ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF POLYSTYRENE / POLYPROPYLENE BLENDS WITH A NEW COMPATIBILIZER

M.Sc. THESIS

Hakan GÖKÇE

Department of Polymer Science and Technology

Polymer Science and Technology Program

Thesis Advisor: Prof. Dr. Nurseli UYANIK

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YENİ BİR UYUMLAŞTIRICI İLE HAZIRLANMIŞ POLİSTİREN / POLİPROPİLEN KARIŞIMLARININ MEKANİK, ISIL VE MORFOLOJİK ÖZELLİKLERİNİN İNCELENMESİ

YÜKSEK LİSANS TEZİ

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Polimer Bilim ve Teknolojileri Programı

Tez Danışmanı: Prof. Dr. Nurseli UYANIK

ARALIK 2013

To my family,

FOREWORD

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December 2013 Hakan GÖKÇE

(Chemical Engineer)

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ABBREVIATIONS

PS	: Polystyrene
PP	: Polypropylene
MW	: Molecular Weight
Tg	: Glass Transition Temperature
DSC	: Differential Scanning Calorimeter
SEM	: Scanning Electron Microscope
MFR	: Melt Flow Rate
Tp	: Significant Melting Peak Temperature
Rpm	: Revolutions per minute
COF	: Coefficient of friction
CP	: Commodity Polymer
EP	: Expensive Engineering Polymer
PP-g-PS	: Polypropylene-graft-polystyrene
LCB	: Long Chain Branching
MWD	: Molecular weight distribution
RC	: Reactive compatibilization
L/D	: Length to diameter ratios
HIPS	: Impact-resistant Polystyrene
EPS	: Expandable Polystyrene
ASTM	: American Society for Testing and Materials
PBE	: Propylene-based Elastomers
SIS	: styrene–isoprene–styrene
SBS	: Styrene butadiene–styrene
SBR	: Styrene– butadiene–rubber
MAH	: Maleic anhydride
St	: Styrene
SEP	: Styrene-ethylene/propylene
SALS	: Small Angle Light Scattering
SEBS	: Styrene-ethylene/butylene-styrene block copolymer
DMA	: Dynamic Mechanical Analysis
CB	: Carbon black
PP-g-MA	: Maleated polypropylene
MWNT	: Multi-walled carbon nanotube
$CaCO_3$	: Calcium carbonate

LIST OF SYMBOLS

ΔG_m	: Gibbs free energy of mixing
ΔH_m	: Enthalpy of mixing
T	: Temperature
ΔS_m	: Entropy of mixing
R	: Ideal gas constant
Φ	: Volume fraction
N	: Degree of polymerization
X	: Interaction parameter
ΔGH	: Free energy of specific action between polymers
V_{ref}	: Reference volume
δ	: Solubility parameter
Δδc	: Critical solubility parameter
Q	: Plastic output
Qd	: Drag flow
Qp	: Pressure flow
Ql	: Leakage flow
K	: Kelvin
™	: Trade Mark
χ	: Degree of crystallinity
ΔH_c	: Fusion enthalpy
ΔH_m	: Crystallization enthalpy

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INVESTIGATION OF MECHANICAL, THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF POLYSTYRENE POLYPROPYLENE BLENDS WITH A NEW COMPATIBILIZER

SUMMARY

Polymeric materials are appreciated for their chemical, physical and economical qualities. The properties of them can be adjusted by controlling their molecular weight (MW) and molecular weight distribution. The successful use of plastic materials is substantially attributable to the incorporation of additives, such as antioxidants, colorants, plasticizers, impact modifiers, heat/UV stabilizers, flame retardants, and extenders. To obtain better properties of polymeric materials, polymer blends can be widely applied as a versatile method in the industry because of their ability to tailor materials for specific applications, at a relatively low cost when compared with the development of a new polymer.

Polymer blends are defined as mixtures of at least two macromolecular substances, polymers or copolymers, in which the ingredient content of the lesser component is higher than 2 wt. %. The performance of polymer blends is determined by the properties and concentrations of blend components, and the final morphology of the blend in the solid state.

From a thermodynamics point of view, polymer blends are classified into two categories as miscible polymer blends and immiscible polymer blends. Unfortunately, miscibility of polymers is limited to a specific set of conditions. Therefore, most polymers are immiscible. The immiscibility of polymer blends does not mean that they have insignificant importance and use. If the interfaces in an immiscible polymer blend are controlled and the morphology of the blend is stabilized, advantageous properties of each component could be exhibited in the end product. This could be achieved by compatibilization. Immiscible but compatibilized polymer blends with intentionally modified morphology and interfaces are called "polymer alloys".

PS is an amorphous thermoplastic polymer with a glass-transition temperature (Tg) between 90^{o}C to 100^{o}C and it has low impact strength at room temperature. On the other hand, PP can be considered as a tough material at room temperature and its tensile strength is quite high. Compatibilized blending of PS with PP can increase the impact strength of PS and it can be used for various purposes in many applications. PS/PP blends with compatibilizers make it also possible to obtain materials with higher gas barrier properties than that of original polystyrenes.

In this study, the effects of the compatibilizer and the composition of the polystyrene/polypropylene (PS/PP) blends, on the morphology, thermal and the

mechanical properties of the samples were investigated. Commercial PP was blended with commercial PS at certain compositions by melt blending via extrusion. The extruder was a 25 mm diameter single screw extruder with L/D ratio of 25 consisted of three heating zones surrounding the screw, a static mixer after the third heating zone and a strand die with four holes. The 3-stage single screw with compression ratio of 2.05 was equipped with dispersive mixing elements in the metering zone. A commercial propylene based elastomer (PBE) was used as a compatibilizer.

The extrusion temperature limits were determined at the beginning of the study by differential scanning calorimetry (DSC) analysis of virgin PS and PP. Then, an optimization study was carried out to determine the optimum temperature profile and the optimum compatibilizer (PBE) amount in the blends.

After this optimization, temperature profile to process the blends was decided to be 190ºC / 195ºC / 195 ºC / 200 ºC / 200 ºC for heating zone 1, heating zone 2, heating zone 3, static mixer and die, respectively. The weight percent of the polymers were varied from 0 to 100. 5 and 10 per hundred resin (phr) compatibilizers were added to prepare 22 samples by melt mixing method. The 11 uncompatibilized samples with the same compositions of PS/PP blends were also prepared as blank samples. Mechanical, thermal and morphological properties of the samples were analyzed by tensile tests, DSC analysis, and scanning electron microscope (SEM) respectively. Melt flow rate was also measured for all of the samples.

Mechanical property analysis of the samples showed that composition of the blends had a pronounced effect on the tensile properties of these materials. The maximum tensile strengths decrease by increasing of PS of all samples content up to 30 wt%, where a minimum value is observed. After this point, the maximum tensile strength increases with further increasing of PS content up to 70 wt%, where a maximum value is obtained. Afterwards there is no significant effect of adding more PS to the tensile strength. Moreover, the maximum tensile strength/PS content curve of the 0 phr (incompatibilized) blend shifting below with the adding of 5 and 10 phr compatibilizer.

Thermal properties of the PP-rich, PP-PS-equal and PS-rich blends were analyzed by differential scanning calorimetry. Both enthalpy of crystallization (obtained by peak integration) and the degree of crystallinity of the blends decrease with higher content of amorphous PS. Enthalpy of fusion results also indicates a reduction of the crystallinity of blends coming from PP by addition of PS. The addition of compatibilizer to the blends further reduces the enthalpy of crystallization and degree of crystallinity compared to the incompatibilized blends in all investigated compositions.

Scanning electron microscopy analysis of the samples showed that compatibilization decreased the size average of the dispersed particle. In the case of PS content larger than 70 wt%, the enhancement of interfacial interaction plays a dominating role related to the mechanical measurements results.

Melt flow rate (MFR) analysis measured at 190^0C that for both incompatibilized and compatibilized PS/PP blends. The MFR results increased when PS content in blends increases. Adding compatibilizers also increase the MFR values and the fluidity. These results indicate that better mixing for both incompatibilized and compatibilized samples is achieved. It is concluded that compatibilization also improved processability.

YENİ BİR UYUMLAŞTIRICI İLE UYUMLAŞTIRILMIŞ POLİSTİREN POLİPROPİLEN KARIŞIMLARININ MEKANİK, TERMAL ve MORFOLOJİK OLARAK İNCELENMESİ

ÖZET

Polimer malzemeler üstün kimyasal, fiziksel ve ekonomik özellikleriyle günümüzün en değerli malzemelerindendir. Polimerlerin özellikleri molekül ağırlıkları ve molekül ağırlığı dağılımları ayarlanarak kontrol edilebilir. Polimer malzemelerin birçok alanda verimli bir şekilde kullanılabilmesi, antioksidan, renklendirici, plastikleştirici, darbe dayanımı arttırıcı, ısı/UV stabilizatörü, alev geciktirici, dolgu maddesi gibi katkı maddelerinin eklenmesiyle mümkün olabilmektedir. Daha iyi özelliklere sahip polimer malzemeler elde etmek için, polimer karışımları veya polimer/dolgu alaşımları endüstride çok yönlü olarak yaygınca kullanılmaktadır. Malzemelerin belirli kullanım alanları için özelliklerinin ayarlanabilmesi, aynı zamanda bu işlem yeni bir malzeme geliştirmeyle kıyaslanınca oldukça kısa zamanda yapılabilmesi buna olanak sağlar.

Polimer karışımları, en az iki makro moleküler maddeden, yani en az iki polimer ya da kopolimerden, oluşan; karışım içinde miktarca daha az bulunan polimerin yüzdesinin % 2'yi geçtiği karışımlardır. Polimer karışımlarının performansı, karışım bileşenlerinin türü ile karışımdaki yüzdeleri ve karışımın katı haldeki morfolojisi tarafından belirlenir.

Termodinamik yaklaşımla polimer karışımları, her oranda karışabilen polimer karışımları ve birbirine karışmayan (çok-fazlı) polimer karışımları olarak iki kategoride sınıflandırılır. Polimerlerin her oranda karışması nadir rastlanan bir durum olup, yalnızca özel şartlarda mümkündür. Bu nedenle polimerlerin birçoğu birbirleri ile karışmaz. Bu durum, çok-fazlı polimer karışımlarının fazla kullanım alanı bulmadığı ve önemsiz olduğu anlamına gelmez. Eğer çok-fazlı bir polimer karışımında ara yüzey kontrol edilebilir ve çok fazlı karışımın morfolojisi kararlı hale getirilebilirse, karışımı oluşturan polimerlerin avantajlı özellikleri elde edilen üründe ortaya konabilir, bu da karışıma uyumlaştırıcı ilave edilerek sağlanabilir. Uyumsuz olan fakat morfolojisi ve ara yüzey uyumluluğu sağlanmış çok-fazlı polimer karışımlarına polimer alaşımları da denir.

Polistiren (PS) camsı geçiş sıcaklığı 90-100^{0}C arasında olan amorf yapıda termoplastik bir polimerdir. PS birçok istenilen özelliğinin yanı sıra oda sıcaklığında düşük darbe dayanımına sahiptir. Diğer taraftan polipropilen (PP), yarı kristal yapıda, camsı geçiş sıcaklığı -20 ile 0^{0}C arasında, ergime sıcaklığı 160-170^{0}C arasında olan termoplastik bir elastomerdir. PP oda sıcaklığında sert bir malzeme olarak bilinir ve çekme dayanımı olukça yüksektir.

PS ile PP'nin karışımları PS'nin darbe dayanımı arttırılması için uygun bir yöntemdir. Uyumlaştırıcılı PS/PP karışımları endüstride çeşitli amaçlar için

kullanılmaktadır. PS/PP karışımları uyumlaştırıcılar ile kullanıldığında homopolistirene göre daha yüksek gaz bariyeri sağladığı görülmektedir.

Bu çalışmada uyumlaştırıcı ve karışım kompozisyonunun morfoloji, termal ve mekanik özelliklere olan etkisi incelenmiştir. Ticari bir PS ve ticari PP, ekstruder kullanılarak, eriyik karıştırma yöntemiyle hazırlanmıştır. Kullanılan ekstruder, 25 mm çapında, L/D'si 25 olan, vidayı çevreleyen üç ısıtma bölgesi, üçüncü ısıtma bölgesinin sonrasında bir statik mikser ve kafadan oluşan tek vidalı bir ekstruderdir. 3 basamaklı ve sıkıştırma oranı 2,05 olan vida, dispersif karıştırma elemanları ile donatılmıştır. Uyumlaştırıcı olarak, propilen esaslı bir elastomer (PBE) kullanılmıştır.

Çalışmanın başında, ekstrüzyon sıcaklık profili, PS ve PP'nin diferansiyel taramalı kalorimetrede (DSC) analizi ile belirlenmiştir. Daha sonra, PS/PP karışımlarının ekstrüzyonu için uygun sıcaklık profili ve hazırlanacak karışımlardaki uygun uyumlaştırıcı yüzdesinin belirlenmesi amacıyla, bir optimizasyon çalışması yapılmıştır.

Optimizasyon çalışması sonucunda PS/PP karışımlarının ekstruzyonu için optimum sıcaklık profili birinci, ikinci ve üçüncü ısıtma bölgesi, statik mikser ve kafa için sırasıyla 190ºC / 195ºC / 195ºC / 200ºC / 200ºC olarak belirlenmiştir. Ağırlıkça polimerlerin yüzdesi 0'dan 100'e kadar olup 5 ve 10 toplam karışıma göre yüzde (phr) oranında uyumlaştırıcı katılarak 22 adet örnek eriyik karıştırma yöntemi kullanılarak hazırlanmıştır. Ayrıca aynı PS/PP oranlarında 11 adet uyumlaştırıcısız örnek de karşılaştırma amaçlı hazırlanmıştır. Tüm örneklerin mekanik, termal ve morfolojik özellikleri, sırasıyla çekme-kopma testleri, DSC analizi ve taramalı elektron mikroskopu ile incelenmiştir. Uyumlaştırıcılı ve uyumlaştırıcısız karışımlar için, eriyik akış hızları da ölçülmüştür.

Örneklerin mekanik karakterizasyonunda, karışımın bileşiminin, ürünlerin kopma-çekme özelliklerini belirgin bir biçimde etkilediğini ortaya koymuştur. PS içeriği ağırlıkça %30 a kadar olan karışımlarda maksimum çekme kuvvetinin düştüğü ve bu noktada bu değerin minimum olduğu gözlenmiştir. Bu noktadan sonra ağırlıkça %70 PS içeriğine kadar olan bölgede maksimum çekme kuvvetinin arttığı ve maksimum değerin %70'de elde edildiği gözlenmiştir. PS içeriğinin daha da arttırılmasının maksimum çekme kuvvetini etkilemediği de görülmüştür. Uyumlaştırıcı eklenmemiş ve 5 ile 10 phr eklenmiş karışımların maksimum çekme kuvveti/PS içeriği eğrilerine bakıldığında, uyumlaştırıcı miktarı arttıkça eğrilerin aşağı kaydığı, yani maksimum çekme kuvveti değerlerinin azaldığı görülmüştür.

Tüm karışımların ısıl özellikleri DSC analizi ile incelenmiştir. Karışımların kristalizasyon entalpisi (tepe noktası integrasyonu ile elde edilen) ve kristallenme derecesi amorf olan PS içeriğinin artmasıyla azalmaktadır. Ergime entalpisi sonuçları da karışımlarda PS oranındaki artışın PP'den gelen kristalliğini azalttığını göstermiştir. Karışımlara uyumlaştırıcı eklenmesinin, kristalizasyon entalpisi ve yüzde kristallilik değerini, uyumlaştırıcısız örneklere göre azalttığı görülmüştür.

Örneklerin taramalı elektron mikroskopu analizi, bütün bileşimler için uyumlaştırmanın dağılan fazın tanecik boyutunda düşüş sağladığını göstermiştir. Bu durum, PS oranı %70'in üzerinde olan örneklerde, çekme mukavemetini de göz önüne alarak, ara yüzey etkileşiminin belirlenmesinde etkin olduğunu ortaya koymuştur.

Eriyik akış hızı (MFR) analizi 190^0C uyumlaştırıcılı ve uyumlaştırıcısız hazırlanmış PS/PP örneklerinde yapılmıştır. Ölçüm sonuçları PS bileşeni arttığında örneklerin MFR değerlerinin arttığını göstermiştir. Uyumlaştırıcı eklenmesi ise akışkanlığı arttırmış ve böylece daha kolay işlenebilirliği de sağlamıştır.

1. INTRODUCTION

Blending of polymers is becoming increasingly important to enhance properties, improve processing or reduce cost. Enhancement of properties of polymers; such as coefficient of friction (COF), adding color, promoting adhesion, increasing output, improving stability, and obtaining easy-opening features, can be achieved by blending. The simplest mixture can be made by mixing the ingredients in the extruder. For more complex mixtures, specialized screw designs or customized compounding equipment may be required to achieve the desired properties. These machines incorporate various mixing modes, such as flow rearrangement (distributive mixing) or high stress levels to breakup particles (dispersive mixing). Complex shear and elongational flow fields may also be used to obtain optimum mixing. The final polymer properties will depend not only on the flow and stress history, which is process dependent, but also on the thermodynamics and the polymers thermal and rheological properties.

