

**RHEOLOGICAL PROPERTIES OF CALCITE FILLED
POLYPROPYLENE RANDOM COPOLYMER COMPOSITES**

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Programme : Chemical Engineering

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**KALSİT KATKILI POLİPROPİLEN RASTGELE KOPOLİMER
KOMPOZİTLERİN REOLOJİK ÖZELLİKLERİ**

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ABBREVIATIONS

App	: Appendix
HDPE	: High Density Polyethylene
LVE	: Linear Viscoelastic Region
MFI	: Melt Flow Index
OIT	: Oxygen Induction Time
PP	: Polypropylene
PP-R	: Polypropylene Random Copolymer
T_g	: Glass Transition Temperature
TKM	: Thermo Kinetic Mixer
T_m	: Melting Temperature
TSE	: Twin Screw Extruder

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RHEOLOGICAL PROPERTIES OF CALCITE FILLED POLYPROPYLENE RANDOM COPOLYMER COMPOSITES

SUMMARY

Composites are brought into usage by being passed through various processes such as injection molding, blow molding, extrusion, compressing molding according to their application field. During these processes, flow behavior of the composite's melt and its viscoelastic properties are extremely important. It has been recognized that addition of filler to the polymer brings a change in processing behavior. At this point, rheology has great importance. To obtain an adequate product, rheological properties of the material must be known. Understanding the rheology of filled melt systems is important not only to optimize processing conditions but also to influence the end properties of the composite product.

The optimization of preparation method for calcite/polypropylene random copolymer (PP-R) composites is achieved by using thermokinetic mixer (TKM) and/or twin screw extruder (TSE). The mixing conditions are chosen to minimize polymer degradation and achieve optimal homogenization of the filler. For this purpose, six different mixing methods are applied. In the first preparation method, the polymer granules are first put in the chamber of TKM and it is operated for 32 seconds. Then required amount of calcite is added in the chamber and it is operated for 15 seconds. In the second preparation method, granules and the required amount of calcite are added together in the chamber of TKM. Then mixer is operated for 22 seconds to have composite. In the third method, polymer granules, required amount of calcite and antioxidant filled PP-R are put in the chamber of TKM. Then it is operated for 22 seconds to obtain composite. In the fourth method, again the PP-R and required amount of calcite are added together in the chamber of TKM. But in this method, pre-mixing time is 12 seconds while it is 5 second in first three methods. The total time is changed from 22 seconds to 29 seconds to achieve optimal filler dispersion in PP-R matrix. In the fifth method, calcite filled PP-R composites are prepared in TSE. Then composite granules are added to TKM. It is operated for 12 second pre-mixing time and totally 22 seconds. In the sixth method, calcite and PP-R are mixed in TSE and composite granules are obtained. These granules are directly press twice under same press conditions which is applied in first five method. The sixth method helps to obtain well dispersed composites and minimum agglomeration, and does not cause PP-R degradation.

Properties of calcites, which are used in this thesis are given in Table S.1. Composites of surface treated (C-s-t) and non-treated various particle sized calcium carbonate (C-s-ut, C-b-ut, C-vb-ut) filled polypropylene with different filler loading have been prepared according to sixth preparation method. Their rheological properties have been studied by shear rate sweep, dynamic strain sweep and small-amplitude oscillatory shear, and compared to those of the corresponding composites of various particle size of calcite at different temperatures. To ascertain the performance of

these composite under stress and temperature, dynamic mechanical analysis has been applied.

Table S.1 : Commercial calcite grades and their properties

code	Commercial Grades	Average Particle Size [μm]	Surface Modification
C-s-ut	A-1	1.85-1.97	untreated
C-s-t	400-E	1.85-1.97	treated with stearic acid
C-m-ut	A-3	2.7-3.3	untreated
C-m-t	KA-2S	2.7-3.3	treated with stearic acid
C-b-ut	A-5	4.7-5.3	untreated
C-b-t	KA-5	4.7-5.3	treated with stearic acid
C-vb-ut	A-30	7.8-10.3	untreated

The zero shear viscosity values of various type of calcite filled PP-R composites is given in Table S.2. The results show that adding calcite to PP-R matrix increases zero shear viscosity. Particle size effect on zero shear viscosity is only distinct at 50 % calcite inclusion. However, in more concentrated systems, it is obviously examined that the smaller particle sized calcite, which is coded as C-s-ut filled PP-R composites has the highest zero shear viscosity. Surface treated calcite, which is coded as C-s-t filled PP-R composite has the lowest viscosity especially at high filler loadings. Because surface treatment reduces interparticular interactions and agglomeration.

Table S.2 : The zero shear viscosity values of calcite filled PP-R composites

Calcite Content [%]	Viscosity [Pa.s]			
	C-s-t	C-s-ut	C-b-ut	C-vb-ut
0	35307	35307	35307	35307
5	38008	39433	39079	38282
10	39189	40608	39970	38478
20	43240	46080	45178	41223
30	44856	49535	47981	46453
40	45105	59480	51910	51468
50	51291	106894	62873	61595

Complex viscosity, storage modulus and loss modulus values at 0.1 and 100 rad/s of C-s-t coded calcite filled PP-R composites is given in Table S.3 as a function of calcite content. Calcite inclusion in PP-R matrix increases complex viscosity, storage and loss modulus. Similar trend is obtained for other type of calcite filled PP-R composites. When frequency increases in oscillation test, the storage modulus increases more than the loss modulus, hence the material damping decreases.

Table S.3 : Oscillation test results of C-s-t-coded calcite filled PP-R composites

Frequency	at 0.1 rad/s			at 100 rad/s		
Content [%]	Complex Viscosity [Pa.s]	Storage Modulus [Pa]	Loss Modulus [Pa]	Complex Viscosity [Pa.s]	Storage Modulus [Pa]	Loss Modulus [Pa]
0	17167	399	1670	1270	113333	57167
5	21267	543	2057	1460	131000	64667
10	22067	543	2137	1530	137000	68267
20	24933	634	2413	1693	151667	75933
30	26467	686	2557	1837	163667	83367
40	28900	761	2790	2010	178667	92767
50	34600	910	3337	2293	202667	106667

It is not understood why crossover frequency at which storage modulus cross loss modulus, is not shifted lower values by increasing calcite content in PP-R matrix. It is probably the reason of not occurring particle network in PP-R matrix.

