloride)/Ethylene-vinyl acetate Copolymer and Poly(vinyl chloride)-Chlorinated ethylene-vinyl acetate Copolymer Mixtures, Journal of Applied Polymer Science, Vol 16, pp. 2239, (1972)

[71] SHUR, Y.J. and DARBY, J.R., Gas Permeation of Polymer Blends 1. PVC/Ethylene-vinyl acetate (EVA) Copolymer, Journal of Applied Polymer Science, Vol 19, pp. 1337, (1975)

[72] SHUR, Y.J. and DARBY, J.R., Gas Permeation of Polymer Blends 2. PVC/Acrylonitrile-butadiene Copolymer Blends, Journal of Applied

Polymer Science, Vol 19, pp. 2143, (1975)

[73] SHUR, Y.J. and DARBY, J.R., Gas Permeation of Polymer Blends 3. PVC/Chlorinated polyethylene, Journal of Applied Polymer Science, Vol 20, pp. 3105, (1976)

[74] SHUR, Y.J. and DARBY, J.R., Gas Permeation of Polymer Blends 3. PVC/Ethylene-vinyl acetate (EVA) Copolymer, Journal of Applied Polymer Science, Vol 20, pp. 3121, (1976)

[75] AKOVALI, G. and ASLAN, S., A Compatibility Study of Waste Poly(ethylene terephthalate) with Poly(vinyl chloride), Journal of Applied Polymer Science, Vol 50, pp. 1747, (1993)

[76] KULSHRESHTHA, A.K., SINGH, B.P. and SHARMA, Y.N., Viscometric Determination of Compatibility in PVC/ABS Polyblends 1. Viscosity-Composition Plots, European Polymer Journal, Vol 24, pp. 29, (1988)

[77] SHIH, K.S. and BEATTY, C.L., Blends of Polycarbonate and Poly(hexamethylene sebacate) 4. Polymer Blend Intrinsic Viscosity Behavior and Its Relationship to Solid State Blend Compatibility, British Polymer Journal, Vol 22, pp. 11, (1990)

[78] BELORGEY, G. and PRUDHOMME, R.E., Miscibility of Polycaprolactone/Chlorinated Polyethylene Blends, Journal of Polymer Science Polymer Physics Edition, Vol 20, pp. 191, (1982)

[79] AUBIN, M. and PRUDHOMME, R.E., Miscibility in Blends of Poly(vinyl chloride) and Polylactones, Macromolecules, Vol 13, pp. 365, (1980)

[80] COLEMAN, M.M. and VARNELL, D.F., Fourier Transform Infrared Studies of Polymer Blends 3. Poly(β-propiolactone)/Poly(vinyl chloride) System, Journal of Polymer Science Polymer Physics Edition, Vol 18, pp. 1403, (1980)

[81] PIGLOWSKI, J. and SKOWROUSKI, T., Properties of Poly(vinyl chloride) Modified with Thermoplastic Polyurethane Elastomers, Angewante Makromolekulare Chemie, Vol 85, pp. 129, (1980)

[82] KALFOGLOU, N.K., Property-Composition Dependence of Polyurethane/Poly(vinyl chloride) Polyblends, Journal of Applied Polymer Science, Vol 26, pp. 823, (1981)

[83] BANDYOPADHYAY, P.K. and SHAW, M.T., Viscoelastic and Engineering Properties of Poly(vinyl chloride) Plasticized with Polycaprolactone Based Polyurethanes, Journal of Applied Polymer Science, Vol 27, pp. 4323, (1982)

[84] XIAO, F.F. and SHEN, D.Y., Studies On The Morphology of Blends of Poly(vinyl chloride) and Segmented Polyurethanes, Polymer, Vol 28, pp. 2335, (1987)

[85] BANDYOPADHYAY, P.K. and SHAW, M.T., Viscoelastic and Engineering Properties of Poly(vinyl chloride) Plasticized with Polycaprolactone Based Polyurethanes, Journal of Applied Polymer Science, Vol 27, pp. 4323, (1982)

[86] ZHU, Y.Q., HUANG, Y.J. and CHI, Z.G., Compatibility of the Blends of Pus with PVC and the Adhesion Behavior of PU to PVC, Journal of Applied Polymer Science, Vol 56, pp. 1371, (1995)

[87] KIM, S.J., KIM, B.K. and JEONG, H.M., Dynamic Mechanical Properties of Poly(vinyl Chloride) and Polyurethane Carboxylate Blends, Journal of Applied Polymer Science, Vol 51, pp. 2187, (1994)

[88] JAGER, H., VORENKAMP, E.J. and CHALLA, G., LCST Behavior in Blends of PMMA with PVC, Polymer Communications, Vol 24, pp. 290, (1983)

[89] SIEGMANN, A. and HILTNER, A., Impact Modification of Poly(vinyl chloride) with Chlorinated Polyethylene 1. Blend Morphology, Polymer Engineering Science, Vol 26, pp. 869, (1984)