At least two polymers blending together to create a new material with different physical properties named as polymer blend. Most polymer blends are immiscible the minor component forms a separate dispersed phase or domain within the major component, and the major component forms a continuous phase or matrix. The phase size and shape is known as the morphology. Blend morphology has a profound effect on final properties and is the subject of much study. Morphology is influenced by;

- interfacial tension (thermodynamics)
- dispersed to continuous phase viscosity ratio
- elasticity of each phase
- component ratios
- mixing and melting order and much more [1].

Polystyrene (PS) is one of the most widely used polymer in industry due to its good physical and chemical properties, low cost and easily processability. Polystyrene can be rigid or foamed. General purpose polystyrene is clear, hard and brittle. This 100%

amorphous polymer is a rather poor barrier to oxygen and water vapor and has a relatively low glass transition temperature. However, some features of PS bring restriction of its application. These features can be improved and its application area can be wider by blending.

Polypropylene (PP) has been used in various applications for human daily life owing to its low density, excellent thermal and mechanical properties and good processability with its appropriate price. But its toughness, strength and stiffness are not sufficient for applications as an engineering plastic. To reinforce PP, polymer blending technique by adding rigid polymers, such as polystyrene (PS) was used [2]. Unfortunately, these PP based polymer blends are usually immiscible [3]. Their blends usually result in serious phase separation, low interfacial adhesion and poor mechanical properties. In order to improve the compatibility of immiscible polymer blends, the usually used method is the addition of one or more compatibilizers. Block and graft copolymers, which have the same or miscible composition with each component in polymer blends to reduce the interfacial tension, decrease the size of dispersed phase and provide specific interaction between two phases. PS/PP blends are known as a typical immiscible system. It is always a great challenge to improve the compatibility between PS and PP homopolymers. The ideal compatibilizer structure used for PS/PP blends would be a block or graft copolymer of polypropylene and polystyrene. Polypropylene-graft-polystyrene (PP-g-PS) copolymer composed of a PP main chain and PS side chains has made great effects on the improvement of the compatibility of PS/PP blends [4].

In this study, commercial PS was blended with commercial PP at certain compositions by melt blending via extrusion. The effects of compatibilization and the composition of the blends, on the mechanical, thermal, and morphological properties of samples were investigated. A commercial propylene based elastomer was used as compatibilizer.

Mechanical characterizations were made by universal testing machine. Thermal properties of blends were characterized by DSC analysis. Morphological characterizations were made by using SEM. MFR measurement were done.

2. THEORY

The development of polymer blends and composites is a very active area of science and technology; of great economic importance not only for the plastics industry but also for many other industries where the use of such products is becoming increasingly more common [5].

Most pairs of polymers are immiscible with each other. Even worse is the fact that they also have less compatibility than would be required in order to obtain the desired level of properties and performance from their blends. Compatibilizers are often used as additives to improve the compatibility of immiscible polymers and thus improve the morphology and resulting properties of the blend. Similarly, it is often challenging to disperse fillers effectively in the matrix polymer of a composite, or to adhere layers of polymers to each other or to other substrates (such as glass or metals) in laminates. Continued progress in the development of compatibilization technologies is, hence, crucial in enabling the polymer industry to gain the full benefits of such approaches to obtaining materials with optimum performance and cost characteristics [5].

2.1 Fundamental Considerations

2.1.1. Performance versus price

As an empirical rule (Rule 1) shown in Equation 1, if a polymeric product remains a commodity material competing for use in commodity-type applications, the price that the average customer is willing to pay will only increase proportionally to the logarithm of the improvement in its performance:

$$\text{Price}_2 \approx \text{Price}_1 + c.\ \ln\left(\text{Performance}_2 / \text{Performance}_1\right) \qquad (1)$$

In this equation, Price2>Price1, Performance2>Performance1 are the corresponding performance levels, "c" is a positive proportionality constant and "ln" is the natural logarithm. See Figure 1 for a schematic illustration. This equation can be generalized

readily to more complex cases where the overall "desirability" for a particular application depends on several performance criteria that have different levels of relative importance [6-7].

The main implication of this equation is that whatever is done to improve the performance of a polymer (blending, incorporation of fillers, lamination, processing in a different way, etc.) must not be allowed to increase by much the sales price required to make a profit if its improved performance remains in the commodity product range. It will be refered to this fundamental limitation on the price that the market will be willing to pay for a commodity polymer as the "commodity trap". It is only if the performance can be increased sufficiently to make the material competitive for higher-valued specialty applications (thus escaping the "commodity trap") that a significant price increase can be allowed.

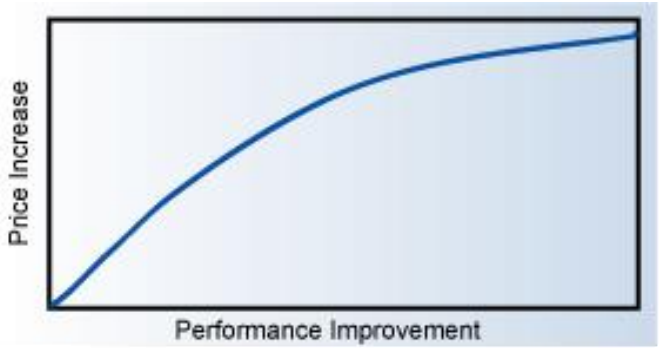


Figure 2.1: Schematic illustration of the "commodity trap".

If an inexpensive polymer (such as a polyolefin) can be modified so that its properties become competitive with those of an expensive engineering plastic, it can escape the "commodity trap" since new potential applications become possible for it. It can then command a significant price premium over the "ordinary" (commodity) grades of the polymer. It must, however, still remain cheaper than the engineering plastic which it displaces in a higher-valued application. See Figure 2 for a schematic illustration.

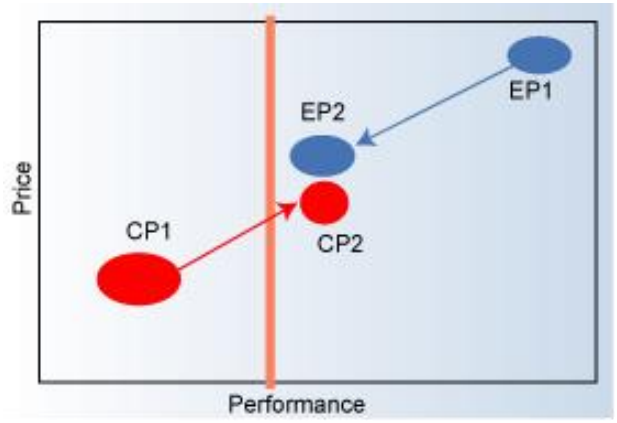


Figure 2.2 : Schematic illustration of two situations where blending and/or compounding are especially attractive from a commercial viewpoint.

In the Figure 2, the thick vertical brown line represents the minimum acceptable performance required to qualify a material for a certain application. The ellipses represent regions on the "price-performance plane". EP1 is an expensive engineering polymer that far exceeds the performance requirements of the application. EP2 is a cheaper blend or composite of EP1 with less expensive ingredients, still exceeding the minimum performance requirements. CP1 is a commodity polymer that does not meet the performance requirements of the application. CP2 is a blend or composite of CP1 hat exceeds the minimum performance requirements and can thus be sold at a substantially higher price.

Most people agree about the desirability of recycling but are unwilling to pay any price premium at all for plastic parts with enhanced recyclability. As a result, the growth rate of post-consumer recycling enabled by the use of compatibilization additives has been considerably slower than it would have been if its environmental benefits really outweighed economic factors in most people's minds. This is clearly an area where new or improved compatibilization technologies can make a significant impact [8-9].

2.2 Polymer Blends Thermodynamics

When two materials are brought together, there must be a decrease in the free energy for them to transform into a single material or miscible blend. This can be expressed mathematically as [10]:

$\Delta G_m < 0$ for miscibility (2.1)

where ΔG_m is the Gibbs free energy of mixing.

The free energy includes enthalpic and entropic contributions:

$\Delta G_m = \Delta H_m - T\Delta S_m$ (2.2)

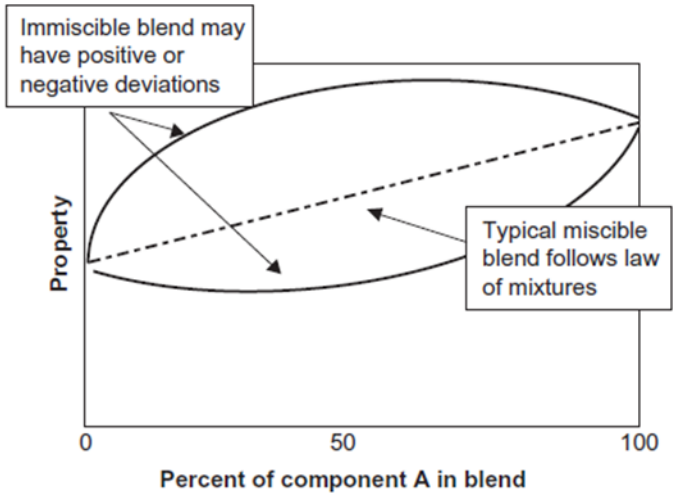


Figure 2.3 : Properties versus percent A in polymer blends.

Where ΔH_m, T, and ΔS_m are the enthalpy of mixing, temperature, and entropy of mixing, respectively.

For most polymer blends, ΔH_m is positive and ΔS_m is nearly zero. Thus, it is rare that polymer blends are miscible. Coleman et al. (1991) derived the following relationship for ΔG_m based on the work of Flory and Huggins:

$$\frac{\Delta G_m}{RT} = \left[\frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B\right] + \chi\Phi_A\Phi_B\left(\frac{\Delta G_H}{RT}\right) \quad (2.3)$$

where, ΔG_m = Gibbs free energy of mixing,

R= ideal gas constant,

T= temperature,

Φ_A= volume fraction of polymer A,

Φ_B= volume fraction of polymer B,

N_A= degree of polymerization of polymer A,

N_B= degree of polymerization of polymer B,

χ=interaction parameter,

ΔG_H= free energy of specific action between polymers, including hydrogen bonding.

The first term on the right side of Eq. (2.3) arises from combinatory entropy. Since N, which is related to molecular weight (MW) and it is large for polymers; this term is approaching to nearly zero. The second-term also arises from entropy and is always positive. The interaction parameter, χ, is defined by:

$$\chi = \frac{V_{ref}}{RT}[\delta_A - \delta_B]^2 \quad (2.4)$$

where, V_{ref} = reference volume,

δ_A= solubility parameter for polymer A,

δ_B= solubility parameter for polymer B.

The final term, $\Delta G_H/RT$, is negative when specific interactions are present.

From Eqs. (2.3) and (2.4), we see that we can improve compatibility by matching solubility parameters and achieve miscibility only when we incorporate specific interactions. Nonpolar polymer blends, such as PP/PE blends, have no specific interactions beyond weak dispersive forces. As we shall see, even though their solubility parameters are nearly equal, they are not miscible. In Eq. (2.4), the solubility parameter is introduced. We can discuss the origin of solubility parameters and how they can be helpful in understanding polymer blends. The energy per unit volume required removing a molecule from a liquid or solid is known as the cohesive energy density. This is illustrated in Figure 2.4.

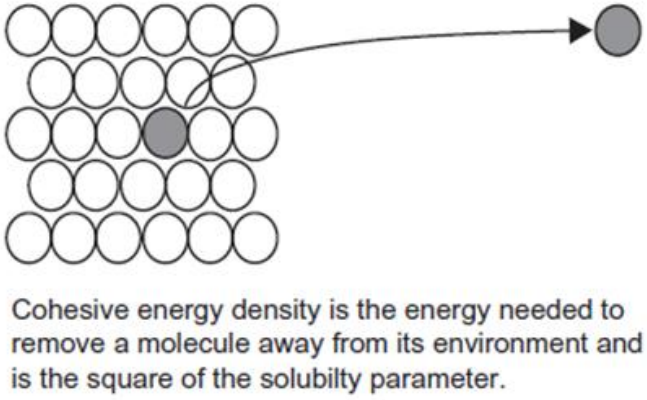


Figure 2.4 : Illustration of cohesive energy density.

The cohesive energy density is a function of the forces that hold the material together. The solubility parameter is the square root of the cohesive energy density. It contains contributions from both nonpolar (dispersive forces) and polar (dipole-dipole and hydrogen bonding) interactions. Comparing solubility parameters is a way to quantify the "like dissolves like" principle of chemistry. For two polymers to be miscible, the difference insolubility parameters should be between 0.1 and 3 Hildebrands, depending on their interaction strength. The critical solubility parameter defined as a difference, $\Delta\delta_c$, below which the polymers may be miscible. As shown in Table 2.1, the value of $\Delta\delta_c$ depends on what interactive forces are present. Table 2.2 lists solubility parameter values for some polymers.

Table 2.1: Critical solubility parameter difference upper limit.

Specific Interactions Involved	Polymer Blend Examples	$\Delta_{\delta critical}$ Hildebrands
Dispersive forces only	Poly(butadiene)-poly(ethylene)	< 0.1
Dipole-dipole	Poly(methylmethacrylate)-poly(ethylene oxide)	0.5
Weak	Poly(vinyl chloride)- butadiene acrylonitrile copolymer	1.0
Weak to modarete	PS acrylonitrile-poly(methylmethacrylate)	1.5
Modarete	PC- polyesters	2.0
Modarete to strong	Polyamide- poly(ethylene oxide)	2.5
Strong	Poly(vinyl phenol)- poly(viynl acetate)	3.0
Very strong	Poly(methylmethacrylic acid)-poly(ethylene oxide)	>3.0

Table 2.2 : Solubility parameters for some polymers.

Polymer	Solubility Parameter (Hildebrands)
PE poly(ethylene)	7.7-8.4
PP poly(propylene)	8.2-9.2
PS poly(styrene)	8.5-9.3
PVC poly(viynl chloride)	9.4-10.8
Polyamide 6	12.6
PET poly(ethylene terephthalate)	10.3

For the PE-PP blend example, it is seen that the difference in their solubility parameters is less than 1 ($\Delta\delta_c$<1). However, since only nonpolar dispersive forces are present, the critical solubility parameter difference ($\Delta\delta_c$) is less than 0.1. Thus, these polymers are not miscible. It should be noted that there is some controversy around solubility parameters in the literature. They are exact for polymers with only physical

interactions. There are errors associated with trying to extend the concept to polymer systems involving hydrogen bonding and other polar interactions and with the indirect methods used experimentally to measure them. These errors typically result in a range that is not very useful for predicting miscibility; hence matching solubility parameters is not a necessary and sufficient condition for the miscibility of polymers. However, they are useful guides for compatibility and, since most polymer blends are not miscible, this maybe their greatest strength. The solubility parameter difference has been related to the interphase thickness between immiscible polymers. Immiscible polymers with a solubility parameter difference of about 0.5 Hildebrands or less may still build up enough strength at the interface for good mechanical properties [1].

2.3 Compatibilization of Immiscible Polymer Blends

Most polymer blends are immiscible and need to be compatibilized. The compatibilization must accomplish; (i) optimization of the interfacial tension; (ii) stabilize the morphology against high stresses during forming; and (iii) enhance adhesion between the phases in the solid state.

Compatibilization is accomplished either by addition of a compatibilizer or by reactive processing. These two categories are;

1. By addition of: (i) a small quantity of a third component that is miscible with both phases; (ii) a small quantity of copolymer whose one part is miscible with one phase and another with another phase; (iii) a large amount of a core-shell, multi-purpose compatibilizer-cum-impact modifier.

2. By reactive compatibilization, which uses such strategies as: (i) trans-reactions; (ii) reactive formation of graft, block or lightly crosslinked copolymer; (iii) formation of ionically bonded structures; and (iv) mechano-chemical blending that may lead to chains' breakage and recombination, thus generation of copolymers (even at liquid nitrogen temperature), etc.

2.3.1 Compatibilization by addition

Historically, the most popular method of compatibilization has been by addition of a third component. In most cases, such an additive was either a block or graft copolymer. Since the key requirement is miscibility, it is not necessary for the copolymer to have identical chain segments as those of the main polymers. It suffices that the copolymer has segments having specific interactions with the main polymeric components, hydrogen bonding, dipole-dipole, dipole-ionic, Lewis acid-base, etc. Theoretical calculations suggest that efficiency of a compatibilizer increases with its MW. However, thermodynamics requires that the added copolymer not only concentrates in the interphase, but also dissolves in both phases, where it may form micelles. It is essential that the compatibilizer be designed to migrate to the interface, broadening the segmental concentration profile. Addition of a block or graft copolymer reduces the interfacial tension and alters the molecular structure at the interface.