The values of linear viscoelastic (LVE) regions are given in Table S.4 for all composites. When the calcite content in PP-R increases, linear viscoelastic region gets narrower. Because interparticle bonding forces are not strong enough to keep the structure intact beyond critical strains such that linear region becomes narrower. As it is seen from Table S.4, effects of particle size and surface treatment on LVE region are not clear.

Table S.4 : LVE regions of varying amount and type of calcite filled PP-R composites

Calcite Content [%]	LVE Regions [strain %]			
	C-s-t	C-s-ut	C-b-ut	C-vb-ut
0	20.5	20.5	20.5	20.5
5	16.0	18.9	15.4	14.7
10	15.4	15.4	15.6	14.6
20	12.1	12.1	11.9	11.8
30	10.1	9.8	10.2	10.4
40	8.0	8.0	8.5	8.3
50	4.0	2.6	4.4	4.5

Viscosities of composites decrease by increasing the temperature. The activation energies of various type of calcite filled PP-R composites are calculated by using Arrhenius-Eyring equation ($\eta = A_0 e^{E/RT}$). The results are given in Table S.5. Adding calcite causes the increase in activation energy. Surface treated calcite, which is coded as C-s-t filled PP-R has a bigger activation energy than untreated calcite, which is coded as C-s-ut filled PP-R composite. But effect of particle size on activation energy is not distinct.

Table S.5 : Activation energy of filled PP-R

Samples		Activation Energy (kJ/mol)
Neat PP-R		34.6
Neat PP-R from Litterateur (Shenoy, 1999)		33.5-41.9
20 % Calcite Filled PP-R	C-s-t	40.0
	C-s-ut	36.5
	C-b-ut	36.5
	C-vb-ut	35.4

The results of dynamic mechanical analysis show that adding calcite in PP-R matrix causes to increase the T_g of composite and to decrease the intensity of the glass transition pick. Elastic modulus value increases by inclusion of calcite. The results of particle size and surface treatment on dynamic mechanical behavior of composites are not definitely explained.

KALSİT KATKILI POLİPROPİLEN RASTGELE KOPOLİMER KOMPOZİTLERİN REOLOJİK ÖZELLİKLERİ

ÖZET

Yeni özellikler kazandırılmış malzeme, uygulama alanına göre çeşitli proseslerden geçerek kullanımımıza sunulmaktadır. Bu prosesler enjeksiyonla kalıplama, üfleme ile kalıplama, ekstrüzyon, sıkıştırma ile kalıplama ve bunların benzerleridir. Bu işlemler sırasında malzemenin akış özellikleri ve viskoelastik özellikleri son derece önemlidir. Polimere katkı maddesi eklemeyele prosesin davranışın değişmesi karşılaşılan bir durumdur. Bu noktada reoloji bilimi ön plana çıkar. İstenilen özelliklerde ürünler elde etmek için malzemelerin reolojik özellikleri bilinmelidir. Katkılı eriyik sistemlerinin reolojisinin anlaşılması sadece proses şartlarını optimize etmek için değil ayrıca kompozit ürünün son özelliklerine etkisi açısından da önemlidir.

Bu çalışmada kalsit/polipropilen rastgele kopolimer (PP-R) kompozitlerinin hazırlama metodunun optimizasyonu termokinetik karıştırıcı ve/veya çift vidalı ekstruder kullanılarak yapıldı. Karışım şartları, polimer degradasyonunu minimuma indirecek ve katkı maddesi dağılımını optimuma çekecek şekilde belirlendi. Bu amaçla altı farklı metod denendi. İlk hazırlama yönteminde, polimer granülleri termokinetik karıştırıcının haznesine konuldu ve karıştırıcı 32 s boyunca çalıştırıldı. Sonra istenilen miktarda kalsit hazneye ilave edilerek 15 s çalıştırıldı. İkinci hazırlama yönteminde, polimer granülleri ve istenilen miktarda kalsit termokinetik karıştırıcının haznesine konuldu. Sonra 22 saniye boyunca kompozit elde etmek için çalıştırıldı. Üçüncü metotta, polimer granülleri, istenilen miktarda kalsit ve antioksidant katkı PP-R termokinetik karıştırıcının haznesine konuldu. Sonra kompozit elde etmek için 22 saniye çalıştırıldı. Dördüncü yöntemde, yine polimer granülleri ve kalsit hazneye konuldu. Fakat bu yöntemde, ilk üç metotta 5 saniye olan ön karıştırma süresi 12 saniye olarak belirlendi. PP-R matriksde optimum katkı maddesi dağılımı elde etmek için toplam karıştırma süresi de 22 saniyeden 29 saniyeye çıkarıldı. Beşinci yöntemde, kalsit katkı PP-R kompozit çift vidalı ekstruderde hazırlandı. Sonra kompozit granüller termokinetik karıştırıcıya konuldu. 12 saniye ön karıştırmalı toplamda 22 saniye boyunca termokinetik karıştırıcı çalıştırıldı. Altıncı yöntemde ise kalsit ve PP-R çift vidalı ekstruderde karıştırıldı ve kompozit granüller elde edildi. Bu granüller daha önceki beş hazırlama metodundaki gibi aynı şartlarda iki kez preslendi. Altıncı yöntem katkısı minimum topaklaşmış ve iyi dağılmış kompozit elde etmeye yardımcı olmaktadır ve de PP-R' nin degrade olmasına sebep olmamaktadır.

Bu tezde kullanılan kalsitlerin özellikleri Tablo Ö.1' de verilmiştir. Yüzey işlemi görmüş (C-t-s) ve yüzey işlemi görmemiş (C-s-ut, C-b-ut, C-vb-ut) kalsit katkı PP-R kompozitler farklı katkı oranlarında altıncı hazırlama metoduna göre hazırlanmıştır. Bu kompozitlerin reolojik özellikleri farklı sıcaklıklarda kayma hızı taraması, dinamik deformasyon taraması ve düşük genlikli osilasyon testleriyle incelenerek belirlenmiştir. Kompozitlerin gerilim ve sıcaklık altındaki performansını belirlemek için dinamik mekanik analiz uygulanmıştır.