[90] CHEN, C.H., WESSON, R.D., COLLIER, J.R. and LO, Y.W., Studies of Rigid Poly(vinyl chloride) Compounds 1. Morphological Characteristics of Poly(vinyl chloride)/Chlorinated Polyethylene (PVC/CPE) Blends, Journal of Applied Polymer Science, Vol 58, pp. 1087, (1995)

[91] KIM, J.H., BARLOW, J.W. and PAUL, D.R., Miscibility of Poly(vinyl chloride) with Styrene/Acrylonitrile Copolymers, Journal of Polymer Science Polymer Physics Edition, Vol , pp. 2211, (1989)

[92] BUCHDAL, R. and NIELSEN, L.E., Effect of Crystallinity on the Dynamic Mechanical Properties of Polyethylenes, Journal of Polymer Science, Vol 15, pp. 1, (1955)

[93] SCHNEIDER, I.A. and CALUGARU, E.M., The Estimation of Phase Modifications in Polymers by the Method of Molecular Probes in Gas Chromatography, European Polymer Journal, Vol 12, pp. 879, (1976)

[94] DEANIN, R.D. and MOSHAR, C., PVC/ABS Polyblends: Practical Properties and Theoretical Problems, Polymer Preprints, American Chemical Society Division Polymer Chemistry, Vol 15, pp. 403, (1974)

[95] BREUER, H., HAAF, F. and STABENOW, J., Investigations of Rubber Modified PVC, Journal of Macromolecular Science and Physics, Vol B14, pp. 387, (1977)

[96] PAVAN, A., RICCO, T. and RINK, M., High Performance Polymer Blends 2. Density, Elastic Modulus, Glass Transition Temperatures and Heat Deflection Temperature of Poly(vinyl chloride), Material Science and Engineering, Vol 48, pp. 9 (1981)

[97] CONGDON, W.L, BAIR, H.E., KHANNA, S.K., KLEMPNER, D. and FRISCH,

K.C., Polymer Alloys, Plenum, Vol II, pp. 255, New York, (1980)

[98] WANG, C.B. and COOPER, S.L., Morphology and Properties of Poly(vinyl chloride)-Poly(butadiene-co-acrylonitrile) Blends, Journal of Polymer Science Polymer Physics Edition, Vol 21, pp. 11, (1983)

[99] CLAS, S.D. and EISENBERG, A., Miscibility of Poly(vinyl chloride) with Ethyl Acrylate 4-Vinyl Pyridine Copolymers, Journal of Polymer Science Polymer Physics Edition, Vol 22, pp. 1529, (1984)

[100] YILGÖR, I., STECKLE, W.P., YILGÖR, E., FREELIN, R.G. and RIFFLE, J.S., Novel Triblock Siloxane Copolymers: Synthesis, Characterization and Their Use as Surface Modifiying Additives, Journal of Polymer Science Part A: Polymer Chemistry, Vol 27, pp. 3673, (1989)

[101] KARAL, O., HAMURCU, E.E. and BAYSAL, B.M., Blends of Polycaprolactone-Poly(dimethyl siloxane)-Polycaprolactone Triblock Copolymer with Poly(vinyl chloride): Preparation and Characterization, Polymer, Vol 38, pp. 6071, (1997)

[102] LOVINGER, A.J., HAN, B.J., PADDEN, F.J.JR. and MIRAU, P.A., Morphology and Properties of Polycaprolactone-Poly(dimethyl siloxane)-Polycaprolactone Triblock Copolymers, Journal of Polymer Science, Vol 31, pp. 115, (1993)

[103] YILGÖR, I. and McGRATH, J.E., Polysiloxane Containing Copolymers: A Survey of Recent Developments, Advances in Polymer Science, Vol 86, pp. 1, (1988)

[104] YILGÖR, I., WARD, R.S. and RIFFLE, J.S., Synthesis and Characterization of Poly(2-ethyloxazoline)-poly(dimethyl siloxane)-poly(2-ethyloxazoline) Triblock Copolymers, Polymer Preprints, Vol 28, pp. 369, (1987)

[105] RIFFLE, J.S., STECKLE, W.P., WHITE, K.A. and WARD, R.S., Polydimethylsiloxane-Poly(ε-caprolactone) Block Copolymers: Synthesis and Applications, Polymer Preprints, Vol 26, pp. 251, (1985)

[106] KARAL, O., HAMURCU, E.E. and BAYSAL, B.M., Effect of Triblock PCL-PDMS-PCL Copolymer on the Properties of Immiscible Poly(vinyl chloride)/Poly(2-ethylhexyl acrylate) (PVC/PEHA) Blends, Macromolecular Chemistry and Physics, in press, (1998)

[107] DAS, G. and BANARJEE, A.N., Role of Methods of Blending on Polymer-Polymer Compatibility, Journal of Applied Polymer Science, Vol 61, pp. 1473, (1996)

[108] SPERLING, L.H., Interpenetrating Polymer Networks and Related Materials, Plenum Press, New York, (1981)

[109] GÜREL HAMURCU, E.E., Synthesis and Characterization of Interpenetrating Polymer Networks, Ph.D Thesis, (1994)

[110] YOUNG, R.J. and LOVELL, P.A., Introduction to Polymers, Chapman and Hall Inc., New York, (1994)