One of the disadvantages of the addition method is the tendency of the added copolymers to form micelles. These reduce the efficiency of the compatibilizer, increase the blend viscosity and may lessen the mechanical performance. For these reasons, the copolymer must be designed in such a way as to:

(i) maximize miscibility of the appropriate part of its macromolecule with the specific polymeric component of the blends,

(ii) minimize its molecular weight just to about the entanglement molecular weight for each interacting block, and

(iii) minimize copolymer concentration in the blend.

Addition of 0.5 to 2 wt% of well-designed, tapered block copolymer has been found sufficient (Brown, 1989).

While reduction of the interfacial tension is relatively simple, the two other functions (stabilization of morphology and improvement of interfacial adhesion in the solid state) rarely are simultaneously achieved. Often, a combination of compatibilizers, or use of other strategies, e.g., crosslinking of one of the three phases (by chemical, thermal or irradiation treatment), may be more appropriate [11].

2.3.2 Reactive compatibilization

The second and the dominant method of compatibilization is based on specific chemical reaction between two polymeric components during mechanical blending. As a result of the process, the chemical reaction takes place within the interphase hence the interfacial agent is produced in situ, with segments from the two homopolymers. Formation of a copolymer at the interface immediately suggests that, by contrast with the compatibilization-by-addition, here the highest MW copolymer is the most desirable – the copolymer is formed within the interphase where it should stay. Reactive processing is an integration of fine polymer chemistry with precisely executed polymer processing (melting, compounding, extruding and forming). It combines the chemical kinetics with flow and thermal properties of the reaction ingredients and products. The conditions for reactive processing require that there is:

i) sufficient dispersive and distributive mixing to ascertain required renewal of the interface;

ii) presence of a reactive functionality, capable to react across the interphase;

iii) sufficient reaction rate making it possible to produce sufficient quantity of the compatibilizing copolymer within the residence time of the processing unit;

iv) stability of the formed chemical structures; and

v) stability of the morphology.

During the reactive processing, during extrusion or injection molding, block or graft copolymers are usually formed. The chemical reaction leads to covalent or, less frequently, ionic bonds [12].

2.4 Methods of Polymer Blending

Mechanical agitation also determines the morphology of polymer blends, hence the end use properties. This section covers the methods of polymer blending and the equipments used for this purpose.

2.4.1 Solution Blending

In this method, the polymers are dissolved in a common solvent. Blend is produced by evaporating the solvent and precipitating the resulting polymer mixture. The use of this method is limited due to the difficulty of solvation of many polymers and difficulty in getting rid of the solvent [13]. Because of the limited use of this method and the method used in this study is melt blending, the melt blending method will be focused on.

2.4.2 Melt Blending

Melt mixing is achieved by mixing the polymers above their melting temperatures via several melt mixing equipment [14]. High shear mixers can generate fine dispersions with droplet diameters smaller than 1 micrometer [15]. Once the ingredients have been fed in the correct proportions into the mixing device hopper, typically an extruder, the polymers and/or additives must be homogeneously blended together. This requires that the polymers be in the molten state. The mixing device melts the polymers, provides a means for mixing, and generates pressure for subsequent operations such as making film when in-line mixing and pelletizing when compounding. Mixing is described as either distributive or dispersive and is illustrated in Figure 2.5.

In distributive mixing, the polymer is rearranged by deformation. Separation and rearrangement of flow and kneading are two examples of distributive mixing. In dispersive mixing, particles are broken up and dispersed within the polymer matrix.

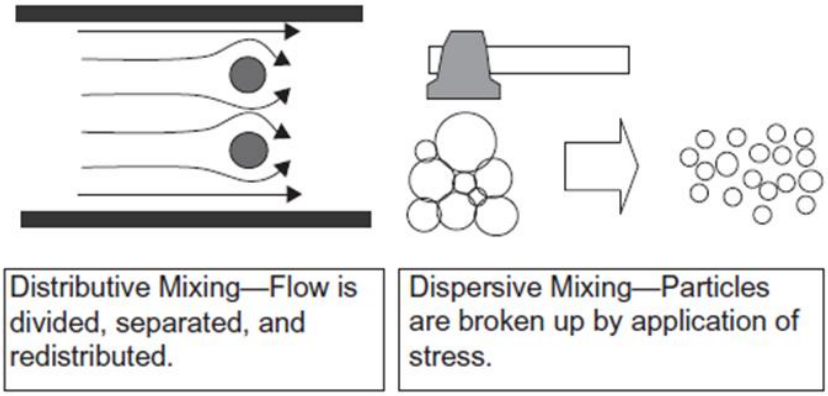


Figure 2.5 : Distributive and dispersive mixing.

Mixing in melt blending is very important in the formation of the final blend morphology. Melt mixing is a complex process involving melting of the solid pellets, distributive mixing (particle elongation), dispersive mixing and droplet coalescence [16]. In order to gain superior properties, both good dispersion and good distribution of the dispersed phase in the matrix is necessary. A good distributive mixing can be achieved by providing convoluted flow paths that split and reorient the flow repeatedly. A good dispersive mixing can be achieved by passing the mixture through small regions of the intense deformation [14, 17] .

Shear stress is important for overcoming the yield stress of the material. The single-screw extruder is the most commonly used device for film production. It efficiently melts the polymer and generates pressure for extruding the polymer through a flat or annular die. It is suitable for many blending applications but has its limitations, many of which can be overcome by optimizing the screw design. Single-screw extruders rely on the difference in friction between the solid polymer pellets and the barrel and screw surfaces to propel the pellets forward. Slippery ingredients may impede the pellet flow and cause surging and other unwanted effects. Single-screw extruders are typically flood fed, meaning the throughput is determined by the extruder screw speed, not how fast the ingredients are fed to the feed hopper. In more sophisticated compounding devices, such as twin-screw extruders, the throughput is decoupled from the screw speed. The output in these devices is determined by the feed rate, and the screw speed can be increased or decreased to change the mixing intensity and energy input. The low melting polymer may also act as a lubricant, impeding the

melting of the high melting component since viscous heat generation from the friction between the polymer and barrel wall is one of the primary avenues for polymer melting.

2.5. Extrusion Process

As the industrial importance of immiscible polymer blends is increasing, it is of crucial importance to understand in detail the fundamental parameters controlling the blend phase morphology during the mixing process because most properties of blends of immiscible polymers depend on the fineness of the phase morphology [18].

2.5.1 Extrusion

Extrusion is a process where the feed is homogeneously delivered to the die to take a desired shape product by being pushed forward with sufficient heat and pressure through the extruder [19]. In batch extrusion systems, the aim is only to take a desired shape product so the feed is already uniform. On the other hand, in continuous extrusion processes, the ingredients are fed together to the extruder and besides taking the shape of the die, homogeneous mixing of the ingredients is also very important.

A general scheme of extrusion processes is given in Figure 2.6. In many extrusion applications, some prior and downstream operations are also necessary. Polymers which are hygroscopic need drying to prevent degradation due to moisture before being fed. In most cases, the polymer will be fed not alone but with some other ingredients such as additives, if a blend is point at issue, the other blend component, compatibilizer etc. So a feed preparation step is usually necessary. After the preparation of true and dry formulation, it is fed to and extruded in the extruder to be melted, mixed, delivered to the die homogeneously and shaped. Then, the product, namely extrudate or throughput or output, is usually cooled by such means as air or water cooling, and collected pullers. Further operations such as printing, annealing may be necessary in some cases. Lastly, the product quality is checked before packaging step [20].

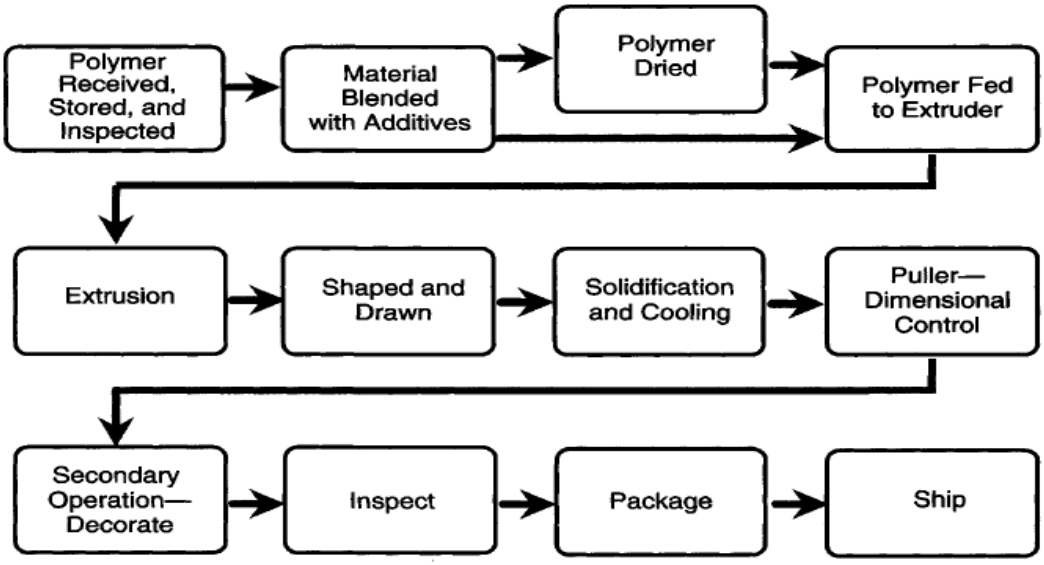


Figure 2.6 : A general scheme of extrusion process.

In a screw extrusion process, polymer is fed from the hopper, and mechanically pushed forward by the rotation of the screw. Along its travel to die, the fed polymer is heated to certain temperatures by the heater bands within the barrel and mainly by the shear created within the extruder to be melted and mixed homogeneously. After reaching to the die by a pumping action, the homogeneous melt is forced through a die orifice that relates to the shape of the product's cross section. The formed melt (extrudate) is cooled as it is being drawn away from the die exit through down-stream equipment (auxiliary equipment includes up-stream and down-stream equipment). Products produced include films, sheets, profiles, pipes, tubes, rods, wire/cable coverings, coatings, filaments, blown shapes, and others.

Each step in this whole extrusion line is very important for the product to be in the desired spec. Any deviation from the determined conditions in any step, for example a change in the extruder temperature profile, screw speed, or cooling temperature, puller speed, drawing ratio, will result in very big differences in the product properties. For instance if screw speed is changed, a homogeneous mixing may not be obtained depending on the residence time, screw itself etc. If the temperature of the cooling bath deviates, a very different product will be obtained depending on different crystallization kinetics [20]. It is convenient to classify extruders as continuous-processing and discontinuous processing according to their mode of

operation. Namely, there are continuous extruders with single-screws or multi screws; continuous disk or drum extruders, which use viscous drag melt actions or elastic melt actions and discontinuous extruders, which use ram and reciprocating actions [21]. Since a single screw extruder is employed in this thesis, only this type of extruder will be mentioned from now on.

2.5.1.1 Single screw extruder components

A single screw extruder has five major equipment components: drive system, feed system, screw-barrel and heaters system, die assembly and control system [20].

The drive system, comprising of the motor, gear box, bull gear, and thrust bearing assembly parts, turns the screw at the required rotating speed over a certain speed range. The drive also provides the required amount of torque to the shank of the screw. Various drive systems, either direct or indirect, are used to meet performance requirements.

The feed system consists of the feed hopper, feed throat, and screw feed section. This part is the solid polymer pellets or powders or their mixture's introduction to the extruder, where the conveying is the result of the weight and solid state fluidity, thus frictional motion of the materials. The solid feed systems that rely on gravity are flood and starve feeding, where feeding rate is determined by the extruder screw speed in the former and is controlled in the latter. Both feed systems have a hopper sitting directly over the extruder feed throat. The feed throat section, attached directly to the extruder barrel, is water jacketed for cooling [20]. The screw, barrel, and heating systems are shown in Figure 2.7. The screw conveys material forward by rotating, contributing to the heating and melting, homogenizing and mixing the melt, and delivering the melt to the die. The barrel and heaters help heat and melt the polymer by controlling the temperature with temperature sensors and control system. There must also be a cooling system over the barrel to prevent temperature raise above set point, which is accomplished usually by air and rarely by water [19].

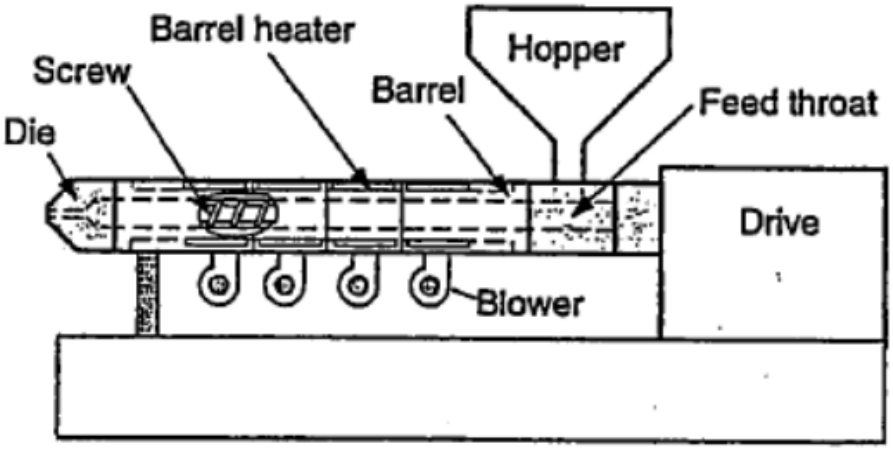


Figure 2.7 : Screw, barrel and heaters in a single screw extruder.

2.6 PS/PP Blends

2.6.1 Polystyrene (PS)

Polystyrene belongs to the group of standard thermoplastics that also includes polyethylene, polypropylene and polyvinylchloride [22]. It is an atactic, amorphous, inexpensive, rigid, easily molded polymer, which possesses good electrical and moisture resistance, with the formula show in Figure 2.23 [23].

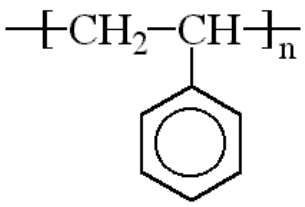


Figure 2.8 : Structure of polystyrene.

Because of the chain-stiffening effect of the benzene ring, the Tg of commercial materials are in the range 90-100°C and isotactic polymers have similar values (approx. 100°C). A consequence of this Tg value plus the amorphous nature of the polymer is that we have a material that is hard and transparent at room temperature. Above its softening point clear polystyrene occurs as a melt, which can be readily processed by techniques such as injection molding or extrusion. Small quantities of lubricants can be used internally or externally as processing aids. The addition of

antistatic agents, UV stabilizers, colorants, compatibilizers and glass fibers is also common [24].

2.6.1.1 Classification of polystyrene

Except the general purpose polystyrene, polystyrene types can be investigated under three main groups as impact-resistant and expandable polystyrene, and polystyrene copolymers.

- **Impact-resistant polystyrene (HIPS)**

The mechanical properties of the relatively brittle PS molding materials can be considerably improved by adding rubbers, generally polybutadiene. Styrene-butadiene molding materials are generally referred to as impact-resistant polystyrene. It is glossy and is an easy to process plastic that is also sturdy and durable. It is furthermore also a rather flexible product that can be used for a diverse range of applications because it can resist high impact. The product is hygienic and visually attractive [24].

The impact-resistant polystyrene is widely used in the food packaging industry because of its unique qualities of strength, hygiene, visual appearance, and ability to retain heat, while also not deforming because of general warm water application. Yogurt holders, plastic cutlery and salad bowls are amongst the products made from high impact polystyrene. It is also used in other industries for packaging such as CD cases, refrigerator linings as well as in the medical industry as trays. Apart from High Impact Polystyrene, various other polystyrenes as mentioned are manufactured and used for packaging.

- **Polystyrene foams (EPS/XPS)**

The cellular structured polystyrene (PS foam) is made by heating polystyrene by different kinds of blowing agents. Generally, two types of PS foam are known and produced in industry: expandable PS (EPS) and extruded PS (XPS). There are both used in insulation industry, but EPS can also be used in packaging material.

EPS is prepared with expandable PS beads which are obtained by suspension polymerization of styrene, are impregnated with pentane. Then they are fed to steam-heated block molds, where expansion and fusion of beads continue.

For XPS productions, firstly, PS pellets and a nucleating agent fed to the primary extruder and melted. A blowing gas is injected and mixed with the molten polymer. The mixture is cooled by passing through a second extruder and then passed through an annular die, where foaming takes place.

The produced foamed PS (EPS/XPS) blocks are sliced for serving to customer [25].

2.6.1.2 Properties of polystyrene

- **Processing properties**

Flow properties may be the most important properties of polystyrene processes. There are two widely accepted industry methods for the measurement of processing properties. These include the melt flow index and the solution viscosity.