Table Ö.1 : Kalsitlerin özellikleri

Kod	Ticari Kodu	Ortalama Parçacık Boyutu [μm]	Yüzey işlem durumu
C-s-ut	A-1	1.85-1.97	Yüzeyi işlenmemiş
C-s-t	400-E	1.85-1.97	Yüzeyi stearik asit ile işlenmiş
C-m-ut	A-3	2.7-3.3	Yüzeyi işlenmemiş
C-m-t	KA-2S	2.7-3.3	Yüzeyi stearik asit ile işlenmiş
C-b-ut	A-5	4.7-5.3	Yüzeyi işlenmemiş
C-b-t	KA-5	4.7-5.3	Yüzeyi stearik asit ile işlenmiş
C-vb-ut	A-30	7.8-10.3	Yüzeyi işlenmemiş

Çeşitli kalsit katkı PP-R kompozitlerin sıfır kayma viskozite değerleri Tablo Ö.2’ de verilmiştir. PP-R matrikse kalsit eklenmesi sıfır kayma viskozite değerlerini arttırmıştır. Parçacık boyutunun sıfır kayma viskozitesine etkisi sadece % 50 kalsit eklenmiş kompozitte belirgindir. Ancak, yüksek katkı içeren kompozitlerde, C-s-ut kodlu, en küçük parçacık boyutlu kalsit katkı PP-R kompozitin sıfır kayma viskozitesinin en büyük olduğu açıkça belirlenmiştir. Özellikle yüksek katkı oranlarında, C-s-t kodlu, yüzeyi işlenmiş kalsit katkı PP-R kompozitinin viskozitesi en küçüktür. Çünkü yüzey işleme parçacıklar arasındaki etkileşimi ve topaklaşmayı azaltır.

Table Ö.2 : Kalsit katkı PP-R kompozitlerin sıfır kayma viskoziteleri

Kalsit miktarı [%]	Viskozite [Pa.s]			
	C-s-t	C-s-ut	C-b-ut	C-vb-ut
0	35307	35307	35307	35307
5	38008	39433	39079	38282
10	39189	40608	39970	38478
20	43240	46080	45178	41223
30	44856	49535	47981	46453
40	45105	59480	51910	51468
50	51291	106894	62873	61595

C-s-t-kodlu kalsit katkı PP-R kompozitlerin kompleks viskozite, depolama ve kayıp modüllerin 0.1 ve 100 rad/s ‘deki değerleri Tablo Ö.3’ de kalsit miktarının fonksiyonu olarak verilmiştir. PP-R matrikse kalsit ilavesi kompleks viskoziteyi, depolama ve kayıp modülleri arttırmaktadır. Diğer kalsit katkı PP-R kompozitler için de benzer sonuçlar elde edilmiştir. Frekans değerinin artması ile depolama modülü kayıp modülüne göre daha fazla artmaktadır. Bu da malzemenin sönümlenmesini (material damping) düşürür.

Table Ö.3 : C-s-t-kodlu kalsit katkılı PP-R kompozitlerin osilasyon testi sonuçları

Frekans	0.1 rad/s değerindeki			100 rad/s değerindeki		
Miktar [%]	Compleks Viskozite [Pa.s]	Depolama Modülü [Pa]	Kayıp Modülü [Pa]	Compleks Viskozite [Pa.s]	Depolama Modülü [Pa]	Kayıp Modülü [Pa]
0	17167	399	1670	1270	113333	57167
5	21267	543	2057	1460	131000	64667
10	22067	543	2137	1530	137000	68267
20	24933	634	2413	1693	151667	75933
30	26467	686	2557	1837	163667	83367
40	28900	761	2790	2010	178667	92767
50	34600	910	3337	2293	202667	106667

PP-R matriks içinde kalsit miktarının artması ile depolama modülünün kayıp modülünü kestiği değer olan kesişme frekansının (crossover frequency) daha düşük değerlere kaymaması beklendiği halde bu sonuçlar elde edilememiştir. Bunun sebebi muthemelen PP-R matrikste parçacık ağının oluşmamış olmasıdır.

Bütün kompozitlerin lineer viskoelastik sınır değerleri Tablo Ö.4' de verilmiştir. PP-R matriks içinde kalsit miktarı arttığında lineer viskoelastik sınır (LVS) beklendiği gibi daralır. Bunun nedeni parçacıklar arası kuvvetlerin yapıyı kritik deformasyon değerlerinde tutacak kadar kuvvetli olmamasıdır. Parçacık boyutunun ve kalsitin yüzeyinin işlenmesinin lineer viskoelastik sınıra etkisi açık değildir.

Table Ö.4 : Kompozitlerin lineer viskoelastik sınırları

Kalsit miktarı [%]	LVS [% Deformasyon]			
	c-s-t	c-s-ut	c-b-ut	c-vb-ut
0	20.5	20.5	20.5	20.5
5	16.0	18.9	15.4	14.7
10	15.4	15.4	15.6	14.6
20	12.1	12.1	11.9	11.8
30	10.1	9.8	10.2	10.4
40	8.0	8.0	8.5	8.3
50	4.0	2.6	4.4	4.5

Sıcaklığın artması ile kompozitlerin viskozitesi azalmıştır. Çeşitli kalsit katkılı PP-R kompozitlerin aktivasyon enerjileri Arrhenius-Eyring denklemi ($\eta = A_0 e^{E/RT}$) kullanılarak hesaplanmıştır. Sonuçlar Tablo Ö.5' de verilmiştir. Kalsit eklenmesi aktivasyon enerjisinde artışa sebep olmuştur. C-s-t kodlu, yüzeyi işlenmiş kalsit katkılı PP-R kompozitin aktivasyon enerjisi C-s-ut kodlu, yüzeyi işlenmemiş kalsit katkılı PP-R'den daha büyüktür. Fakat parçacık boyutunun değişimi ile aktivasyon enerjisinin değişimine ait ilişki net olarak ortaya konamamıştır.

Table Ö.5 : Kompozitlerin aktivasyon enerji değerleri

Numune		Aktivasyon Enerjileri (kJ/mol)
katkısız PP-R		34.6
Literatürden katkısız PP-R (Shenoy, 1999)		33.5-41.9
% 20 kalsit katkılı PP-R	C-s-t	40.0
	C-s-ut	36.5
	C-b-ut	36.5
	C-vb-ut	35.4

Dinamik mekanik analiz sonuçları PP-R matrikse kalsit eklenmesinin kompozitin T_g ' sini yükselttiğini ve camı geçiş pik şiddetini düşürdüğünü göstermiştir. Elastik modül değeri kalsit ilavesi ile artar. Ayrıca parçacık boyutunun ve yüzey işleminin dinamik mekanik davranış üzerine etkisi net olarak ortaya konamamıştır.