[111] BILLMEYER, F.W., Textbook of Polymer Science, Wiley-Interscience, USA, (1971)

[112] COLEMAN, M.M., GRAF, J.F. and PAINTER, P.C., Specific Interactions and the Miscibility of Polymer Blends, Technomic Publishing Co., Pennsylvania, (1991)

[113] FOLKES, M.J. and HOPE, P.S., Polymer Blends and Alloys, Blackie Academic and Professional, UK, (1993)

[114] BROWN, H.R., CHAR, K., DELINE, V.R. and GREEN, P.F., Effects of a Diblock Copolymer on Adhesion Between Immiscible Polymers 1. PS-PMMA Copolymer Between Ps and PMMA, Macromolecules, Vol 26, pp. 4155, (1993)

[115] THOMAS, S. and PRUDHOMME, R.E., Compatibilizing Effect of Block Copolymers in Heterogeneous Polystyrene-Poly(methyl methacrylate) Blends, Polymer, Vol 33, pp. 4260, (1992)

[116] BUCKNALL, D.G. and HIGGINS, J.S., The Compatibilizing Effect of Diblock Copolymer on the Morphology of Immiscible Polymer Blends, Polymer, Vol 33, pp. 4419, (1992)

[117] KRUSE, W.A., KIRSTE, R.G., HAAS, J., SCHMITT, B.J. and STEIN, D.J., Experimental Evidence for the Molecularly Disperse Character of the Mixture of Two Polymers and the Determination of the Chemical Potential in These Mixtures, Macromolecular Chemistry, Vol 177, pp. 1145, (1976)

[118] FISCHER, E.W., WENDORFF, J.H., DETTENMAIER, M., LIESER, G. and VOIGT-MARTIN, I., Chain Conformation and Structure in Amorphous Polymers as Revealed by X-Ray, Neutron, Light and Electron Scattering, Journal of Macromolecular Science and Physics, Vol 12, pp. 41, (1976)

[119] YU, H., Methods for Determining Polymer-Polymer Miscibility, Advances in Chemistry Series, Vol 99, pp. 1, (1971)

[120] ZEMAN, L. and PATTERSON, D., Effect of the Solvent on Polymer Incompatibility in Solution, Macromolecules, Vol 5, pp. 513, (1972)

[121] ROBARD, A., PATTERSON, D. and DELMAS, G., The Δx Effect and Polystyrene-Poly(vinyl methyl ether) Compatibility in Solution, Macromolecules, Vol 10, pp. 706, (1977)

[122] BERGHMANS, H. and OVERBERGH, N., Crystallization and Melting of the System Isotactic Polystyrene-Poly(2,6-dimethyl phenylene oxide), Journal of Polymer Science Polymer Physics Edition, Vol 15, pp. 1757, (1977)

[123] MIYA, M., IWAMOTO, R. and MIMA, S., FTIR Study of Intermolecular Interactions in Polymer Blends, Journal of Polymer Science Polymer Physics Edition, Vol 22, pp. 1149, (1984)

[124] GARTON, A., COUSIN, P. and PRUDHOMME, R.E., An Examination of Specific Interactions of Esters and Polyesters with Chlorinated Solvents by Infrared and Nuclear Magnetic Resonance Spectroscopies, Journal of Polymer Science Polymer Physics Edition, Vol 21, pp. 2275, (1983)

[125] COLEMAN, M.M. and PAINTER, P.C., Hydrogen Bonded Polymer Blends, Progress in Polymer Science, Vol 20, pp. 1, (1995)

[126] NIELSEN, L.E., Mechanical Properties of Polymers, Reinhold Publishing Co., USA, (1962)

[127] SEARS, J.K. and DARBY, J.R., The Technology of Plasticizers, John Wiley Publication, New York, (1982)

[128] LIZYMOL, P.P. and THOMAS, S., Miscibility Studies of Polymer Blends by Viscometry Methods, Journal of Applied Polymer Science, Vol 51, pp. 635, (1994)

[129] SCHRÖDER, E., MÜLLER, G. and ARNDT, K.F., Polymer Characterization, Academic-Verlag, Berlin, (1989)

[130] HUGGINS, M.L., The Viscosity of Dilute Solutions of Long Chain Molecules 4. Dependence on Concentration, Journal of American Chemical Society, Vol 64, pp. 2716, (1942)

[131] KRIGBAUM, W.R. and WALL, F.T., Viscosities of Polymeric Binary Mixtures, Journal of Polymer Science, Vol 5, pp. 505, (1950)

[132] SCHWAHN, D., MORTENSEN, K. and MADEIRA, H.Y., Studies of Critical Phenomena and Phase Transitions with SANS and DKD (double crystal diffraction) in the Polymer Blend PVME-PSD, Material Res.Society Symposium Series, Vol 79, pp. 351, (1987)

[133] PAULY, S., BRANDRUP, J. and IMMERGUT, E.H., Polymer Handbook, VI, Wiley Interscience Publication, USA, (1989)

[134] COMYN, J., Polymer Permeability, Elsevier Science, UK, (1986)

[135] RIM, P.B. and RUNT, J.P., Melting Point Depression in Crystalline Compatible Polymer Blends, Macromolecules, Vol 17, pp 1520, (1984)