The melt flow index is measured by ASTM method as a measure of the melt viscosity at 200 °C and a 5 kg load. The melt flow index of polystyrene is generally controlled by adjustment of the molecular weight of the material and by the addition of such lubricants as mineral oil. Polystyrenes are commercially produced with melt flow ranges of less than 1 to greater than 50, although the most widely available grades generally have melt flows between 2.0 and 20 g per 10 min.

Solution viscosity is another method for measuring the molecular structure of the polystyrene. Solution viscosity can be measured as an 8% solution in toluene and increases with increasing molecular weight.

- **Mechanical properties**

Polystyrenes have very low impact strengths of less than 0.5 ft-lb. Commercially available impact polystyrene grades can be obtained with values of 1.0-4.0 ft-lb. Generally, polystyrenes are not produced with greater than 15% total rubber because

of polymerization processing constraints. Nevertheless, impact properties can be increased substantially without additional rubber by the proper control of rubber particle size, percentage of grafting, cross-linking, and percentage of gel.

Tensile and flexural properties are also important representation of the strength of polystyrenes. Increasing the rubber modification of polystyrene generally leads to lower tensile strength, crystal grades being stiff and brittle. Tensile strength is also decreased by the addition of lubricants, such as mineral oil. Flexural strengths for polystyrenes can be obtained from 5000 to 18000 psi and are also decreased by the addition of rubber and other additives to the polystyrene. Elongations can be obtained from 1% for polystyrene to 100% for some impact polystyrene grades.

- **Thermal properties**

Annealed heat distortion is one popular method for measuring the resistance to deformation under heat for polystyrenes. The heat distortion temperature is decreased by the addition of rubber, mineral oil, or other additives to polystyrene.

The glass transition temperature for unmodified polystyrene is 373 K, and the glass transition temperatures for polybutadienes are 161-205 K, subject to the cis, trans, and vinyl content.

- **Optical properties**

Crystal polystyrene is a transparent and colorless polymer; high impact polystyrene is generally opaque as a result of the rubber particles. Developmental grades of translucent impact polystyrenes have been produced but have not gained wide acceptance. The major optical; property for high impact polystyrene is gloss. Gloss is a measure of the percentage of light reflected is generally controlled by the size of the rubber particle. In general, the smaller rubber particle gives higher gloss. Values from 20 to 95% reflectance are commercially available [26].

2.6.2. Polypropylene (PP)

Polypropylene (PP) - This polyolefin is readily formed by polymerizing propylene with suitable catalysts, generally aluminum alkyl and titanium tetrachloride. Polypropylene properties vary according to molecular weight, method of production, and the copolymers involved. Generally polypropylene has demonstrated certain advantages in improved strength, stiffness and higher temperature capability over polyethylene. Polypropylene has been very successfully applied to the forming of fibers due to its good specific strength which is why it is the single largest use of polypropylene. Polypropylene also happens to be one of the lightest plastics available with a density of 0.905 g/cm^3.

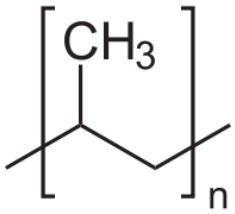


Figure 2.9 : Structure of polypropylene.

Polypropylene is a versatile member of polyolefins which are profoundly affected by stereoregularity (Figure 2.25). This thermoplastic polymer is used in a wide variety of applications including packaging, textiles, stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers and automotive components [27].

The isotactic polypropylene is prepared with various modifications of Ziegler-Natta coordination catalysis, producing polymers with varying degrees of stereoregular order with isotacticity up to 98%. Syndiotactic polypropylene is prepared with soluble coordination catalysis and the stereoregularity attained is generally lower than that of isotactic polymers. Atactic polypropylene can be obtained by extraction with boiling n-heptane from isotactic polypropylene of lower stereoregularity [28].

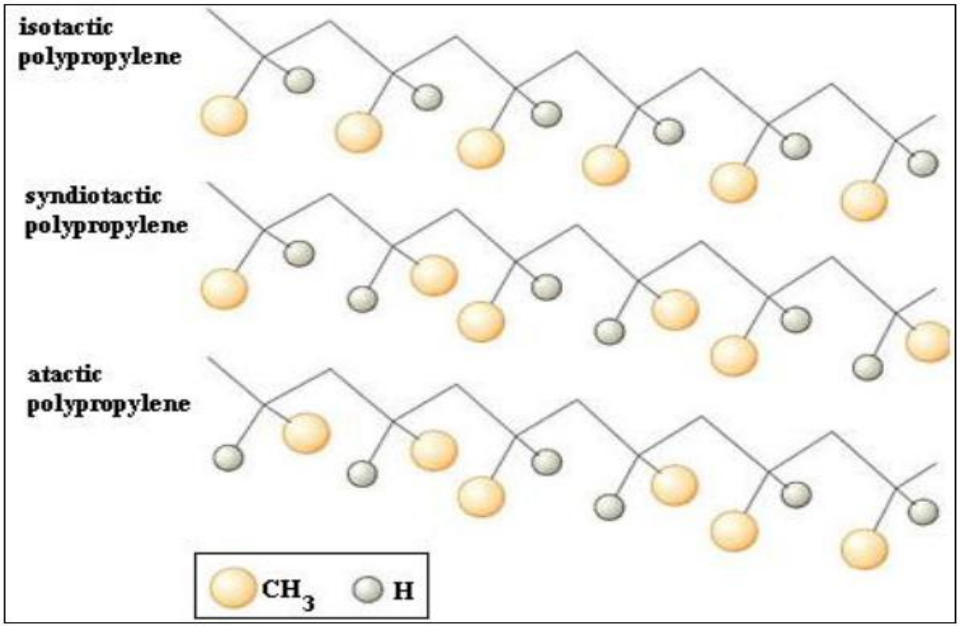


Figure 2.10 : Structure of isotactic, syndiotactic and atactic polypropylene.

2.6.2.1 Properties of Polypropylene

The mechanical and thermal properties of polypropylene can vary based on the isotacticity, the molecular weight and its distribution and % crystallinity. Since PP is a viscoelastic material like other thermoplastics, its mechanical properties are strongly dependent on time, temperature and stress.

- **Density**

Polypropylene is the lightest among the commonly used thermoplastics and has a density of 0.9 g/cm^3.

- **Thermal properties**

Polypropylene has a glass transition temperature and a crystalline melting point of -10ºC and 160-170ºC, respectively. Moreover, it has a maximum continuous use temperature of 100ºC, which is significantly higher than those of the other commodity plastics and some other engineering plastics.

- **Mechanical properties**

The mechanical properties of isotactic PP depend on its % crystallinity. Due to its relatively high melting temperature, the crystalline phase maintains mechanical strength up to rather high temperatures. It has high tensile strength, stiffness and hardness due to its crystallinity. However, an increase in molecular weight leads to a reduction in tensile strength, stiffness, hardness but an increase in impact strength of polypropylene.

- **Electrical properties**

Polypropylene has an excellent electrical insulating property. It has outstandingly high resistivity, low dielectric constant and negligible power factor.

- **Solubility**

Polypropylene is soluble only at elevated temperatures due to its crystalline character. Isotactic PP is soluble in "good" solvents such as xylene, tetralin, chlorinated aromatic and aliphatic hydrocarbons, etc. above 80ºC [29].

2.6.3 Propylene based elastomers (PBE)

New PBE are olefinic specialty elastomers based on proprietary metallocene technology. They are semicrystalline copolymers of propylene and ethylene and they bring new capabilities to the film industry [30].

-Unique combination of elasticity, flexibility, adhesion, drapability and toughness

-Potential not seen in conventional elastomers or resins

They are compatible with many other polymers. Low crystallinity copolymers of propylene (>80 wt%) and ethylene. Densities are between 0.855 and 0.871 g/cm^3.

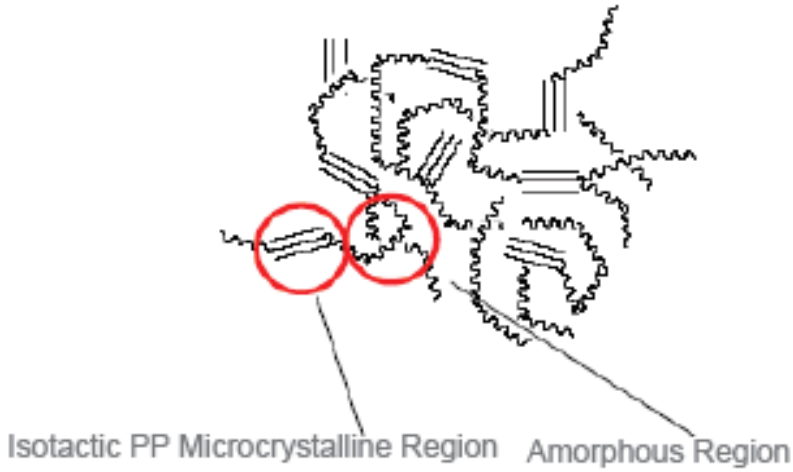


Figure 2.11 : Amorphous and microcrystalline region of PBE.

New PBE's strengths are;

- Elasticity
- Excellent compability with PP and PE
- Excellent adhesion to PP and PE
- Maintain clarity of PP

New PBE's

- Enhance the performance of many film applications
- Suitable for cast film, blown film and extrusion coating
- Enable low SIT / high hot tack and strong seal strengths
- Can be processed on conventional extrusion equipment
- Compatible with most polyolefins
- Food Law compliant for food packaging applications[30]

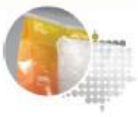
	Cast PP	Stretch Hoods	Raffia modification	PP woven sacks	Stretch Cling	Surface Protection
						
Application description	Sealant resin	Elastic engine	hPP blend partner	Extrusion Coating & Lamination	Blend partner in skin	Adhesive resin in coextrusion

Figure 2.12 : Application description of PBE's.

2.6.4. PS/PP Blends

Polystyrene (PS) and polypropylene (PP) as well as their blends belong to the most often used polymeric materials. In particular, PP-based materials have important applications in medicine. However, PP/PS blends exhibit relatively low impact strength, low wear resistance and high friction. In fact, PS is much more brittle than all other engineering polymers for which brittleness has been determined.

The disadvantageous characteristics of the PS/PP blends can easily be explained by poor compatibility of the components. Here lies the reason why compatibilizers are added to immiscible blends. Compatibilizers increase the miscibility of the components of the blend by reducing interfacial tension; that tension largely determines properties of multiphase systems. The important literature on the improvements of PS/PP blends are given as below in chronological order.

Raghu and co-workers studied the mechanical, thermal, rheological, and morphological properties of polypropylene (PP)/polystyrene (PS) blends compatibilized with styrene–isoprene–styrene (SIS), styrene butadiene–styrene (SBS), and styrene– butadiene–rubber (SBR). The incompatible PP and PS phases were effectively dispersed by the addition of SIS, SBS, and SBR as compatibilizers. The PP/PS blends were mechanically evaluated in terms of the impact strength, ductility, and tensile yield stress to determine the influence of the compatibilizers on the performance properties of these materials. SIS- and SBS-compatibilized blends showed significantly improved impact strength and ductility in comparison with SBR-compatibilized blends over the entire range of compatibilizer concentrations. Differential scanning calorimetry indicated compatibility between the components upon the addition of SIS, SBS, and SBR by the appearance of shifts in the melt peak of PP toward the melting range of PS. The melt viscosity and storage modulus of the blends depended on the composition, type, and amount of compatibilizer. Scanning electron microscopy images confirmed the compatibility between the PP and PS components in the presence of SIS, SBS, and SBR by showing finer phase domains [31].

In a work of Zhang and co-workers polypropylene (PP)/polystyrene (PS) blends modified with reactive monomers, such as maleic anhydride (MAH) and styrene (St),

and in situ formed PP/PS blends were prepared by melting extrusion. The crystallization and melting behavior and the dynamic mechanical properties of the PP/PS blends, including the structure of the grafted copolymer, were investigated. The results indicated that the addition of MAH hardly influenced the crystallization temperature of PP in the blends, but the addition of MAH and St increased the crystallization temperature of PP in its blends. The blends showed no remarkable variety for the melting temperature, but the shapes of the melting peaks were influenced by the addition of the reactive monomers. In addition, a significant increase in the storage and loss moduli of all the modified PP/PS blends was observed [32].

Li and co-workers studied the role of styrene-ethylene/propylene (SEP) diblock copolymer in controlling morphology development of polypropylene/polystyrene (PP/PS) blends. According to SALS, a certain amount of SEP was located at the phase boundary, forming a relatively thick transition layer penetrating into the homopolymers. For PP/PS (1/99) and PP/PS (20/80) blends, the incorporation of SEP into PP/PS blends resulted in a decrease in domain size following an emulsification curve as well as a uniform size distribution, and consequently, a fine dispersion of PP domains in the PS matrix. However, for PP/PS (45/55) blends, the addition of SEP results in a non-monotonous change in domain size. Due to the penetrating transition layer, adhesion between phases was improved, making it possible for applied stress to transfer between phases and leading to a more uniform stress distribution when blends were broken; accordingly, a more complicated morphology fluctuation of the fracture surfaces appeared [33].

Brostow and co-workers prepared various concentrations of polypropylene (PP) and polystyrene (PS) blends with styrene-ethylene/butylene-styrene block copolymer (SEBS) added as a compatibilizer between the two main polymers. They investigated the effect of SEBS on processing, morphology and thermophysical properties of the blends. The compatibilizing agent improves the blend morphology since smaller particles of the dispersed PS phase in the PP matrix blends are obtained; adding more than 5 % SEBS has no further effect on the blends. The presence of SEBS lowers the crystallinity of the PP-rich phase - as reflected in the enthalpy of fusion and also in the enthalpy of crystallization [34]. Brostow and co-workers used styrene-

ethylene/butylene-styrene (SEBS) block copolymer as the compatibilizer for PP + PS blends. They investigated effects of the presence of SEBS on tribological and mechanical properties; dynamic mechanical analysis (DMA) was also performed. Since the copolymer causes formation of smaller particles of the dispersed PS phase in PP matrix blends, there is improved energy transmission and dissipation resulting in higher impact strength. The SEBS additive is relatively soft and causes a decrease in stress at break but an increase in elongation at break in tensile testing. In most cases the friction of the compatibilized blends is higher although in PS-rich blends they find a decrease. Scratch testing shows a change in wear mechanisms when SEBS is added to PP/PS. In incompatibilized blends they observe adhesive wear, with crazes formed in the middle of the wear track. A compatibilized blend shows more ductile behavior and ploughing wear [35].

Al-Saleh and his friends study on using selective localization of carbon black (CB) at the interface of immiscible polymer blends in order to reduce the percolation threshold concentration and enhance the conductivity of the blends. CB was successfully localized at the interface of polypropylene/polystyrene (PP/PS) blend by introducing styrene- butadiene-styrene (SBS) tri-block copolymer to the blend. In CB–PP/PS/SBS blends, CB has higher affinity for the polybutadiene (PBD) section of the SBS copolymer, whereas in CB PP/PS blends, CB prefers the PS phase. PP/PS interface is one of the preferred locations for the SBS copolymer in the (PP/PS) blend; at which the PBD section of the SBS copolymer forms a few nanometers thick layer able to accommodate the CB nano-particles. The influence of SBS addition on the morphology and electrical properties of various PP/PS blends filled with 1 vol% CB were studied. SBS influence on the conductivity of PP/PS blends was found to be a function of the PP/PS volume ratio and SBS loading. The most dramatic increase in conductivity was found in the (60/40) and (70/30) PP/PS blends upon the addition of 5 vol% SBS. 5 vol% SBS was found to be the optimum loading for most blends. Using 10 vol% of SBS was reported to deteriorate electrical conductivity of the conductive co-continuous PP/PS blends. For all blends studied, SBS addition was found to compatibilize the blends. Finer morphologies were obtained by increasing SBS loading [36].

Wu and co-workers investigated the effects of the blend composition and rotation speed on the morphological evolution of polypropylene (PP)/polystyrene (PS) blends in a twin-screw extruder. When PS was the major component, the rate of melt and the rate of dispersion played final roles in the morphological development of the polymer melts. However, when PP was the major component, the rate of dispersion and the rate of coalescence played key roles. A high tendency to coalesce occurred at a high rotation speed and/or a high content of the dispersed phase. When the PP/PS blend composition was close to 1, a co continuous morphology was observed to transmute into a coarse one with increasing rotation speed. Attempts were made to correlate the morphology and mechanical properties [37].

Al-Saleh and co-workers studied mechanical properties and morphology of carbon black (CB)-filled polypropylene/polystyrene (PP/PS) blends with and without styrene-butadiene-styrene (SBS) triblock copolymer as a function of PP/PS volume ratio and CB content. Incompatibility of the PP/PS blends was found to negatively influence the blends' tensile properties. Addition of 5 vol% SBS to the CB-filled PP/PS blends was found to compatibilize the blends by reducing the interfacial tension and enhancing the interfacial adhesion. In general, SBS addition enhanced the yield stress of the co-continuous CB-filled PP/PS blends, reduced the Young's modulus and enhanced the elongation at yield for all blends studied. For the (70/30) PP/PS blends with and without SBS, yield stress of the blends filled with up to 3 vol% CB is close to that of the unfilled (70/30) PP/PS blends. Increasing CB loading to 5 vol% considerably increased the yield stress for the blends with and without SBS. A gradual increase in Young's modulus was reported with increasing CB content in the (70/30) PP/PS blends with and without SBS. Increasing CB loading up to 5 vol% did not influence the elongation at yield of the (70/30) PP/PS blend without SBS [38].