1. INTRODUCTION

Polymer materials have become a substantial material in our daily life and nearly all branches of industry by showing important developments through last 20-25 years. Polymers differ from steel and other conventional materials because of their structure and their application fields are expanded by introducing their useful aspects. The main purposes of the polymers and polymer composites are to produce materials, which are as light as possible, as durable as steel, economic and resistible to high temperature applications.

According to the usage of materials, it is wanted materials to have suitable properties such as flexibility, lightness, endurance to environmental (humidity, sunray, etc.), impact strength, hardness, thermal expansion coefficients, fatigue, cracking, breaking, tensile and flexural strength. It is extremely rare case that all the desired features appear in only a metal, a ceramic or a polymer material. Therefore, whether the features of the polymers are improved or new properties are gained to the polymers by adding fillers into them.

Composites represent an important class of engineering materials. The incorporation of mineral fillers into thermoplastics has been widely practiced in industry to extend them and to enhance certain properties. Fillers often increase the performance of polymeric products. They also frequently lower the material cost. The degree of improvement depends on the judicious choice of filler origin, particle size and shape, the fraction of filler, and the surface treatment promoting interaction between the polymer matrix and filler.

Mineral fillers such as calcite, titanium dioxide, talc, silica, mica, and clay have become important materials in the polymer industry due to their ability to fulfill the above roles. Among these, calcite is the most common filler. Calcite is known as isotropic particles because of its shapes; thus, it affects the compounds equally in all directions. Other particles such as talc, mica, and clay are anisotropic as they consist of two dimensional layered silicate sheets (disc-like shape) and they are often oriented in thermoplastic parts.

Polypropylene (PP) is extensively used in automobile, electronic appliance, and piping applications. However, its application is somewhat limited due to its high shrinkage rate and relatively poor impact resistance at room or low temperatures. To improve its toughness and dimensional stability, PP fillers with rigid inorganic particles such as calcium carbonates (CaCO_3), is widely used in industry.

Composites are brought into usage by being passed through various processes according to their application field. These processes are injection molding, blow molding, extrusion, compressing molding and such as similar processes. During these processes, flow behavior of the composite's melt and its viscoelastic properties are extremely important. It has been recognized that addition of filler to the polymer brings a change in processing behavior. The presence of the filler increases the melt viscosity leading to increase in the pressure drop across the die but gives rise to less die swell due to decreased melt elasticity. The decrease in melt elasticity can raise the critical shear rate at which melt fracture during extrusion starts to occur and hence one could often consider increasing throughput rate in the case of filled polymer melt processing. At this point, rheology becomes an important issue. To obtain an adequate product, rheological properties of material must be known. In other words, understanding the rheology of filled melt systems is important not only to optimize processing conditions but also to influence the end properties of the composite product.

In this study, CaCO_3 is used as fillers in polypropylene random copolymer (PP-R) matrix. Firstly, the optimization of preparation method for calcite/PP-R composites is achieved by using thermokinetic mixer (TKM) and/or twin screw extruder (TSE). Then, the effects of CaCO_3 of varying particle size content (5–50 wt %), type of surface modification (untreated, stearic acid-treated), and temperature on rheological properties of PP-R/ CaCO_3 composites are investigated and reported.

2. POLYMERS

Polymers are high molecular weight organic substances that have usually been synthesized from low molecular weight compounds through the process of polymerization, using condensation reaction or addition reaction.

In condensation polymerization, the reaction takes place between two polyfunctional molecules to produce one larger polyfunctional molecule with the possible elimination of a small molecule such as water. Long reaction times are essential for forming high molecular weight polymers by this type reaction (Shenoy, 1999).

In addition polymerization, the reaction is initiated by a free radical which is usually formed due to the decomposition of a relatively unstable component in the reacting species. In this reaction, repeating units add one at a time to the radical chain, and reasonably high molecular weight polymers can be formed in a short time by this polymerization (Shenoy, 1999).

There are many possible classifications of polymers. One is according to the general types of polymerization processes used to produce them are mentioned before. Two other useful classifications are by their structure and based on their properties.

2.1 Linear, Branched or Network Polymers

Polymers can be classified according to their structure as linear, branched or a cross-linked as shown in Figure 2.1.

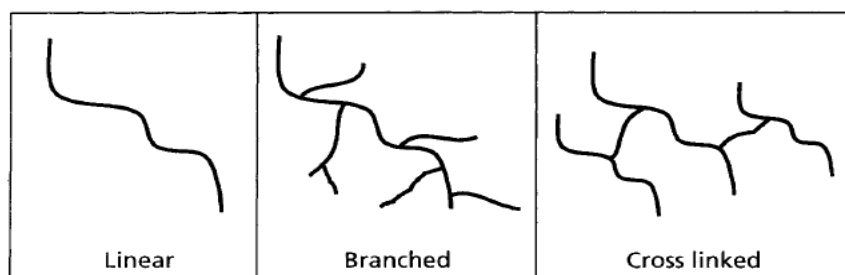


Figure 2.1 : Structures of polymer chain (Ram, 1997)

The linear chain does not have branches or chemical links with neighbouring chains, has only physical links, called entanglements.

The branched chain consists side subchains. Many branches are short but they are able to decrease the crystallinity in the polymer, due to steric hindrance. Existence of longer branches affects the flow properties by decreasing viscosity. It affects to improve the workability in melt. However, extremely long branches which has entanglements between adjacent branches, can reverse the effect by increasing viscosity caused.

A lattice network structure is obtained by primary bonds. Increasing the degree of cross-linking causes the chain gradually loses capability to dissolve and its mobility. Then, it finally reaches the thermosetting state.

2.2 Thermoplastics, Thermosets and Rubbers (Elastomers)

Thermoplastics can be made to soften and take on new shapes by application of heat and pressure. The changes that occur during this process are physical rather than chemical and hence products formed from such polymers can be remelted and reprocessed (Shenoy, 1999).