[136] TÖTSCH, W. and GAENSSLEN, H., Poly vinyl chloride, Environmental Aspects of a Common Plastic, Elsevier Science Publishers Ltd., Great Britain, (1990)

[137] TITOW, W.V., PVC Technology, Elsevier Applied Science Publishers, Vol 1, London, (1984)

[138] TITOW, W.V., PVC Technology, Elsevier Applied Science Publishers, Vol 2, London, (1984)

[139] MARK, H.F. and GAYLORD, N.G., Encyclopedia of Polymer Science and Technology, Interscience Publishers, Vol 14, New York, (1972)

[140] GARTON, A., AUBIN, M. and PRUDHOMME, R.E., FTIR of Polycaprolactone/Poly(vinylidene chloride-co-Acrylonitrile) Miscible Blends, Journal of Polymer Science: Polymer Letters Edition, Vol 21, pp. 45, (1983)

[141] NISHI, T., KWEI, T.K. and WANG, T.T, Physical Properties of Poly(vinyl chloride)-Copolyester Thermoplastic Elastomer Mixtures, Journal Applied Physics, Vol 46, pp. 4157, (1975)

[142] HUARNG, J.C., MIN, K. and WHITE, J.L., Phase Equilibrium in the Binary and Ternary Blend System: Polycaprolactone-Polyvinyl chloride-Styrene Acrylonitrile Copolymer, Polymer Engineering Science, Vol 28, pp. 24, (1990)

[143] MARK, J.M., Silicon Containing Polymers, in ZEIGLER, J.M. and GORDON FEARON, F.W., Silicon Based Polymer Science, American Chemical Society, Vol 224, Washington, DC, (1990)

[144] DVORINC, P.R. and LENZ, R.W., High Temperature Siloxane Elastomers, Hüthig and Wepf Verlag, Heidelberg, (1990)

[145] ROCHOW, E.G., Silicon and Silicones, Springer-Verlag, Berlin, (1987)

[146] KÖNCZÖL, L., DÖLL, W., BUCHHOLZ, U. and MÜLHAUPT, R., Ultimate Properties of Epoxy Resins Modified with a Polysiloxane-Polycaprolactone Block Copolymer, Journal Applied Polymer Science, Vol.54, pp. 815 (1994)

[147] OWEN, M.J. and KENDRICK, T.C., Surface Activity of Polystyrene-Polysiloxane-Polystyrene ABA Block Copolymers, Macromolecules, Vol 3, pp. 458, (1970)

[148] BURREL, H., in Polymer Handbook (BRANDRUP, J. and IMMERGUT, E.H.), Wiley-Interscience Publication, Vol IV, New York, (1975)

[149] VANKREVELEN, D.W., Properties of Polymers, Their Estimation and Correlation with Chemical Structure, Elsevier Science Edition, New York, (1976)

[150] YORKGITIS, E.M., EISS, N.S., TRAN, C., WILKES, G.L. and McGRATH, J.E., Siloxane Modified Epoxy Resins, Advance Polymer Science, Vol 72, pp. 79, (1985)

[151] MURAYAMA, T., Dynamic Mechanical Analysis of Polymeric Material, Elsevier Science, New York, (1978)

[152] SAWYER, L.C. and GRUBB, D.T., Polymer Microscopy, Chapman and Hall, Cambridge, (1987)

[153] Gas Permeability Testing Operator Instructions, Manual, Brugger Feinmechanik GMBH, München

[154] FOX, T.G., Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System, Bulletin of American Physical Society, Vol 1, pp. 123, (1956)

[155] BUTTERS, G., Particulate Nature of PVC-Formation, Structure and Processing, Applied Science, London, (1982)

[156] CHEN, C.H., WESSON, R.D., COLLIER, J.R. and LO, Y.W., Studies of Rigid Poly(vinyl chloride) (PVC) Compounds II. Determination of the Fusion Level, Journal Applied Polymer Science, Vol 58, pp. 1093, (1995)

[157] CHEN, C.H., WESSON, R.D., COLLIER, J.R. and LO, Y.W., Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. IV. Fusion Characteristics and Morphology Analyses, Journal of Applied Polymer Science, Vol 58, pp. 1107, (1995)

[158] YANAGASE, A., MASAKAZU, I., YAMAMOTO, N. and ISHIKAWA, M., Mechanism of Enhanced Impact Strength of Poly(vinyl chloride) Modified by Acrylic Graft Copolymer, Journal of Applied Polymer Science, Vol 60, pp. 87, (1996)

[159] YANAGASE, A., MASAKAZU, I., YAMAMOTO, N. and ISHIKAWA, M., Effect of Modifier Characteristics on Toughness of Poly(vinyl chloride), Journal of Applied Polymer Science, Vol 62, pp. 1387, (1996)

[160] HAMURCU, E.E. and BAYSAL, B.M., Solubility Parameter of a Poly(dimethyl siloxane) Network, Journal of Polymer Science, Polymer Physics Edition, Vol 32, pp. 591, (1994)

[161] ERBİL, H.Y., YAŞAR, B., SÜZER, Ş. and BAYSAL, B.M., Surface Characterization of The Hydroxy - Terminated Poly(ε-Caprolactone)/Poly(dimethyl siloxane) Triblock Copolymers By Electron Spectroscopy For Chemical Analysis and Contact Angle Measurements, Langmuir, Vol 13, pp. 5484, (1997)

Appendix A

Calculations of T_g Values of Ternary Blends

Calculated T_g values of ternary blends are predicted according to Fox equation described in Section 5.2.3.