Straat and co-workers prepared conducting polymeric materials from polypropylene (PP)/polystyrene (PS), together with carbon black (CB). An immiscible 1:1 blend of PP and PS to which 4 wt% CB was added exhibited a very low melt draw-down ratio at rupture compared with PP with the same content of CB. By adding 5 wt% SEBS (styrene-ethylenebutene- styrene block copolymer), the ultimate melt draw-down

ratio increased about 10 times, which made the material more suitable for melt spinning [39].

Rajkiran and co-workers studied the effect of organically modified clay on the morphology, phase stability and mechanical properties of polypropylene (PP) and polystyrene (PS) blends, using three molecular weight grades of PP. Maleated polypropylene was used, at a PP-g-MA/organoclay ratio of 1, to preferentially promote dispersion of the organoclay in the PP matrix. The MMT content was fixed at 3 wt% based on the PP/PP-g- MA/MMT phase and the PS content was varied from 0-100 wt% in the blend. The organoclay resides in the PP phase and at the PP/PS interface. The dispersed PS particle size is significantly reduced by the presence of MMT, with maximum decrease observed for the low viscosity PP compared to its blend without MMT. The blends with MMT did not show any change in onset of co-continuity, though MMT shifts the phase inversion composition toward lower PS contents. The phase stability of the blend was significantly improved by the presence of MMT; for blends annealed at 210^0C for 2 h the dispersed phase particle size increased by as much as 10x without MMT with little change was noted with MMT present in the blend. The tensile modulus of blends improved with the addition of MMT at low PS contents. Blends based on the highest molecular weight grade PP showed increase in the tensile yield stress up to 40 wt% PS in the absence of MMT. The tensile strength at break for blend increased slightly with MMT while elongation at break and impact strength decreased in the presence of MMT [40].

Krishnan and co-workers prepared nanoclay composites based on polypropylene (PP) / polystyrene (PS) blends by melt mixing. They studied the effect of modified clays on the properties of nanocomposites and evaluated the degree of dispersion and morphology of nanocomposites. Nanocomposites prepared from modified clays show improved tensile modulus and strength as compared to those prepared from unmodified clay. Vinyl silane modified nanocomposites show maximum improvement in mechanical properties, suggesting that vinyl silane provides better interfacial interaction. Thermogravimetric analysis show improved thermal stability of PP/PS/clay nanocomposites. The dynamic mechanical analysis reveals higher storage moduli over a temperature range of 40–125 ^{0}C for nanocomposites, and the extent of increase in the storage modulus is dependent on the type of clay [41].

In a work of Hwang and co-workers electrical, rheological properties and phase change behavior of polypropylene (PP)/ polystyrene (PS) blends filled with multi-walled carbon nanotube (MWNT) were investigated. Two kinds of masterbatch were used to prepare ternary blends of PP, PS, and MWNT, and the effects of the kinds of masterbatch were confirmed by phase morphology of ternary blends and the distribution of MWNT. From thermodynamic analysis, MWNT is expected to locate in PS phase and it shows a good agreement with the TEM observations. The ternary composites show the lowest conductive percolation threshold and fine morphologies when most MWNT particles are located at the interface. Time sweep test were carried out to monitor the phase coalescence of the ternary blends and MWNT migration and agglomeration in the PS phase during annealing.

The higher filler concentration, storage modulus is increased, moreover, as use of PPMB, the increase of storage modulus is predominant. The presence of MWNT in the interface results a fine morphology in ternary blends with low percolation value. During annealing process, MWNT prevent the coalescence of PS phases, especially, PPMB plays an effective role as a compatibilizer in immiscible blends. Crystallization and thermal degradation of PP/PS ternary blends were also studies to confirm the improvement of compatibility. From the above results it could be concluded that the compatibility of the PP/PS blends was increased. Moreover, by introducing PPMB during extrusion, the compatibility of immiscible PP/PS blends could be more enhanced [42].

In the study of Fortelny and co-workers the effect of molecular structure of styrene–butadiene block (SB) copolymers on the morphology, tensile properties, impact strength, and micro hardness of polypropylene/polystyrene (PP/PS) (80/20) blends was studied. The addition of SB copolymers substantially reduces the size of dispersed PS particles formed at mixing. The distribution of SB copolymers between the interface and bulk phases is controlled by the length of styrene blocks in SB, but a decrease in the size of PS particles at mixing correlates with total molecular weight of SB copolymers. For a substantial part of compatibilized blends, PS particles aggregate rapidly during compression molding.

Blends containing PS particles with well-developed honeycomb structure show lower yield stress, higher plasticity, and lower tensile impact strength than the blends having PS particles with simple or undeveloped honeycomb structure. Micro hardness of PP/PS blends is additive and of PP/ PS/SB blends is lower than the additive due to the effect of SB copolymers on crystalline structure of PP matrix [43].

In a work of Wang and her friends wanted to improve compatibility between PP/PS blends and different types of fillers were prepared by melt compounding techniques. The effects of the MCM-41 and PP-g-MAH on the mechanical and crystallization properties of PP/PS composites were investigated. The results of mechanical tests showed that the co-incorporation of MCM-41 filler and PP-g-MAH gave rise to much better tensile and impact strength than adding of MCM-41 and PP-g-MAH respectively due to different interfacial structure between the fillers and the matrix. DMA attested that the good adhesion between PP/PS blend was obtained by adding MCM-41 and PP-g-MAH fillers [44].

In the study Xu and his friends examined the influence of SBS loading and the compounding process on morphology, electrical conduction and thermal stabilities of CB-filled PP/PS blends. Simultaneous measurement of conductive and rheological behaviors was adopted to determine the CB aggregation and the phase coalescence during annealing of the composites. The immiscible CB/PP/PS composite with CB rather homogeneously dispersed in the PS phase exhibits the highest resistivity. SBS compatibilizer at appropriate loading can significantly lower the electrical resistivity of the composites by partially trapping CB particles in the PP/PS interfacial region [45].

In a work of Zhang and coworkers β-polypropylene/polystyrene (β-PP/PS) blends were prepared with PP, PS, and a novel supported β-nucleating agent or β-nucleated PP and PS. The β-PP/PS blends were compatibilized by PP-g-MA, PP-g-GMA, POE-g-MA, and EVA-g-MA, respectively. For exploring the effect of PS amount and compatibilizers on the β-nucleation of PP, crystallization behavior and melting characteristics, the β-crystal content and crystal morphology of β-PP are characterized. The results indicated that the PP with high content of β-crystal was

obtained by addition of $CaCO_3$ supported β-nucleating agent (β -NA) into PP. The b-nucleation, crystallization behavior, and melting characteristics, and the β-crystal content of β-PP in these blends were not influenced by addition of PS and its amount. However, the increased content of PS decreased the size of β-spherulites of PP in these blends. The β-nucleation of PP in compatibilized blends slightly depended on the compatibilizers. β-PP/PS blends with high β-crystal content can easily be prepared [46].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene (PP)

PP homopolymer was the commercial Luban^{TM} isotactic PP supplied from Oman Polypropylene LLC company. The melt flow rate (190°C/2.16 kg) and heat deflection temperature (under 0.45 MPa) are 5.4 g/10 min and 85ºC respectively. The density is declared 910 kg/m^3 by the company.

3.1.2 Polystyrene (PS)

PS was the commercial polystyrene supplied from Total Petrochemicals. The melt flow rate (190°C/2.16 kg) is 2.1 g/ 10 min.

3.1.3 Propylene based elastomer (PBE)

Vistamaxx was the commercial propylene based elastomer obtained from ExxonMobil Chemical Company. The melt flow rate (190°C/2.16 kg) is 8.3 g/ 10 min. The density is declared to be minimum 855 kg/m^3 and maximum 871 kg/m^3 by the company.

3.2 Equipments

3.2.1 Extruder

A single screw extruder with a diameter of 25 mm and L/D of 25 was used to prepare PS / PP blends by melt mixing method. The scheme of the extruder is given in Figure 3.1.

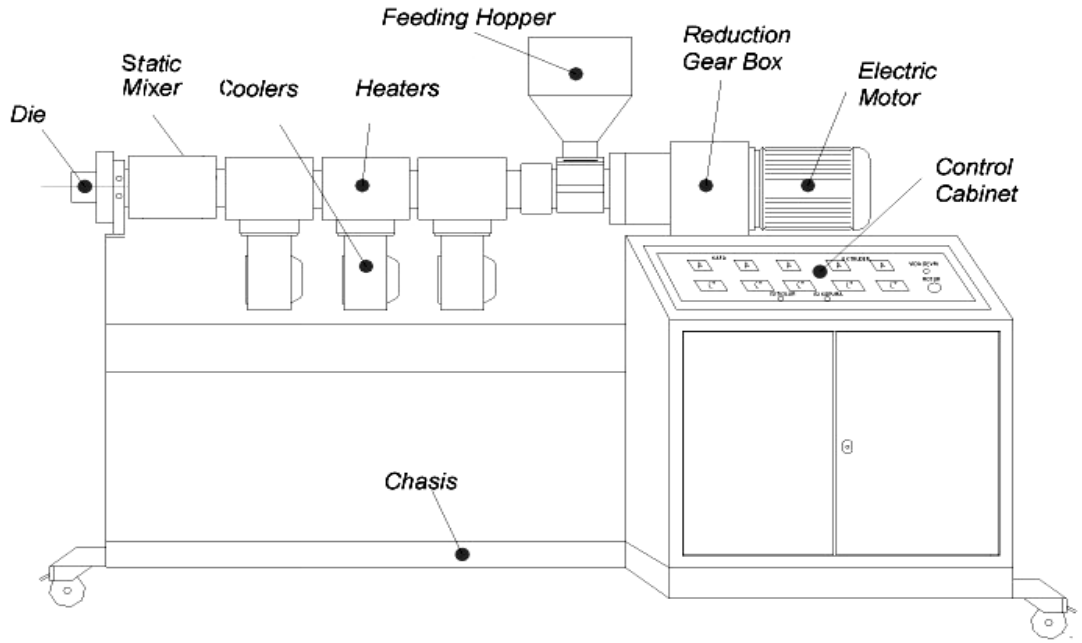


Figure 3.1 : Single screw extruder.

The motor is a 3 KW, 1450 rpm AC electric motor to supply the power for the movement of the screw. The reduction gear, with a 3KW gear resistance, has a reduced turning speed of 97 rpm box to deliver AC motor torque. Temperature control is achieved by PID control of ceramic heaters, which are placed over each zone and air blowers which were attached to every section for cooling action. The heaters have a capacity of giving 3 watts per every cm² of the barrel surface and are divided in 3 sections. Every ceramic heater section is surrounded with a cover. All the controllers are introduced in a control board. The control board contains an AC motor invertor which can change the motor speed by adjusting the frequency. Temperature of the barrel measured by PT 100 sensors and controlled by PID controllers.

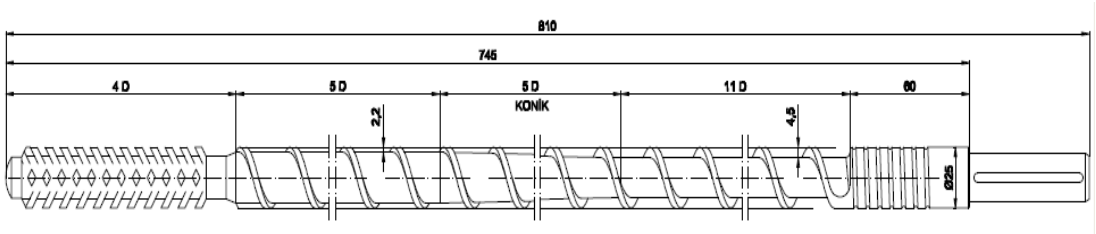


Figure 3.2 : Screw configuration.

The screw of the extruder has 3 stages, which consists of universal single flights in the feeding and transition zones with distributive pineapple mixing elements in the metering zone. The compression ratio (ratio of metering section flight depth/feeding section flight depth) is 2.05. The screw configuration is given in Figure 3.2.

A static mixer is placed between the barrel and the die. The pressure before the die is monitored by the pressure gauge.

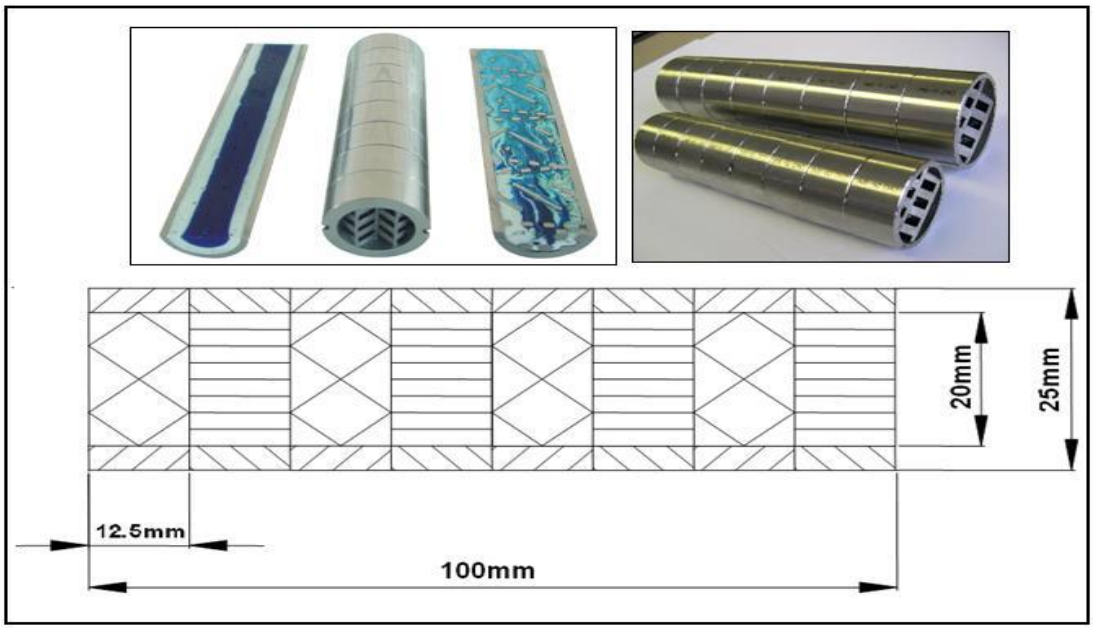


Figure 3.3 : Static mixer.

In order to further increase the degree of mixing, a static mixer is placed between the barrel and die. This static mixer which is given in Figure 3.3 consists of eight mixing elements.

3.2.2 Universal testing machine

A Zwick/Roel Z.05 universal testing machine was performed for the evaluation of tensile properties of the blends. The machine had 500 N capacities, sizes to 12x30 mm stainless steel Zwick pincer grips. The load cell was capable of applying 500 N force and testing samples up to 200 mm/min speed.

3.2.3 Differential scanning calorimetry analysis

Thermal analysis of the samples were done with a Mettler Toledo DSC1 Differential Scanning Calorimetry equipment. The analysis were done for all blends and pure PS,

PP and compatibilizer between 30ºC and 200ºC at 10ºC/min heating rate under inert atmosphere. Glass transition temperatures (T_g), melting temperatures (Tm), the peak temperature (Tp), the enthalpy of crystallization, and the enthalpy of fusion values of the compounds were obtained using a differential scanning calorimeter (DSC).

3.2.4 Scanning electron microscopy

The morphologies of the samples were investigated by scanning electron microscopy (FE-SEM, FEI Quanta FEG 450) was used to examine the samples after fracture in liquid nitrogen. The specimens were coated with gold by means of vapor deposition using vacuum sputtering in order to avoid excessive charging during imaging.

3.2.5 Melt flow index device

HAAKE Melt Flow MT was used to measure melt flow rate (MFR) values of the samples. It is equipped with a standard 8 mm in length and 3 mm in diameter die, a standard 6.35 mm in length and 9.4772 mm in diameter piston, and a standard load to apply 2.16 kg force during the extrusion.

3.3. Experimental Procedure

3.3.1. Optimization

The aim of this study is to analyze the effects of composition and compatibilization on mechanical, thermal, and morphological properties of PS/PP blends which are prepared by melt mixing via a single screw extruder. Firstly, an optimum temperature profile was necessary. For this reason, the processing limits were determined by DSC analysis of homo PS, homo PP and compatibilizer (PBE) at the beginning of the study. The lower limit of the processing temperatures was being determined by PP as 190ºC, which is higher than melting temperature of PP and the upper limit was being determined by PS as 200ºC, which is lower temperature than PS degradation temperature.