Thermosets are normally rigid. They cannot melt on heating and they decompose if the temperature is high enough. Examples of thermosets are the epoxy resins, such as araidites, and the phenol- or urea-formaldehyde resins.

Elastomers are rubbery polymers that deform when stress is applied and revert back to the original shape upon release of the applied stress. They are often capable of rapid elastic recovery. They have lightly crosslinked molecular network above their glass transition temperatures. They are natural rubbers or synthetic rubbers.

2.3 Crystalline, Semi-Crystalline or Amorphous Polymers

Polymers can also be classified as crystalline, semi-crystalline or amorphous polymers depending on their degree of crystallinity. A crystal is basically an orderly arrangement of atoms in space. Polymers that are able to crystallize under suitable temperature conditions are called crystalline polymers. The primary transition temperature, when a crystalline polymer transforms from a solid to a liquid, is the melting temperature designated T_m (Shenoy, 1999).

On the other hand, an amorphous polymer does not crystallize under any conditions. The phase transition for this type of polymers occurs from the glassy state to rubbery state at a temperature termed the glass transition temperature and often designated T_g (Shenoy, 1999).

Most thermoplastics have both T_g and T_m . This is because it is relatively difficult to get to the extreme case of a completely crystalline polymer with an ideal formation of single crystals having the relative arrangement of atoms strictly the same throughout the volume. In fact, deviations from the completely ordered arrangement as well as completely disordered arrangement always exist. Thus, it is the degree of crystallinity that truly determines whether a polymer could be classified as a crystalline, amorphous or semi-crystalline polymer (Shenoy, 1999).

2.4 Homopolymers, Copolymers and Terpolymers

If a single repeating unit such as A or B exists in a polymer, it is termed a homopolymer. Thus, homopolymer is AAAAAAAAAA or BBBBBBBB.

When two different monomers are used in the polymerization process, the result is a copolymer. The repeating units A and B both exist in the polymerized product and their varying configurations give different types of copolymers.

(I) Random copolymer: AA BAA AB BA BBB

(II) Alternating copolymer: AB AB AB AB AB

(III) Block copolymer: AAAA BBBB AAAA BBBB AAAA

(IV) Graft copolymer: AAAAAAAAAAAAAA
 B B
 B B

On the other hand, a polymer consists of three different monomers called as terpolymer.

3. FILLERS

Filler is a solid material capable of changing the physical and chemical properties of materials by surface interaction or its lack thereof and by its own physical characteristics. Filler categorization can be done in a number of different ways (Wypych, 2000).

3.1 Filler Types

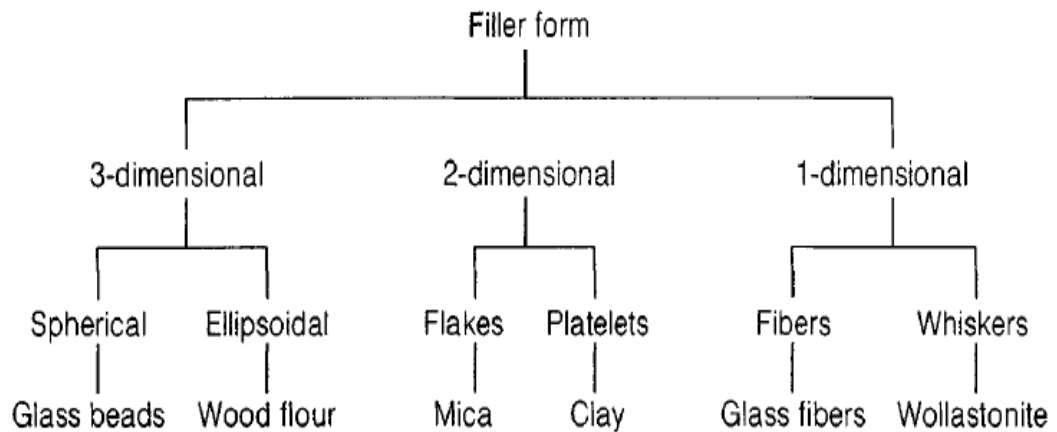
3.1.1 Rigid or flexible fillers

The shape or configuration of rigid fillers does not change within the polymer matrix. Example of such type of fillers are calcium carbonate, titanium dioxide. On the other hand, flexible fillers are those fillers whose spatial configuration within the polymer matrix is not rigidly defined. For example, asbestos fibers, nylon fibers, polyester fibers, etc. would lie in folded, coiled or twisted positions within the polymer matrix.

3.1.2 Spherical, ellipsoidal, plate like or fibrous fillers

Fillers can be classified based on their physical form and shape as shown in Table 3.1.

Table 3.1 : Filler classification by physical form (Shenoy, 1999).



3.1.3 Organic or inorganic fillers

Classification of fillers can also be based on their chemical form. Organic fillers fall within the subcategory of cellulose such as wood flour, lignins such as processed lignin, proteins such as keratin and synthetics such as polyesters. On the other hand, inorganic fillers include carbonates such as calcium carbonates, oxides such as aluminum oxide, silicates such as mica, sulfates such as calcium sulfate, carbon such as carbon black, metal powders such as aluminum and so on.

3.2 Filled Polymers

Using of fillers in polymers is to modify specific mechanical properties such as toughness or impact strength, stiffness, strength and dimensional stability, mechanical damping, or to reduce cost of products or to reduce permeability to gases and liquids, or to increase heat deflection temperature, or to modify electrical properties.

When stiffness, strength and dimensional stability are desirable, the polymers are extended with rigid fillers; for increased toughness as in the case of high-impact polypropylene, deformable rubber particles are added; asymmetric fillers such as fibers and flakes increase the modulus and heat distortion temperature; and electrical and thermal properties are modified by the use of metallized fibrous fillers.

Selection of a filler is a science and various factors would have to be considered in the choice such as, cost and availability, wettability or compatibility with the polymer, effect on polymer flow characteristic, physical properties.

The effect of fillers on polymer flow characteristics, namely, the rheology must be carefully assessed as that determines its processibility and hence rheology is very important.

3.3 Filler Polymer Interactions

When a filler is added to a polymer with the specific idea of reinforcement, it is expected that the reinforcing filler component that is strong and stiff should bear most of the load or stress applied to the system while the polymer, which is of low strength, fairly tough and extensible, should effectively transmit the load to the filler.