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} \qquad (A.1)$$

For PVC/PEHA/Tegomer (98.01/0.99/1) blend ,the calculated T_g value can be calculated as follows:

T_g = glass transition temperature of ternary PVC/PEHA/Tegomer blend
T_{g1} = glass transition temperature of PVC = 352 K
T_{g2} = glass transition temperature of PEHA = 223 K
T_{g3} = glass transition temperature of Tegomer = 187 K
w_1 = weight fraction of PVC in the blend
w_2 = weight fraction of PEHA in the blend
w_3 = weight fraction of Tegomer in the blend

$$\frac{1}{T_g(\text{blend})} = \frac{0.9801}{352} + \frac{0.0099}{223} + \frac{0.01}{187}$$

T_g(blend) = 348 K (75°C)

T_g values for ternary ternary blend systems were also calculated without taking into account the presence of the minor component in the mixture.

For ternary PVC/PEHA/Tegomer (98.01/0.99/1) blend, the minor component (PEHA in this case) in the mixture was neglected.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

T_{g1} = glass transition temperature of PVC
T_{g2} = glass transition temperaturte of Tegomer
w_1 = weight fraction of PVC
w_2 = weight fraction of Tegomer

$$\frac{1}{T_g(\text{blend})} = \frac{0.99}{352} + \frac{0.01}{187}$$

T_g(blend) = 349 K (76°C)

Appendix B

Determination of the Viscometric Interaction Coefficients, b_{12} and Compatibility Parameters, Δb for Polymer Blends

For binary PVC/Tegomer (99/1) blend, b_{12} and Δb values were calculated as follows:

b_{11} is related to the constant k, in the Huggins equation[130], when component 1 is in the solution alone. This also applies to b_{22}.

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \qquad (B.1)$$

$$b_{11} = k_1[\eta_1]^2 \qquad (B.2)$$

b_{11}(PVC) and b_{22}(Tegomer) were obtained from the slope of η_{spm}/C vs. C plot for homopolymers (Figure 5.14).
b_{12} is the interaction coefficient calculated from below equation:

$$\eta_{spm} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \qquad (B.3)$$

Concentration of stock solution = 2 g/dl
Concentration of PVC in the mixture = C_1 = 0.198/0.1 = 1.98 g/dl
Concentration of Tegomer in the mixture = C_2 = 0.002/0.1 = 0.02 g/dl
η_{spm} of PVC/Tegomer(99/1) blend = 2.48
$[\eta_1]$ = intrinsic viscosity of PVC = 0.739 (Table 5.9)
$[\eta_2]$ = intrinsic viscosity of Tegomer = 0.1336 (Table 5.9)
b_{11} = 0.252 (Table 5.9)
b_{22} = 0.016 (Table 5.9)

$$2.48=(0.739)(1.98)+(0.1336)(0.02)+(0.252)(1.98)^2+(0.016)(0.02)^2+2b_{12}(1.98)(0.02)$$

$$b_{12} = 0.33$$

The interaction coefficient between two polymers, b_{12}^* can be theoretically calculated as follows:

$$b_{12}^* = (b_{11} + b_{22}) / 2 \qquad (B.4)$$

For binary PVC/Tegomer (99/1) blend,

$$b_{12}^* = (0.252 + 0.016) / 2 = 0.134$$

The compatibility parameter, Δb calculated as follows:

$$\Delta b = b_{12} - b_{12}^{*} \qquad \text{(B.5)}$$

$\Delta b = 0.33 - 0.134 = 0.196$ (Table 5.10)

For binary PVC/PEHA (99/1) blend,

b_{11} (PVC) = 0.252 (slope of η_{spm} / C vs C plot) (Figure 5.16)
b_{22} (PEHA) = 0.631 (slope of η_{spm} / C vs C plot) (Figure 5.16)

Concentration of stock solution = 2 g/dl
Concentration of PVC in the mixture = C_1 = 0.198/0.1 = 1.98 g/dl
Concentration of PEHA in the mixture = C_2 = 0.002/0.1 = 0.02 g/dl
η_{spm} of PVC/PEHA (99/1) blend = 2.5
$[\eta_1]$ = intrinsic viscosity of PVC = 0.739 (intercept of η_{spm} / C vs C plot)
$[\eta_2]$ = intrinsic viscosity of PEHA = 1.6048 (intercept of η_{spm} / C vs C plot)

$$2.50=(0.739)(1.98)+(1.6048)(0.02)+(0.252)(1.98)^2+(0.631)(0.02)^2+2b_{12}(1.98)(0.02)$$

$b_{12} = 0.208$

$b_{12}^{*} = (0.252 + 0.631)/2 = 0.4415$

$\Delta b = 0.208 - 0.441 = -0.233$ (Table 5.10)