After knowing the processing limits, experiments with several temperature profiles were carried out. As a result of these experiments, the temperature profile was decided to be 190°C / 195°C / 1955°C / 200°C / 200°C for zone 1, zone 2, zone 3, static mixer and die respectively. Then, residence time measurements at 50 rpm was done by dye detecting method with the use of blue colored PP-based mastebatches, which were found to be between 1.1 – 1.4 minutes. After the temperature profile

determination, optimum compatibilizer amount was determined. According to the literature, compatibilizer was useful between 5 – 10 phr for different compositions of PS/PP blends. So, the weight percent of the polymers were varied from 0 to 100 with 5 and 10 phr compatibilizers were added to prepare 22 samples by melt mixing method. Also 11 samples were prepared with the same compositions of PS/PP ratios without compatibilizer for comparison purposes.

3.3.2. Preparation of PS/PP blends

In this study, different compositions of PS/PP blends with and without compatibilizer were extruded at 50 rpm in order to investigate the effects of composition and compatibilization on mechanical, thermal, and morphological properties of PS/PP blends.

300 grams of polymer was prepared for each batch for melt mixing in extruder. Compatibilizer was added to the PS/PP resin compositions as phr. The PS, PP and compatibilizers pellets were premixed by shaking in a large – closed container by hand for 5 minutes before being fed to the extruder. Temperatures of the zone 1, zone 2, zone 3, static mixer and die were 190°C / 195°C / 195°C / 200°C / 200°C respectively. The strands from the die were collected on a metal plate and pelletized after complete solidification. The die swelling was observed especially compatibilized blends, due to the properties of PBE. Die swelling comes from the flow rate through the polymer flow stream. Physical entanglements may relax, if the time scale of the polymer within the die is long enough. When the polymer stream leaves the die, the remaining physical entanglements cause the polymers in the die stream to regain a portion of its former shape and spherical volume, in order to return to the roughly spherical conformation that maximizes entropy. The mixtures prepared in extruder were collected from die and the middle of these productions was taken as samples of the mixtures, because effective mixing takes place at this point. Strands types of specimens prepared for the mechanical measurement tests.

3.3.3 Mechanical property characterization

Specimens were cut with a cutter. Then dimensional measurements were taken place. Suitable specimens were placed between gauge. The tensile tests were carried out at 100 mm/min rate according to ISO 6259 (specifies a short-term tensile test method for determining the tensile properties of thermoplastics pipes) standards. From the

measured stress and strain values, maximum tensile strength and E-modulus were calculated from the average of at least 5 specimens tested. The tensile strength, were averaged from at least 5 tested specimens with the errors calculated as ±7%.

For the comparison of the mechanical tests results on the blends; mechanical properties of homo PS and homo PP specimens were measured and calculated.

3.3.4 Thermal property characterization

The thermal properties of the blends were determined by differential scanning calorimetry (DSC). The heating scans were carried out at 10ºC/min rate in the temperature range of 30ºC - 200ºC in the DSC analysis of the blends. The enthalpy of crystallization and the enthalpy of fusion were calculated from the thermograms by evaluating the area under the melting curves. Parameters of crystallization and melting were taken from the second run curves.

3.3.5 Melt flow rate determination

The melt flow rate (MFR) of PS/PP blends were measured at 190ºC with 2.16 kg load according to ASTM D1238 standard.

3.3.6 Morphological characterization

The aim is to examine two-phase morphology with PS (or PP) particles dispersed in the PP (or PS) matrix. The changes of morphology in blends by addition of compatibilizer were examined.

4. RESULTS AND DISCUSSION

In this study, PS/PP blends were prepared according to the procedure given in the Section 3.3.2. Compatibilizer PBE was used in blends with two compositions as 5-10 phr. Homo PS, homo PP and the PS/PP blends with compatibilizer were prepared. The prepared 33 samples were characterized and the measurements results of the mechanical, thermal and morphological properties of the blends were given.

4.1 Evaluation of Mechanical, Thermal and Morphological Properties

4.1.1 Tensile test result of blends

Tensile tests were performed with universal test machine at 25^0C. The tensile properties of the materials are shown in Table 4.1 and Table 4.2. The values of all the mechanical parameters are calculated as 5 specimens for each composition and the data of samples is plotted on Figures from 4.1 to 4.6. From these results, it is clear that composition and compatibilization of the blends have a pronounced effect on the mechanical properties of these materials.

Table 4.1 : Maximum tensile strength values of the PS/PP blends with 0-5-10 phr compatibilizers.

PS Content (%)	PP Content (%)	0 Comp. (MPa)	5 phr Comp. (MPa)	10 phr Comp. (MPa)
0	100	66	56	55
10	90	53	52	52
20	80	51	46	42
30	70	48	44	42
40	60	58	48	45
50	50	64	56	54
60	40	71	64	62
70	30	74	67	67
80	20	76	70	71
90	10	77	69	71
100	0	78	71	71

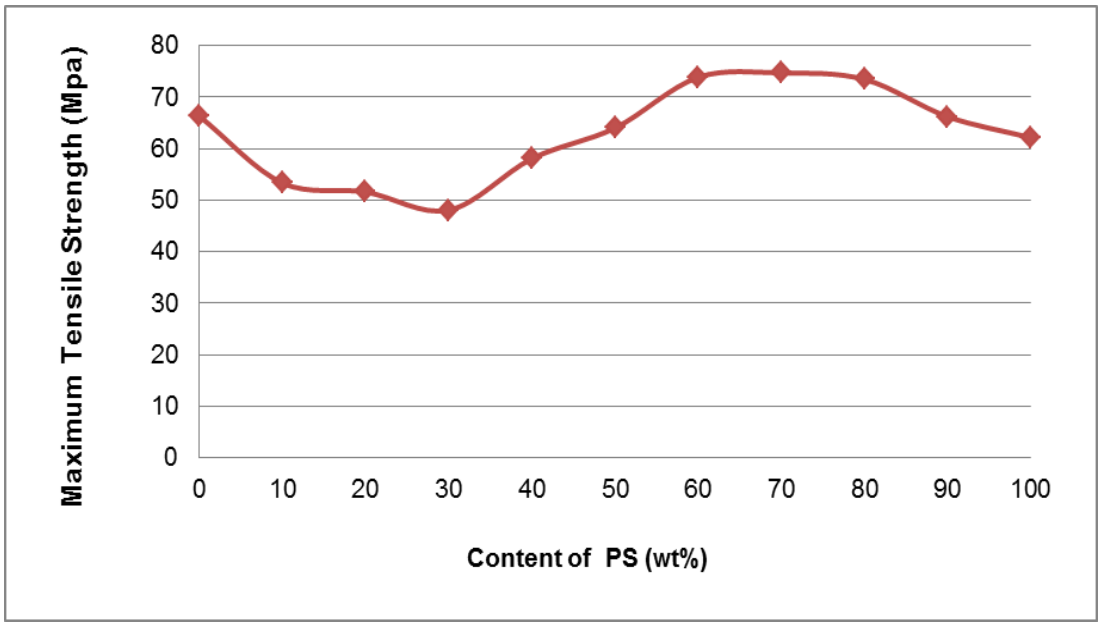


Figure 4.1 : Maximum tensile strength of the PS/PP blends without compatibilizer.

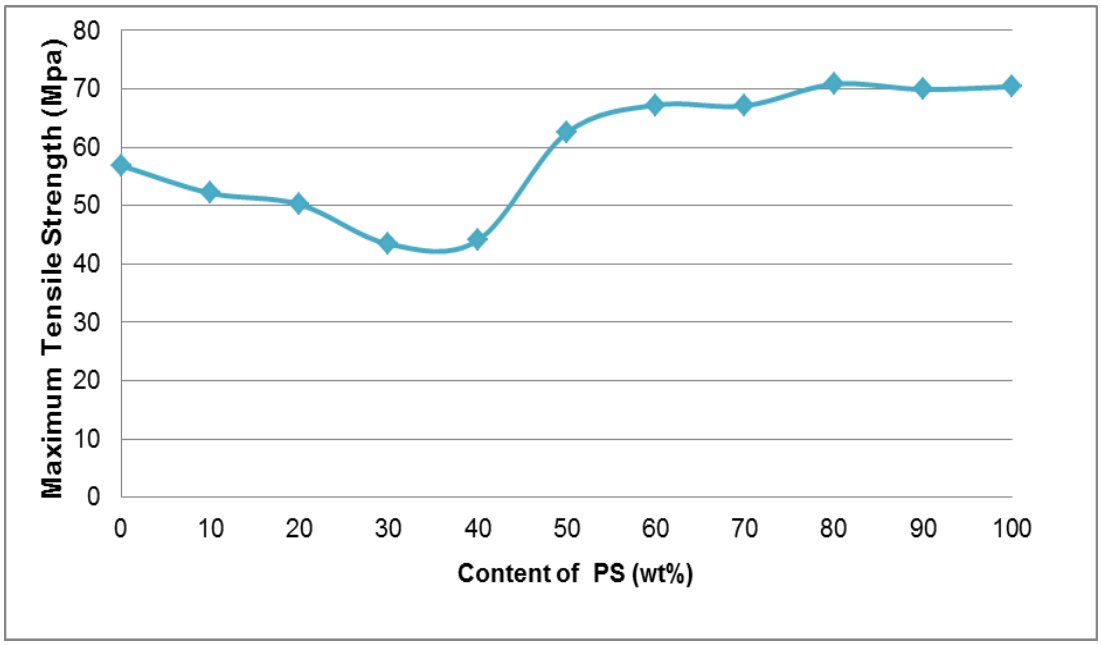


Figure 4.2 : Maximum tensile strength of the PS/PP blends with 5 phr compatibilizer.

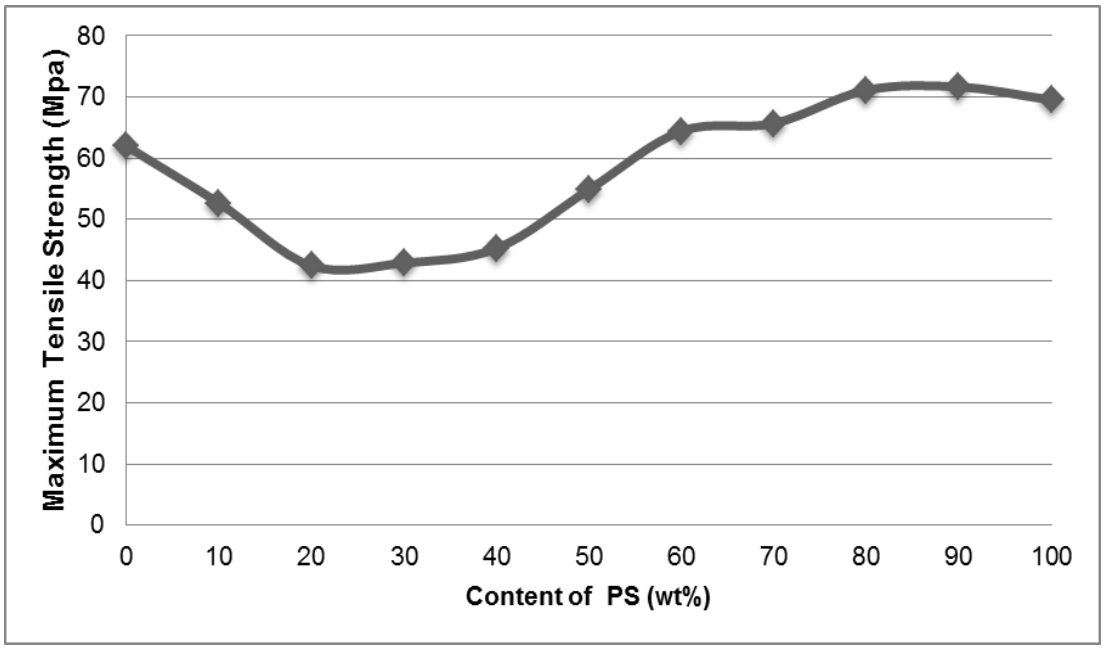


Figure 4.3: Maximum tensile strength of the PS/PP blends with 10 phr compatibilizer.

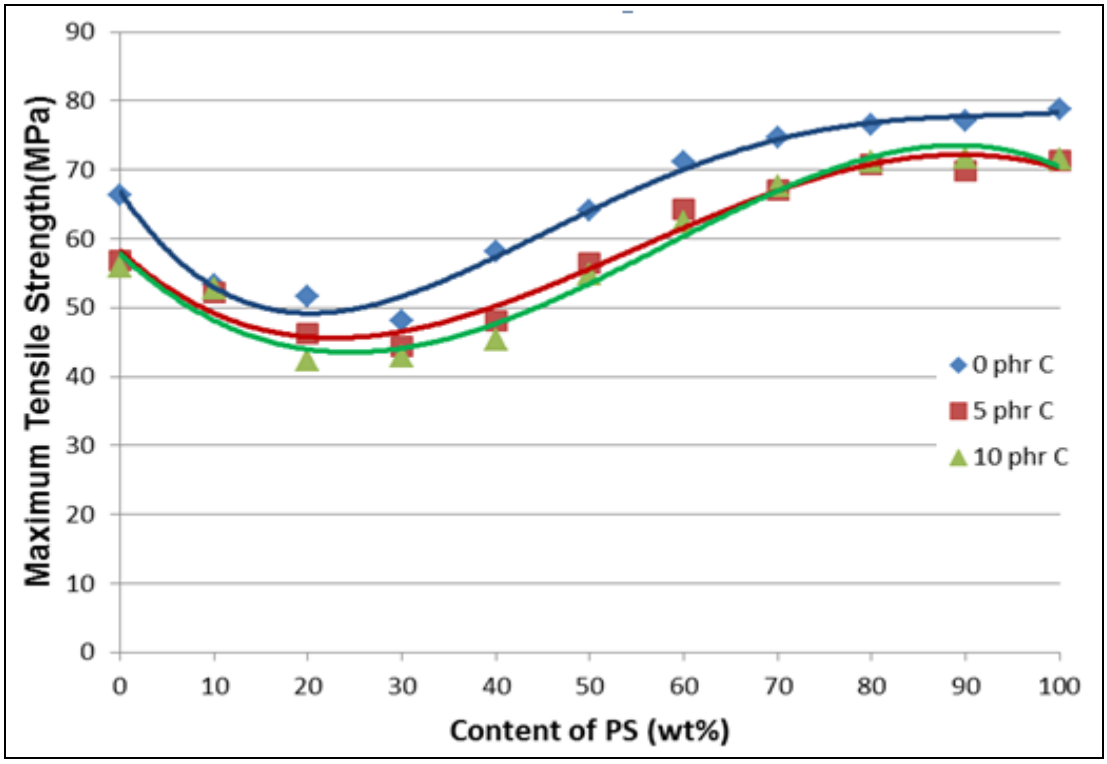


Figure 4.4: Maximum tensile strength values of the PS/PP blends with 0-5-10 phr compatibilizers.

The maximum tensile strengths decrease by increasing of PS of all samples content up to 30 wt%, where a minimum value is seen. Afterwards, the maximum tensile strength increases with further increasing of PS content. When PS content is less than 70 wt% the maximum tensile strength decreases as adding of compatibilizer and the compatibilizer acts as rather a softening-material. The maximum tensile strength is found to increase as increasing of compatibilizer content when PS content is larger than 70 wt%.

Table 4.2 : Modulus of Elasticity of the PS/PP blends with 0-5-10 phr compatibilizer.