Maximum reinforcement benefits would be achieved from fillers when conditions occur in accordance with this concept. In order that the load transfer takes place effectively, the matrix must have sufficiently high cohesive and interfacial shear strength. Thus, apart from the filler and the polymer, it is the inevitable region between them, namely, the interphase that plays a vital role in filled polymer systems. The interphase is the region separating the filler from the polymer. It comprises the area in the vicinity of the interface. It would be synonymous with the words 'interfacial region' but different from the term 'interface', which would be the contacting surface where two materials under consideration meet (Shenoy, 1999).

It is the behavior of the interphase during service that finally decides the performance of the filled polymer product. It is, therefore, prudent to understand the interphase through a careful study of the polymer.

Three possible types of filler-polymer interactions can be visualized. The filler may be only physically present in a nonpolar polymer without an interaction at all. The filler then less acts as a diluent and is expected to weaken the material by its presence. On the other hand, the filler is physically present in the polymer and its surface is either wetted by the polymer because of the inherent polymer affinity for the filler or because the filler is appropriately surface treated to provide this affinity. A physical bond is developed causing an increase in the frictional resistance to the movement of the filler. The strength of the mechanical bonding between the filler and the polymer define the mechanical properties. Moreover, the filler establishes a true chemical bond with the polymer. This causes in an exceptional strengthening effect.

There are a number of factors, which affect filler-polymer interaction.

3.3.1 Filler geometry

Filler geometry is related with the surface area. Surface area of the filler depends upon the particle size, particle shape, and porosity of the filler. The smaller particle sized filler has the bigger surface area. The bigger surface area leads to high interfacial area, hence strong interfacial bonds. However, large interfacial area would lead to physico-chemical instability resulting in agglomeration of the filler due to high interfacial energy.

3.3.2 Filler surface

Apart from surface area, frictional properties of the filler surface plays an important role in the filler-polymer interaction. Friction implies the presence of a compressive force normal to the interface. Smooth filler surfaces do not offer opportunity for keying adhesion of the polymer but they are more easily wetted than those with less regular surfaces.

3.3.3 Wettability

Good wetting provides an intimate contact between the filler and the polymer. That foregoing condition leads to good bonding. In filled polymer systems, if a polymer does not wet the filler then there is entrapment of air bubbles, which act as stress risers and represent areas of zero load transfer, thereby weakening the filled polymer product. Wettability also affects the ease of dispersion of the filler.

3.3.4 Filler surface treatment

It is difficult to form a strong bond between the filler and the matrix due to poor wettability of the filler especially in nonpolar, high melt viscosity polymeric systems, and due to the presence of contaminants or multimolecular layers of water on the mostly hydrophilic surfaces of fillers, which prevents physical or chemiadsorption of the polymer molecules. The interfacial bond can be enhanced and the mechanical performance of the composites improved by suitable surface treatment.

Surface treatment can greatly change the surface energy of a filler. For example, coating calcium carbonate with stearic acid reduces its surface energy from 200 to 40 mJ/m². This transforms the original hydrophilic surface into a hydrophobic one, reducing the water absorption and greatly weakening the forces of attraction between the particles. This has the benefit of reducing the tendency to agglomerate and helps to improve the free flow of the powder. Further important advantages are the easier dispersion of the particles in the polymer matrix (Omya, 2004).

4. RHEOLOGICAL CONCEPTS

Rheology is a relatively young branch of natural science that deals with the flow properties of materials and relationships between forces (stresses) and deformations of material bodies. That's why in this work, first flow properties of the polymer composites are mentioned, then behavior of the composites are examined.

Filled polymer rheology is basically concerned with the description of the deformation of filled polymer systems under the influence of applied stresses. Softened or molten filled polymers are viscoelastic materials in the sense that their response to deformation lies in varying extent between that of viscous liquids and elastic solids. In purely viscous liquids, the mechanical energy is dissipated into the systems in the form of heat and cannot be recovered by releasing the stresses. On the other hand, an ideal solids deform elastically such that the deformation is reversible and the energy of deformation is fully recoverable when the stresses are released.

4.1 Flow Classification

Flow is broadly classified as shear flow and extensional flow. However, in the present work, the discussion is restricted to only simple shear flow that occurs when a fluid is held between two parallel plates. Simple shear flow could be of the steady or unsteady type. Similarly extensional flow could be steady or unsteady. In the case of extensional flow, it is often difficult to keep the measuring apparatus running for a long enough time to achieve steady state conditions and therefore unsteady conditions are quite often encountered.

Thus, flow is classified under three headings:

1. Steady simple shear flow
2. Unsteady simple shear flow
3. Extensional flow.

4.1.1 Steady simple shear flow

Fluid deformation under steady simple shear flow can be described by considering the situation in Figure 4.1 where the fluid is held between two large parallel plates separated by a small gap d_y and sheared as shown in Figure 4.1.

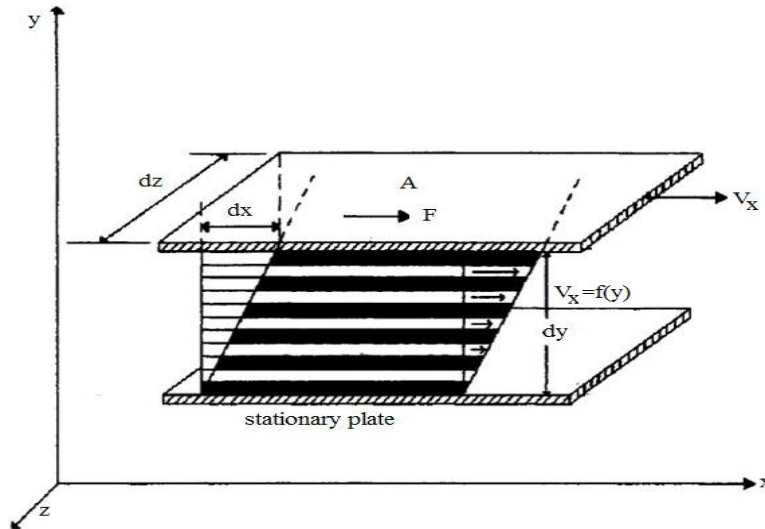


Figure 4.1 : Simple shear flow of a fluid trapped between two parallel plates.