For ternary blends of PVC/PEHA/Tegomer, we have treated PVC/PEHA system as the component 1 and Tegomer as the component 2 in Equation (B.3)

b_{11} (PVC/PEHA (99/1)) = 0.234 (Table 5.10)
b_{22} (Tegomer) = 0.016 (Table 5.9)

Concentration of stock solution = 2 g/dl
Concentration of PVC/PEHA (99/1) blend in the mixture=C_1=0.198/0.1=1.98 g/dl
Concentration of Tegomer in the mixture = C_2 = 0.002/ 0.1 = 0.02 g/dl
η_{spm} of ternary PVC/PEHA/Tegomer (98.01/0.99/1) blend = 2.47
$[\eta_1]$ = intrinsic viscosity of PVC/PEHA (99/1) blend = 0.778
$[\eta_2]$ = intrinsic viscosity of Tegomer = 0.1336

$$2.47=(0.778)(1.98)+(0.1336)(0.02)+(0.234)(1.98)^2+(0.016)(0.02)^2+2b_{12}(1.98)(0.02)$$

$b_{12} = 0.171$

$b_{12}^{*} = (0.234 + 0.016)/2 = 0.125$

$\Delta b = 0.171 - 0.125 = 0.046$ (Table 5.10)

Appendix C

Calculations of Permeability Coefficients and Activation Energies of Permeation (E_p) Values of CO_2, O_2 and N_2 for Blends

Table C.1 q and P values of PVC homopolymer at different temperatures

T(°C)	$q(CO_2)$	$P(CO_2)$	$q(O_2)$	$P(O_2)$	$q(N_2)$	$P(N_2)$
5	2086	$8.47x10^{-14}$	1960	$7.96x10^{-14}$	1766	$7.17x10^{-14}$
10	2276	$9.24x10^{-14}$	2192	$8.90x10^{-14}$	1743	$7.07x10^{-14}$
20	2650	$1.07x10^{-13}$	2276	$9.24x10^{-14}$	2005	$8.14x10^{-14}$
30	2611	$1.06x10^{-13}$	2315	$9.40x10^{-14}$	2009	$8.16x10^{-14}$
40	3128	$1.27x10^{-13}$	2763	$1.22x10^{-13}$	2251	$9.14x10^{-14}$
50	3472	$1.41x10^{-13}$	3029	$1.23x10^{-13}$	2374	$9.64x10^{-14}$

Table C.2 q and P values of PVC/Tegomer(96/4) blend at different temperatures

T(°C)	$q(CO_2)$	$P(CO_2)$	$q(O_2)$	$P(O_2)$	$q(N_2)$	$P(N_2)$
5	2956	$1.20x10^{-13}$	3030	$1.23x10^{-13}$	2044	$8.30x10^{-14}$
10	3793	$1.32x10^{-13}$	3400	$1.38x10^{-13}$	2345	$9.52x10^{-14}$
20	4409	$1.79x10^{-13}$	3793	$1.54x10^{-13}$	2704	$1.10x10^{-13}$
30	4162	$1.69x10^{-13}$	3842	$1.56x10^{-13}$	2857	$1.16x10^{-13}$
40	4557	$1.85x10^{-13}$	4039	$1.64x10^{-13}$	3005	$1.22x10^{-13}$
50	5394	$2.19x10^{-13}$	4630	$1.88x10^{-13}$	3153	$1.28x10^{-13}$

Table C.3 q and P values of PVC/Tegomer (94/6)blend at different temperatures

T(°C)	$q(CO_2)$	$P(CO_2)$	$q(O_2)$	$P(O_2)$	$q(N_2)$	$P(N_2)$
5	2988	$1.21x10^{-13}$	2611	$1.06x10^{-13}$	2064	$8.38x10^{-14}$
10	3448	$1.40x10^{-13}$	2704	$1.10x10^{-13}$	2547	$1.03x10^{-13}$
20	3990	$1.62x10^{-13}$	3202	$1.30x10^{-13}$	3103	$1.26x10^{-13}$
30	3497	$1.42x10^{-13}$	2882	$1.17x10^{-13}$	2783	$1.13x10^{-13}$
40	3793	$1.54x10^{-13}$	3202	$1.30x10^{-13}$	2956	$1.20x10^{-13}$
50	4458	$1.81x10^{-13}$	3793	$1.54x10^{-13}$	3276	$1.33x10^{-13}$

Table C.4 q and P values of PVC/Tegomer (92/8)blend at different temperatures

T(°C)	$q(CO_2)$	$P(CO_2)$	$q(O_2)$	$P(O_2)$	$q(N_2)$	$P(N_2)$
5	2893	$1.51x10^{-13}$	2988	$1.56x10^{-13}$	2318	$1.21x10^{-13}$
10	3601	$1.88x10^{-13}$	2691	$1.40x10^{-13}$	2375	$1.24x10^{-13}$
20	3352	$1.75x10^{-13}$	2759	$1.44x10^{-13}$	2471	$1.29x10^{-13}$
30	3200	$1.67x10^{-13}$	3103	$1.62x10^{-13}$	2644	$1.38x10^{-13}$
40	3716	$1.94x10^{-13}$	3601	$1.88x10^{-13}$	3103	$1.62x10^{-13}$
50	4195	$2.19x10^{-13}$	4195	$2.19x10^{-13}$	3793	$1.98x10^{-13}$