PS Content (%)	PP Content (%)	0 Comp. (MPa)	5 phr Comp. (MPa)	10 phr Comp. (MPa)
0	100	181	226	258
10	90	248	244	259
20	80	237	267	273
30	70	302	311	368
40	60	299	325	365
50	50	346	342	372
60	40	356	367	432
70	30	398	394	435
80	20	410	435	450
90	10	453	473	489
100	0	475	477	498

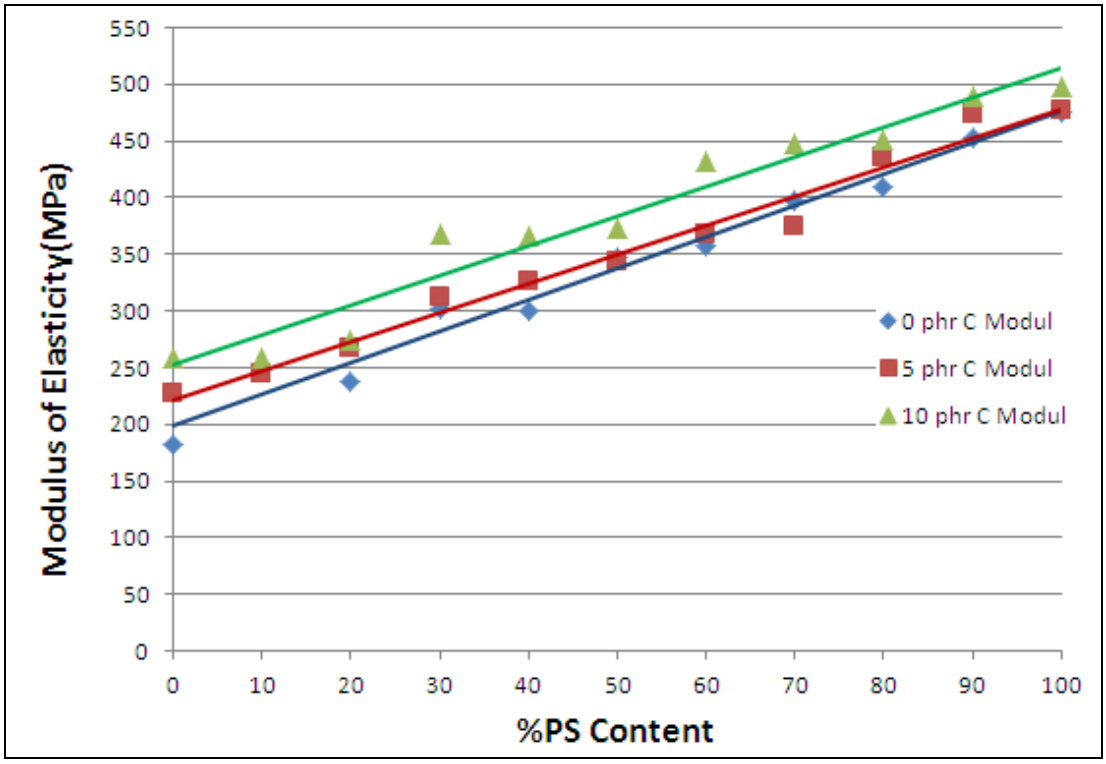


Figure 4.5 : Modulus of Elasticity of the PS/PP blends with 0-5-10 phr compatibilizer.

Young's Modulus (modulus of elasticity) equals to the ratio of the applied load per unit area of cross section to the increase in length per unit length. PS is a brittle thermoplastic polymer. On the other hand PP can be considered a tough material at room temperature. Addition of PS to the PP increase the modulus of elasticity so it is clearly seen that increasing of PS content increases the Young's modulus of the PS/PP blends in all investigated samples. The modulus of elasticity values of the materials are collected in Table 4.2.

PBE is propylene based elastomer, so adding compatibilizer reduces the brittleness. Adding tough material further reduces the modulus of elasticity and this is shown in the Fig. 4.5 and 4.6 with the comparison of Fig.4.4.

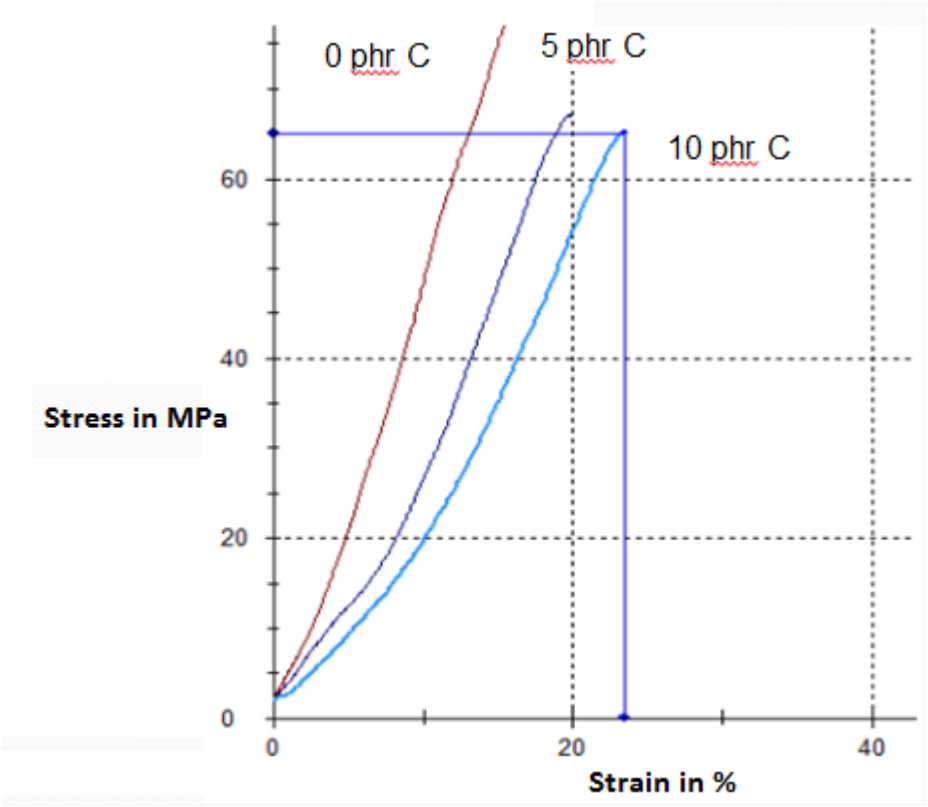


Figure 4.6 : % Strain values of the PS/PP blends with 0-5-10 phr compatibilizers.

4.1.2. Thermal tests results of the blends

Thermal properties of the PS-rich, PS-PP-equal and PP-rich blends were analyzed by differential scanning calorimetry. Samples were heated from room temperature to 200 °C, kept at this temperature for 5 minutes, and then cooled to room temperature at 10 °C /minute. Parameters of crystallization data showed in Figure 4.7, 4.9, 4.11 gained from this run. The heat of crystallization data were calculated and given in Table 4.3. They were then reheated to 200 °C at the same heating rate. Parameters of melting data showed in Figure 4.8, 4.10, 4.12 gained from this run.

All of the thermographs had one melting peak belonging to PP phase. By using the software of DSC analyzer, the first derivative of heat flow change with respect to temperature change were calculated in order to determine the start and end temperatures of the melting regions. Onset and peak temperatures were taken from the second run curves. By using these data, linear baselines were drawn to determine the onset and the peak (Tp) temperatures (Table 4.4.). From the second run the calculated heat of fusion with heat of crystallization values were given in Table 4.3.

Addition of PS to PP reduces the intensity and the width of the crystallization peaks due to higher contents of the amorphous phase. Crystallization peak is significantly displaced to lower temperatures only in the 30/70 blend; this can be explained by a disruption of the structure of PP.

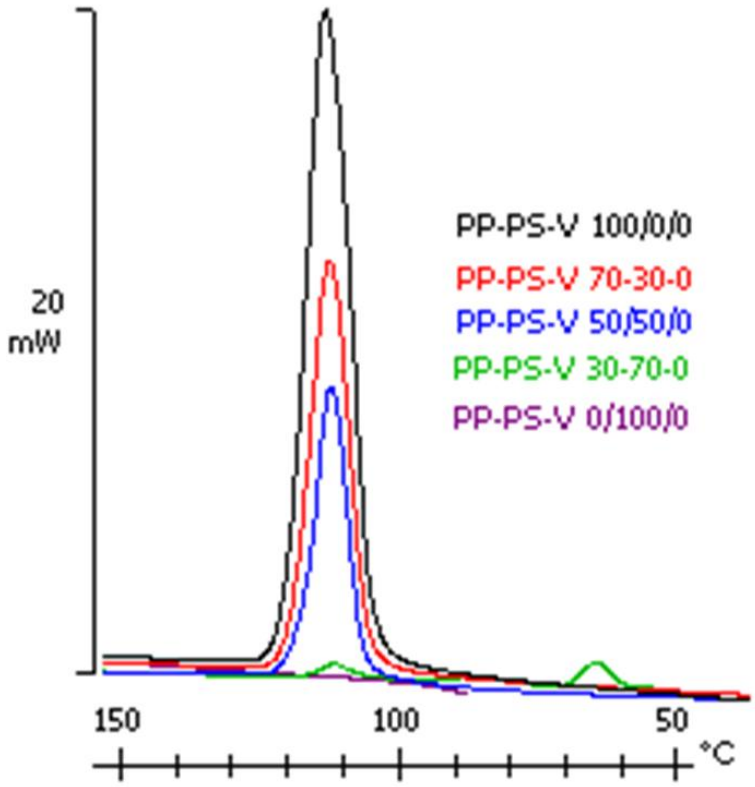


Figure 4.7 : Crystallization peaks of exothermic DSC curves of incompatibilized PS/PP blends.

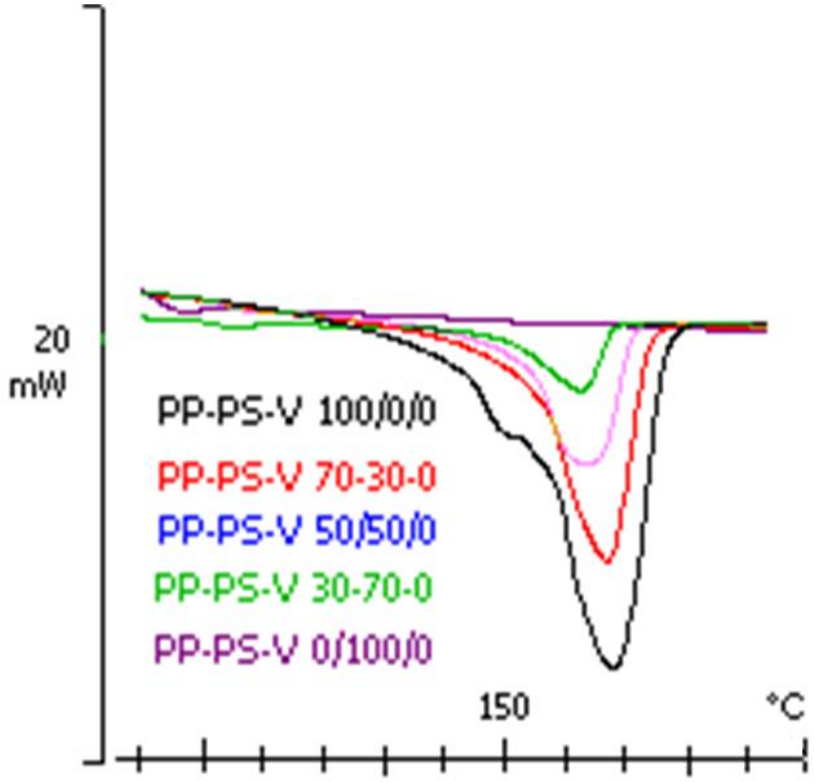


Figure 4.8 : Melting peaks of binary PS/ PP blends as a function of PS content.

Both enthalpy of crystallization (obtained by peak integration) and the degree of crystallinity of the blends decrease with higher content of amorphous PS (Table 4.3). Enthalpy of fusion results also indicates a reduction of the polypropylene crystallinity by addition of PS (Figure 4.8, Table 4.3.). The addition of compatibilizer to the blends further reduces the enthalpy of crystallization and degree of crystallinity compared to the incompatibilized blends in all investigated compositions (Figure 4.9, 4.10, 4.11, 4.12).

The reduction of crystallinity is more pronounced by adding 5-10 phr of PBE (Table 4.3). Effects of the presence of the compatibilizer on melting behavior of our blends are presented in Figure 4.10 - 4.12.

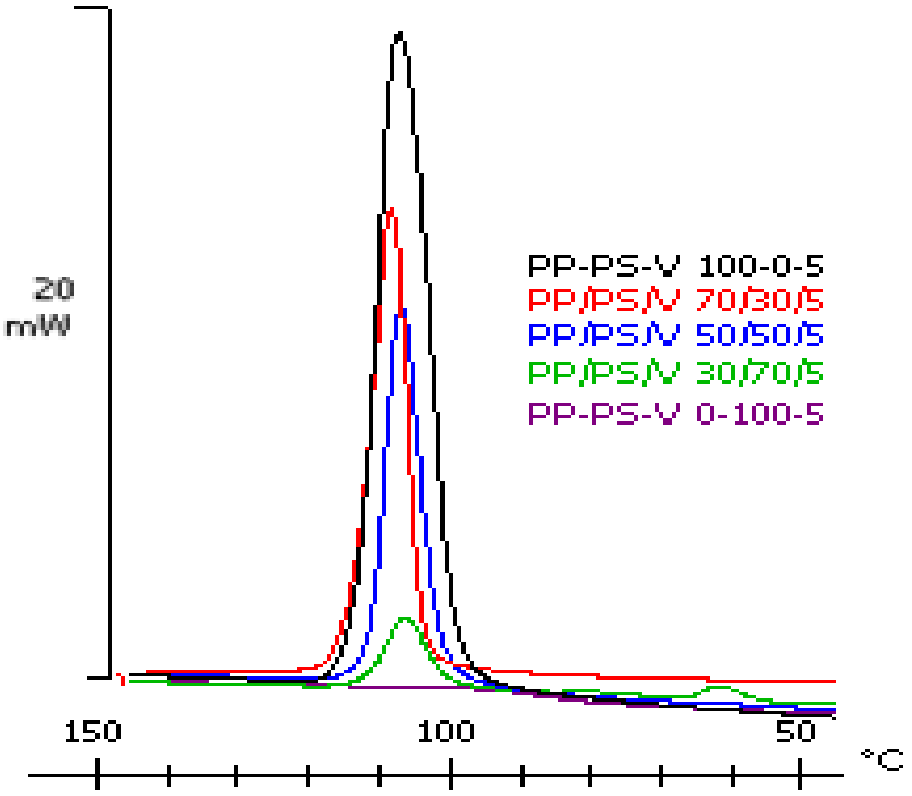


Figure 4.9 : Crystallization peaks of PS/PP blends compatibilized with 5phr PBE.

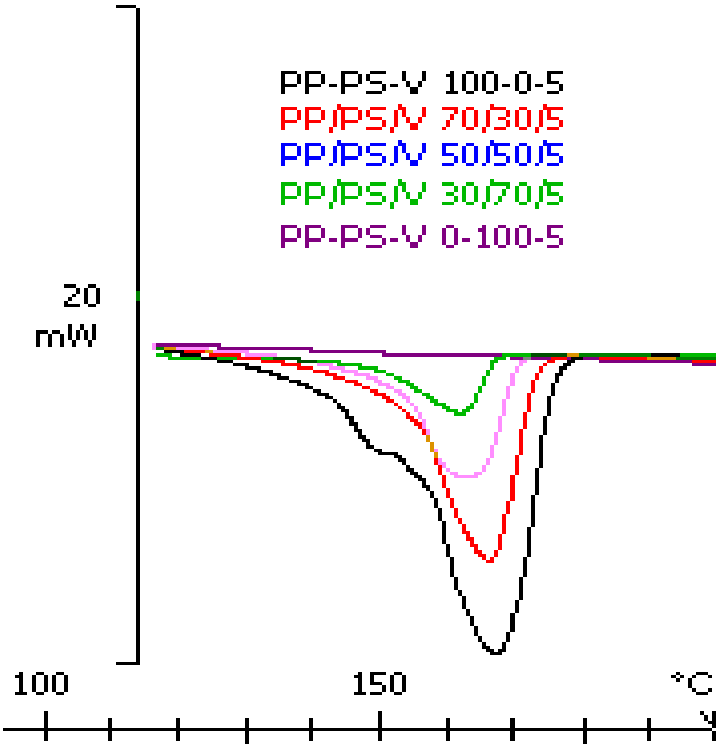


Figure 4.10 : Melting peaks of endothermic DSC curves of compatibilized PS/PP blends with 5 phr PBE.

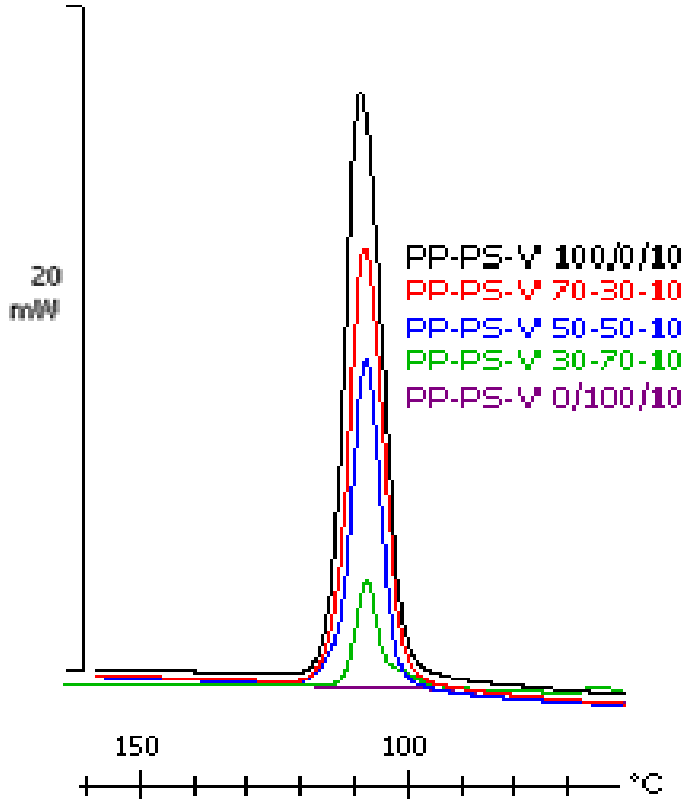


Figure 4.11 : Crystallization peaks of PS/PP blends compatibilized with 10phr PBE.