The lower plate is stationary. The upper plate is moving at a constant velocity of v_x under the action of a force applied to it. A thin layer of fluid adjacent to each plate moves at the same velocity as the plate, assuming the no-slip condition at the plate surfaces. Molecules in the fluid layers between these two plates move at velocity function of y . Under steady-state conditions, the force required to produce the motion becomes constant and is related to the velocity.

Shearing flows are found in many polymer processing operations, for example in injection molding, extrusion, in many reometer flows.

4.1.1.1 Shear rate

The velocity profile of the fluid between two plate is given by $dv_x/dy = \dot{\gamma}_{yx}$. This term can be a function of time. The absolute value of $\dot{\gamma}_{yx}$ is called shear rate $\dot{\gamma}$. For steady shear, flow is independent of time (Bird et all, 1987).

This velocity gradient can also be given in Equation 4.1.

$$\frac{dv_x}{dy} = \frac{d}{dy} \left[\frac{dx}{dt} \right] = \frac{d}{dt} \left[\frac{dx}{dy} \right] \quad (4.1)$$

The term $[dx / dy]$ in Equation 4.1 represents the deformation of the material which is defined as the shear strain. Shear strain is designated as γ . Hence, the shear rate is the rate of shear strain or the rate of deformation (Shenoy, 1999).

4.1.1.2 Shear stress

The force per unit area $[F/A]$ required to shear the material between two parallel plates is defined as the shear stress. It is basically a function of the velocity gradient. Shear stress is designated as τ .

$$\tau_{yx} = \frac{F}{A} = f \left(\frac{dv_x}{dy} \right) \quad (4.2)$$

It must be noted that τ_{yx} in equation 4.2 is just one component of the stress and, in principle, there are a number of components of stress that must be specified to completely define the state of stress.

4.1.2 Unsteady simple shear flow

Unsteady simple shear flow would occur when the stresses involved are time-dependent. Small-amplitude oscillatory flow, stress growth, stress relaxation, creep and constrained recoil are some examples of such types of flows.

4.1.2.1 Small-amplitude oscillatory shear flow

Small-amplitude oscillatory shear flow is often referred to as dynamic shear flow. Fluid deformation under dynamic simple shear flow can be described by considering the fluid within a small gap dy between two large parallel plates of which the upper one undergoes small amplitude oscillations in its own plane with a frequency ω as shown in Figure 4.2. The velocity field within the gap can be given by Equation 4.3. $\dot{\gamma}$ is not a constant as in steady simple shear. Instead it varies sinusoidally and is given by Equation 4.4 where ω is angular frequency, $\dot{\gamma}_0$ is shear rate amplitude and t is at any time.

$$v_x = \dot{\gamma} y \quad (4.3)$$

$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t \quad (4.4)$$

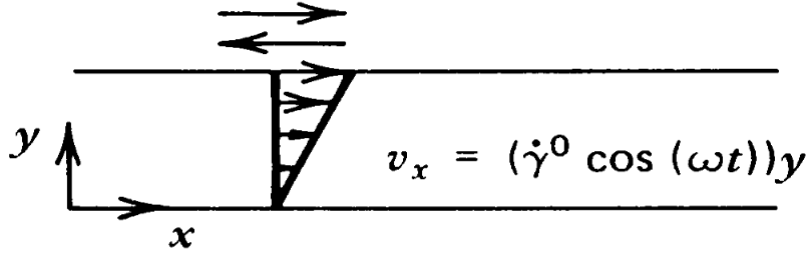


Figure 4.2 : Small amplitude oscillatory shear flow of a fluid trapped between two parallel plates (Bird et al, 1987).

The shear stress in simple dynamic shear flow is expressed in terms of the amplitude and phase shift functions of the frequency as Equation 4.5 and 4.6. In these equations, δ is the phase angle, γ_0 and τ_{yx}^0 are the amplitudes of the strain and stress, respectively, and G' and G'' are linear viscoelastic material functions, respectively, referred to as the dynamic storage modulus and dynamic loss modulus.

$$\tau_{yx}(t) = \gamma_0 (G'(\omega) \sin \omega t + G''(\omega) \cos \omega t) \quad (4.5)$$

$$\tau_{yx}(t) = \tau_{yx}^0 \sin(\omega t + \delta) \quad (4.6)$$

Dynamic storage modulus is given by Equation 4.7, whereas loss modulus is given by Equation 4.8.

$$G'(\omega) = \frac{\tau_{yx}^0}{\gamma_0} \cos \delta \quad (4.7)$$

$$G''(\omega) = \frac{\tau_{yx}^0}{\gamma_0} \sin \delta \quad (4.8)$$

The phase angle, δ , between the stress and strain is normally given by the loss tangent. It is defined as the ratio of loss to storage modulus in Equation 4.9.

$$\tan \gamma = \frac{G''(\omega)}{G'(\omega)} \quad (4.9)$$

It is also possible to define a complex viscosity, η^* , in terms of G' and G'' .

$$\eta^*(i\omega) = \frac{G''(\omega)}{\omega} - i \frac{G'(\omega)}{\omega} \quad (4.10)$$

The real and the imaginary parts of the Equation 4.10 are defined as dynamic viscosity, η' , and imaginary part of the complex viscosity, η'' , respectively. Thus Equation 4.11 is written corresponding to 4.10.

$$\eta^*(i\omega) = \eta'(\omega) - i \eta''(\omega) \quad (4.11)$$

4.1.2.2 Stress growth

The aim of a stress growth experiment is to observe how the stresses change with time as they approach their steady shear flow values. This is done by presuming the fluid sample to be at rest for all times previous to $t=0$. All components of stress are zero in the fluid when steady shear flow is initiated at $t=0$. For times $t>0$ when a constant velocity gradient is imposed, the stress is monitored with respect to time till it reaches steady state value (Bird et al., 1987).

4.1.2.3 Stress relaxation

Stress relaxation is an observation of how the stress decays with time. This can occur either after cessation of steady shear flow or after a sudden shearing displacement. In the first case, the motion of a fluid is undergoing steady shear flow with a finite constant shear rate and then the flow is suddenly stopped at time t equal to zero. After that time the stress is observed with respect to time till it becomes insignificant or dies out. If the shear rate in the preceding steady shear flow is increased, the stress would relax monotonically to zero and more rapidly.