Table C.5 q and P values of PVC/Tegomer (90/10)blend at different temperatures

T(°C)	$q(CO_2)$	$P(CO_2)$	$q(O_2)$	$P(O_2)$	$q(N_2)$	$P(N_2)$
5	3005	$1.22x10^{-13}$	2808	$1.14x10^{-13}$	2044	$8.30x10^{-14}$
10	3596	$1.46x10^{-13}$	2906	$1.18x10^{-13}$	2374	$9.64x10^{-14}$
20	3793	$1.54x10^{-13}$	2990	$1.21x10^{-13}$	2709	$1.10x10^{-13}$
30	4064	$1.65x10^{-13}$	3621	$1.47x10^{-13}$	2547	$1.03x10^{-13}$
40	4581	$1.86x10^{-13}$	3694	$1.50x10^{-13}$	3111	$1.26x10^{-13}$
50	5492	$2.23x10^{-13}$	3867	$1.57x10^{-13}$	3800	$1.54x10^{-13}$

Table C.6 Activation energies of permeation for PVC/Tegomer blends

Composition of the blend,(wt %)		$E_p(CO_2)$ kJ/mol	$E_p(O_2)$ kJ/mol	$E_p(N_2)$ kJ/mol
PVC	Tegomer			
100	0	7.78	8.05	9.70
96	4	8.72	9.80	11.97
94	6	10.09	11.32	15.17
92	8	11.43	12.20	14.60
90	10	12.14	14.36	16.26

Gas permeability (q) in ml/(m^2.day.bar) was determined using the following equation:

$$q = \frac{3.41 \times 10^7 \times V}{N \times T} \quad \frac{ml}{m^2 \times day \times bar}$$

The straight line is obtained from the plotter of the gas permeability testing appliance.

N = $\Delta t / \Delta n$ is the slope in s/scale division
V = the measurement volume = 0.5732 cm^3 (this is given on the upper part of the permeation cell)
T = room temperature in K

For PVC homopolymer, gas permeability for O_2 at 20°C was calculated as follows.

N = 293
T = 20 + 273 = 293 K
V = 0.5732 cm^3

$$q\ (O_2) = \frac{3.41 \times 10^7 \times 0.5732}{293/10 \times 293} = 2276\ ml / m^2.d.bar$$

If the plotter output is used "log 10", the slope measured on the diagram is divided by 10.

$$P = 1.16 \times 10^{-14} \times q \times l' \quad ml.cm / cm^2.sec.Pa$$

1.16×10^{-14} is the multiplication factor to obtain P in ml.cm / cm^2 .sec.Pa
l'= polymer film thickness in cm (0.0035 cm)

$$P = 1.16 \times 10^{-14} \times 2276 \times 0.0035 = 9.24 \times 10^{-14}\ ml.cm / cm^2.sec.Pa$$ (Table C.1)

Activation energies of permeation for homopolymer PVC and PVC/Tegomer blends were calculated using the following equation:

$$P = P_0 \exp(-E_p/RT) \qquad (C.1)$$

P, P_0 in cm^3 (273.15 K; 1.013×10^5 Pa)xcm/cm^2xsxPa

E_p (activation energy of permeation) in kJ/mol
T is the temperature in K
R is the gas constant (8.3144×10^{-3} kJ/mol)

Equation C.1 can be written,

$$\ln P = \ln P_0 - E_p/RT \qquad (C.2)$$

The intercept of ln P vs.1/T graph gives the value of P.
The slope of ln P vs. 1/T graph gives the E_p value.

For PVC homopolymer, ln P vs. 1/T graph was shown in Figure C.1 using the values in Table C.1 and E_p of O_2 for PVC was obtained (Table C.6).