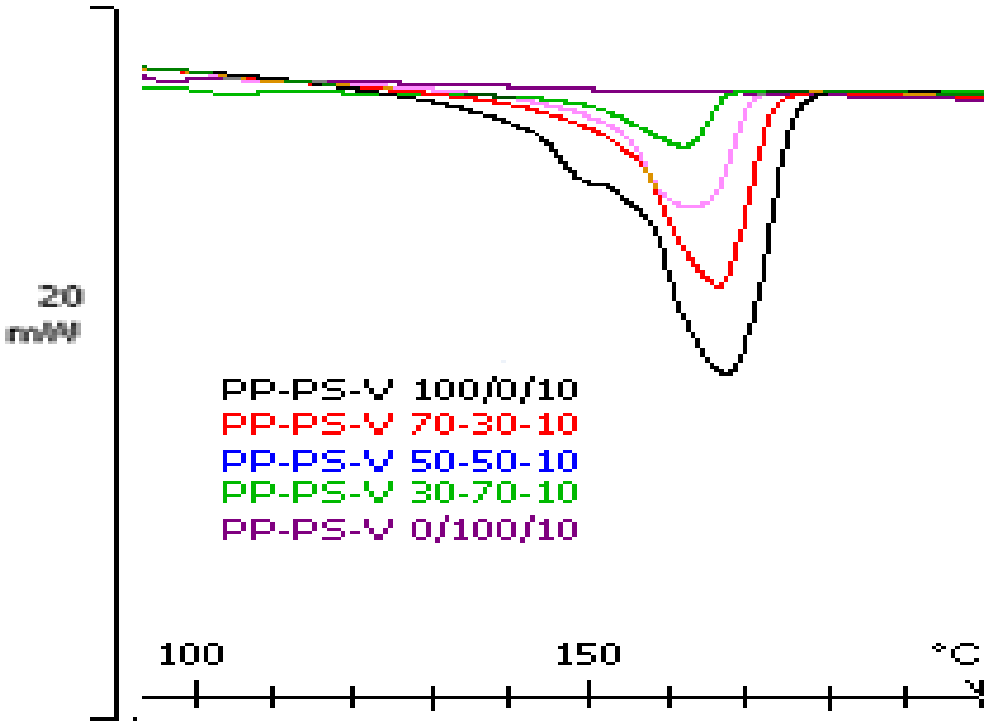


Figure 4.12 : Melting peaks of endothermic DSC curves of compatibilized PS/PP blends with 10 phr PBE.

When PS content increases degree of crystallinity of blends also decreases. Moreover addition of PS also reduces the intensity and the width of the crystallization peaks due to higher contents of the amorphous phase (Table 4.3.). In light of this information it can be clearly seen that from the Table 4.4, addition of PS reduces the onset and the peak temperature. The addition of compatibilizer to the blends further reduces the degree of crystallinity in all investigated compositions and onset and peak temperature reduce related with compatibilizer addition.

Table 4.3 : Results of DSC analysis; fusion enthalpy ΔHm, crystallization enthalpy ΔHc and degree of crystallinity χ of PP homopolymer and PS/PP blends.

Sample (PP/PS/PBE)	**ΔHm (J/g)**	**ΔHc (J/g)**	**% Crystallinity (χ)**
100/0/0	84.7	93.1	40.8
100/0/5	76.4	82.1	36.8
100/0/10	78.1	88.3	36.7
70/30/0	51.5	60.6	24.8
70/30/5	46.7	59.5	22.5
70/30/10	41.7	52.1	20.1
50/50/0	36.8	44.9	17.7
50/50/5	34.3	41.7	16.5
50/50/10	32.8	40.7	15.8
30/70/0	21.1	10.7	10.2
30/70/5	20.2	16.8	9.7
30/70/10	15.8	19.3	7.6

PS is 100% amorphous polymer and increasing amount of PS further reduces the crystallinity degree. In addition to that addition of compatibilizer also affected the crystallinity of the blends. These result are showed in Table 4.3.

The onset and the peak (Tp) temperatures were showed in Table 4.4 for the blends.

Table 4.4 : Thermal properties of the PS/PP blends.

Sample (PP/PS/PBE)	**PP Melting Temperatures**	
	Onset (°C)	**Tp (°C)**
100/0/0	153.3	166.3
100/0/5	152.6	166.7
100/0/10	152.4	166.2
70/30/0	153.2	165.7
70/30/5	152.1	164.5
70/30/10	151.6	164.2
50/50/0	152.2	162.5
50/50/5	149.5	163.0
50/50/10	150.8	164.0
30/70/0	147.9	161.4
30/70/5	147.0	162.9
30/70/10	145.7	163.8

For the incompatibilized blends addition of PS reduces the intensity and the width of the crystallization peaks and it causes the reduction on onset and the peak temperatures. For 5-10 phr added blends, adding PS content also decreases the onset and the peak temperatures.

If a compatibilizer effect wants to be investigated on onset and peak temperatures, adding of compatibilizer decreases the onset temperature. On the other hand it increases the peak temperature. It is thought that this temperature rising comes from the crystallization domains of the compatibilizer. Adding more compatibilizer to the blends further decrease the onset and increase the peak temperatures.

4.1.3 MFR result of the blends

The melt flow rate (MFR) of PS/PP blends were measured according to ASTM D1238 standard. The MFR results obtained increase when PS contents in blends increase. Adding compatibilizers also increase the MFR values and increase the fluidity. Both results showed a better mixing for both incompatibilized and compatibilized blend samples, this means that compatibilization also improved processability. The results are given in Figures 4.13.

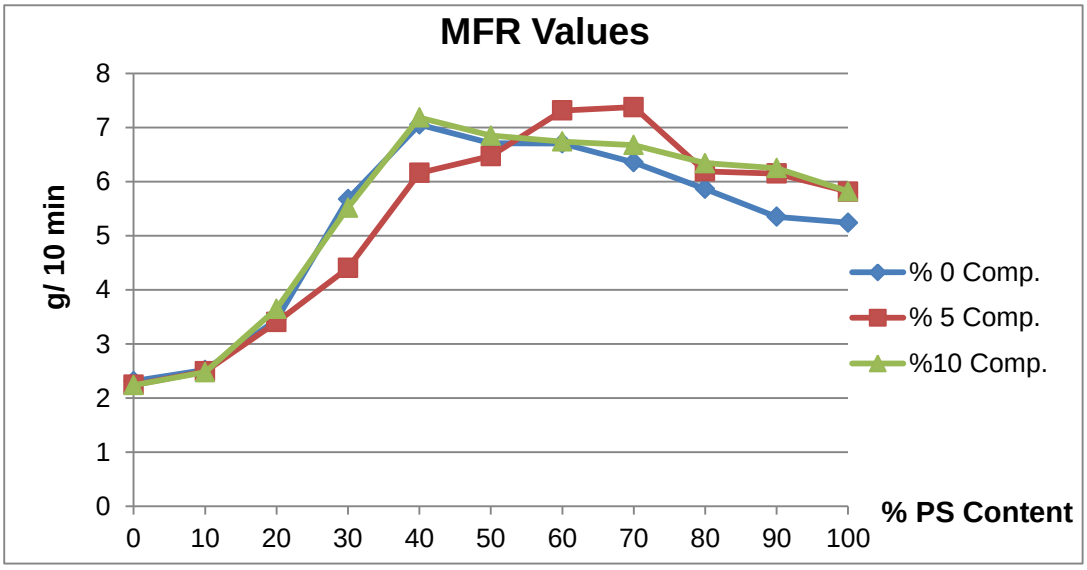
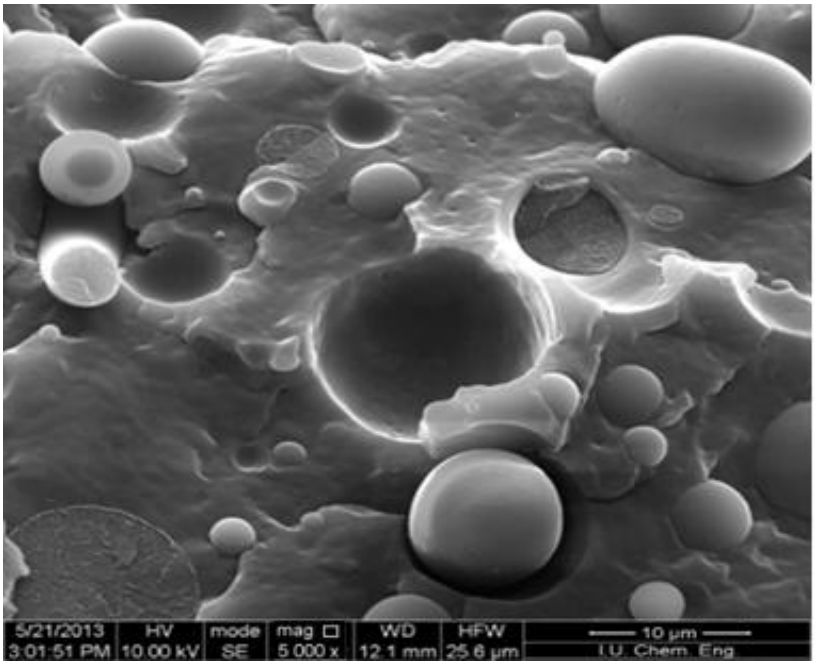


Figure 4.13 : Effect of PS content and the compatibilizer on the MFI of PS/PP (by wt. %) blends.

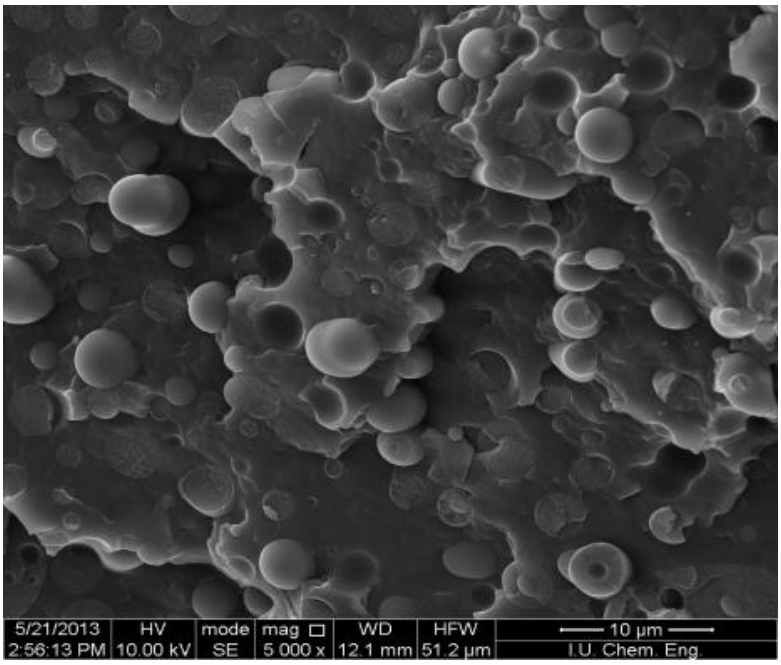
4.1.4. Morphological results of the blends

In order to characterize blend morphology and structure, the samples were analyzed by scanning electron microscope (SEM). Figure 4.14.a shows the image of the uncompatibilized PS/PP 30/70 blend. Two-phase morphology with PS particles dispersed in the PP matrix can be seen, a result of high interfacial tension between the components. Also, holes formed during stretching on the fractured specimen can be observed. The addition of compatibilizer to binary blends changes their morphology. The polypropylene-based elastomer is located at the interface between PS and PP (Figure 4.14.b, 411.c). The size of the dispersed PS particles is reduced at both compositions, namely 5 and 10 phr of the added compatibilizer; the effect is more pronounced at 10 phr of compatibilizer (Figure 4.14. c). A better adhesion of the dispersed phase in the matrix can be recognized – along with a decrease in the number of holes.

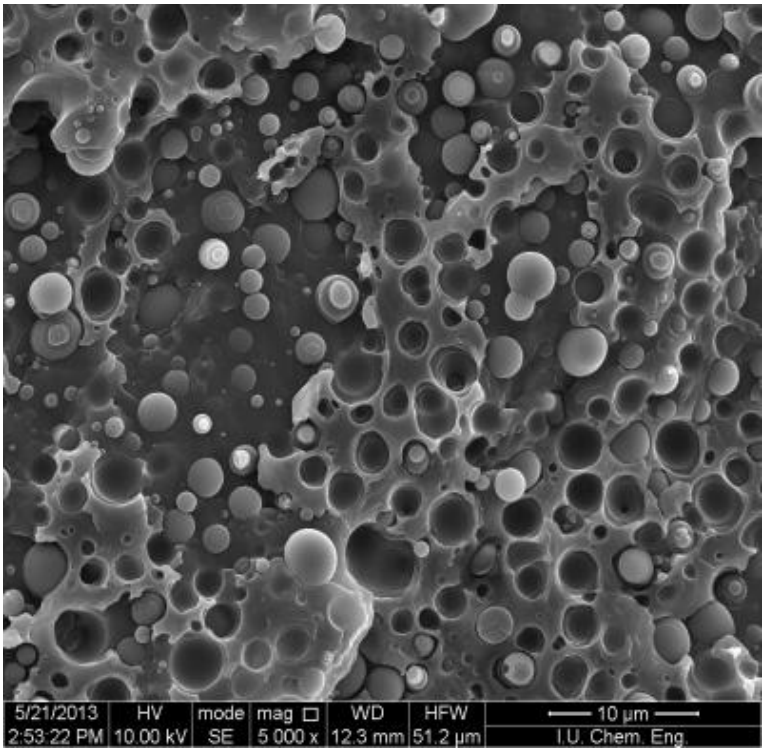


(a)

Figure 4.14 : SEM microphotographs of a) PS/PP 70/30, b) PS/PP/PBE 70/30/5, c) PS/PP/PBE 70/30/10.



(b)



(c)

Figure 4.14 (cont'd): SEM microphotographs of a) PS/PP 70/30, b) PS/PP/PBE 70/30/5, c) PS/PP/PBE 70/30/10.

5. CONCLUSION

In this study, PS/PP blends were prepared with and without PBE compatibilizer. The effects of this compatibilizer and the composition of the blends, on the mechanical, thermal, and the morphological properties were investigated.

Different compositions of PS/PP blends with and without compatibilizer were extruded after the PS, PP and PBE pellets were premixed by shaking in a large – closed container by hand for 5 minutes before being fed to the extruder. The strands from the die were collected on a metal plate and pelletized after complete solidification.

Mechanical property analysis of the samples showed that composition and compatibilization of the blends had a pronounced effect on the tensile properties of these materials.

Mechanical results showed that the maximum tensile strengths decrease by increasing of PS content up to 30 wt% where a minimum value is seen. Compatibilizer acts as a softening material on that range. After this point, the maximum tensile strength increases with further increasing of PS and when PS content is 70 wt% maximum values can be seen. Although the same trend is observed at the 5 and 10 phr compatibilizer added blend graphs, but the curves are shifted below with the increasing compatibilizer content, which tends to lower maximum tensile strength values. On the other hand, adding compatibilizer increases the % strain values.

Melt flow rate (MFR) analysis were carried out for both incompatibilized and compatibilized PS/PP blends. Increased PS content of the blends resulted in increased MFR for both incompatibilized and compatibilized samples. MFR values did not differ significantly for both incompatibilized and compatibilized PP-PS-equal and PP-rich blends. In PS-rich blends MFR of the compatibilized PP-PS samples were greater than that of incompatibilized ones, which shows that compatibilization improved processability of the blends.

Thermal properties of the PP-rich, PP-PS-equal and PS-rich blends were analyzed. Addition of PS to PP reduces the intensity and the width of the crystallization peaks due to higher contents of the amorphous phase. Both enthalpy of crystallization (obtained by peak integration) and the degree of crystallinity of the blends decrease with higher content of amorphous PS. Enthalpy of fusion results also indicates a reduction of the polypropylene crystallinity by addition of PS.

The addition of compatibilizer to the blends further reduces the enthalpy of crystallization and degree of crystallinity compared to the incompatibilized blends in all investigated compositions. T_{onset} and T_p values are not changed in PP-rich blends, on the other hand, in PP-PS equal and PS-rich blends T_{onset} values decreases with increasing PS content and/or adding compatibilizer, at the same time T_{peak} values increases.

Scanning electron microscope analysis of the samples showed that addition of compatibilizer decreased the particle size of the blends. The holes were observed during streching on the fractured specimen. The propylene-based elastomer is located at the interface between PP and PS. The size of the dispersed PS particles is reduced at both compositions, namely 5 and 10 phr compatibilizer; the effect is more pronounced at 10 phr compatibilizer. A better adhesion of the dispersed phase in the matrix can be recognized – along with a decrease in the number of holes.

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