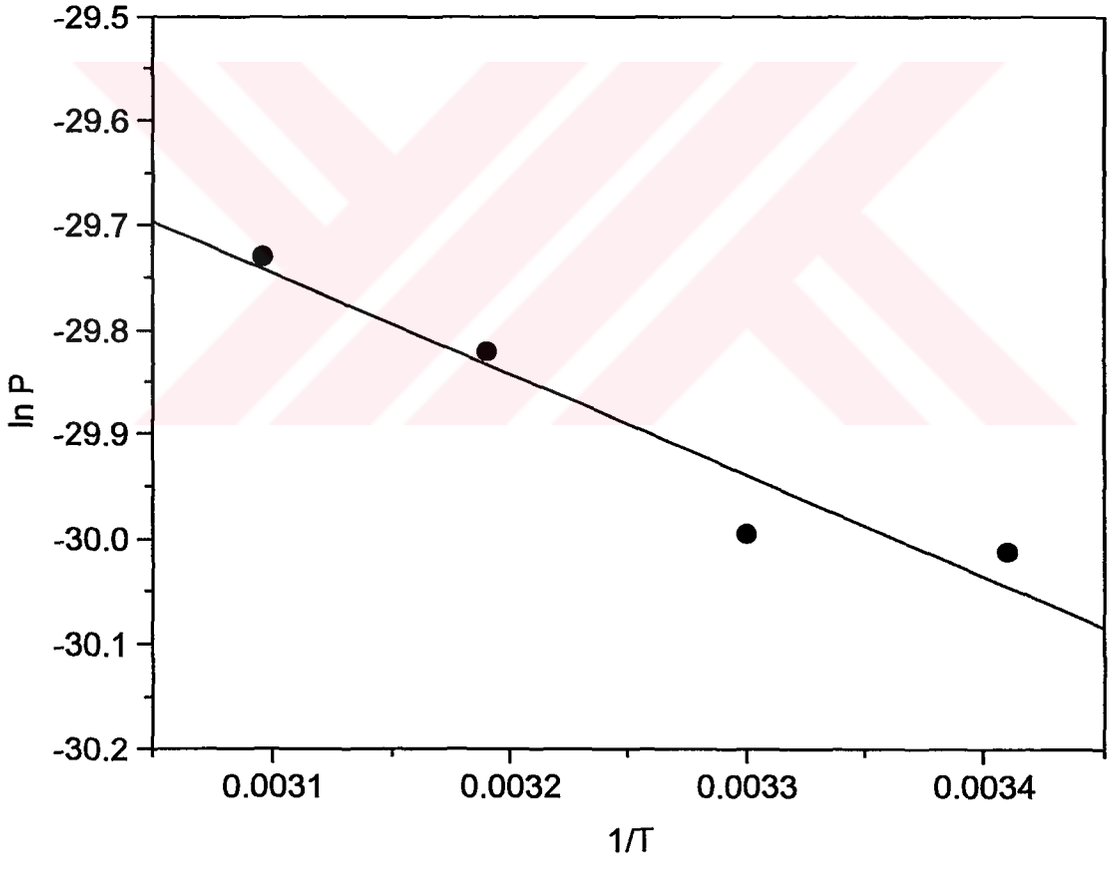


Figure C.1 ln P vs. 1/T graph of PVC homopolymer for O_2

Slope = $-E_p/R = -967.43$ $\quad -E_p\ (O_2) = -967.43/8.3144 \times 10^{-3} = 8.05$ kJ/mol for PVC

Appendix D

Experimental and Theoretical Densities of Polymer Blends

Theoretical densities of polymer blends were calculated according to the additivity of volumes rule:

$$V_A + V_B = V_T$$

$$\frac{m_A}{d_A} + \frac{m_B}{d_B} = \frac{m_A + m_B}{d_{mixture}}$$

m_A = mass of PVC homopolymer
m_B = mass of Tegomer
d_A = density of PVC homopolymer
d_B = density of Tegomer
$d_{mixture}$ = density of the mixture

For binary PVC/Tegomer (90/10) blend,

$m_{PVC} = 0.90$ g.
$m_{Tegomer} = 0.10$ g.
$d_{PVC} = 1.246$ g/cm^3
$d_{Tegomer} = 1.08$ g/cm^3

$$\frac{0.90}{1.246} + \frac{0.1}{1.08} = \frac{1}{d_{mixture}}$$

$d_{mixture} = 1.227$ g/cm^3

Experimental densities of polymer blends were calculated bu using pycnometer and Archimedean principle is applied.

For PVC/Tegomer (90/10) blend,

m (pycnometer) = 18.3988 g
m (pycnometer+water) = 44.5864 g
m(water) = m(pycnometer+water) - m(pycnometer)

$$V(water) = \frac{m(water)}{d(water)_{(20°C)}} = \frac{26.1876}{0.99823} = 26.2340 \text{ cm}^3$$

V(polymer) = V(total) - V(water)

$$d(\text{polymer}) = \frac{m(\text{polymer})}{V(\text{polymer})}$$

m(polymer) = 0.0329 g
m(pycnometer+polymer+water) = 44.5933 g
m(polymer+water) = 26.1945 g
m(water) = 26.1616 g
V(water) = 26.208 cm^3
V (polymer) = 26.2340 - 26.208 = 0.026 cm^3
d(polymer) = 0.0329/0.0260 = 1.2648 g/cm^3

Table D.1 Experimental and Calculated densities of PVC/Tegomer Blends

Composition of the blend (wt%)		density (g/cm^3)	
		exp.	calc.
PVC	Tegomer		
99	1	1.360	1.244
98	2	1.350	1.242
96	4	1.290	1.238
94	6	1.280	1.234
92	8	1.310	1.230
90	10	1.265	1.227

BIOGRAPHY

Okşan Karal was born in Ankara in 1969. She graduated from Marmara University, Faculty of Education, Department of Chemistry Teaching in 1992.

She attended as a M.Sc. student to the Institute of Science and Technology of Istanbul Technical University and obtain M.Sc. degree in Chemistry in 1994.

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She has been working as a researcher in Chemistry Department at TUBITAK Marmara Research Center since 1994. She is the co-author of four research paper in international scientific journals and also has six presentations in national and international symposiums.