In the second case, a constant shear rate lasting only for a brief time interval is imposed. The decay of the stress that is generated by this sudden small displacement is observed and known as the relaxation modulus. The stress would decrease monotonically with time. For small shear displacements the relaxation modulus is known to be independent of shear rate (Shenoy, 1999; Bird et al., 1987).

4.1.2.4 Creep

Instead of controlling the shear rate and measuring the resulting stresses, a prescribed time dependent shear stress is applied and measured the resulting shear strain. In the creep experiment, a constant shear stress is applied to a fluid that was previously at rest and stress-free. It is convenient to measure the shear strain in the material relative to the application of the shear stress (Bird et al., 1987).

The response of the sample to the applied stress is sometimes described by the creep compliance $J(t, \tau)$. The steady-state compliance J_e is defined as $\dot{\gamma}/\tau$. If the driving shear stress, τ , is small enough then the value of the compliance is independent of the driving shear stress (Shenoy, 1999; Bird et al, 1987).

4.1.2.5 Constrained recoil (creep recovery)

If the shear stress is suddenly removed from a viscoelastic fluid undergoing steady shear flow and if the separation between the plates is held constant, the fluid will recoil to some position it previously occupied. The recovery of the fluid is described by the shear strain during measured relative to the time when the shear stress is removed (Bird et al, 1987).

Input and the output of the creep recovery test is illustrated in Figure 4.3. The recoil of strain after the stress is removed. After the stress has been removed from a viscoelastic material, the deformation reverses itself.

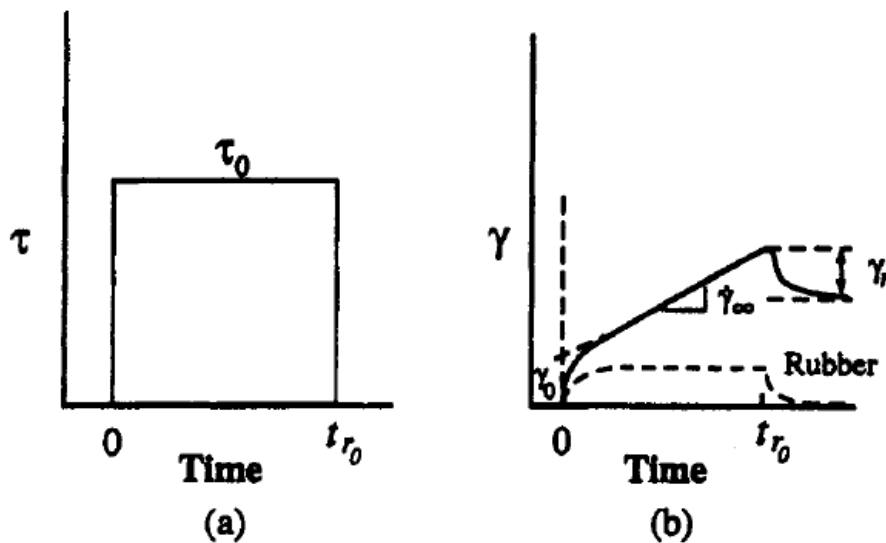


Figure 4.3 : Creep recovery test (Macosko, 1994)

4.1.3 Extensional flow

Extensional flow differs from both steady and unsteady simple shear flows in that it is a shear-free flow. In such a flow, the volume of a fluid element must remain constant. Extensional flow can be visualized as that occurring when a material is longitudinally stretched (Shenoy, 1999).

The shear free flow that has been most used in experimental rheology is uniaxial extension, also called simple extension, which is axisymmetric flow with stretching in the direction of the axis of symmetry. The effect of uniaxial extension on the shape of an initially cubic fluid element is sketched in Figure 4.4 (Dealy and Wissbrun, 1999).

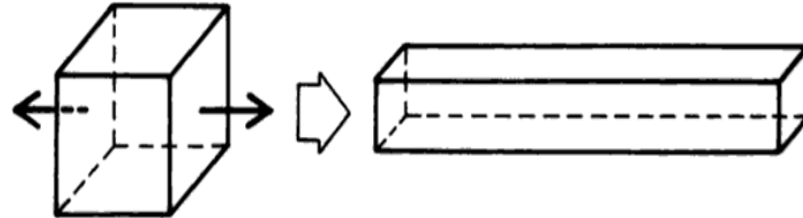


Figure 4.4 : Effect of simple extension on an initially cubical fluid element (Dealy and Wissbrun, 1999).

There is another axisymmetric extensional flow, and this is biaxial extension. In this deformation there is compression along the axis of symmetry and stretching in the radial direction, as shown in Figure 4.5. This exhausts the possibilities for non-axisymmetric deformations, but there are many possible non-axisymmetric shear free flows. The simplest of these is planar extension, in which the velocity in one cartesian direction is zero, as shown in Figure 4.6.

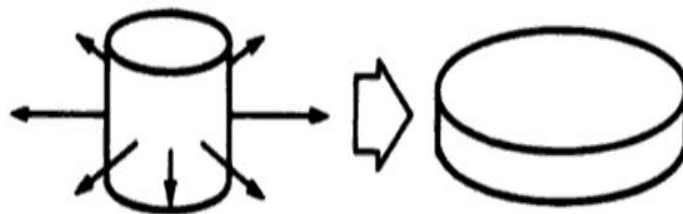


Figure 4.5 : Change in shape of a fluid element during biaxial extension (Dealy and Wissbrun, 1999).

The material function of prime importance in extensional flow is the extensional viscosity which is basically a measure of the resistance of the material to flow when stress is applied to extend it (Shenoy, 1999).

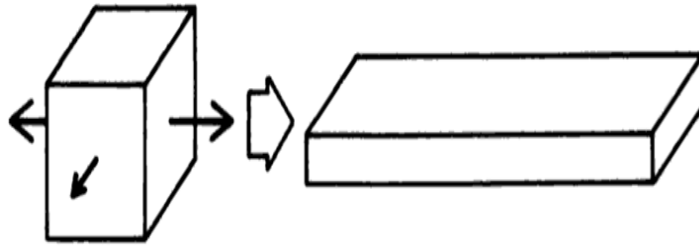


Figure 4.6 : Change in shape of a fluid element during planar extension (Dealy and Wissbrun, 1999).

4.2 Classification of Flow Behavior

Flow's behavior can be classified into two categories as Newtonian and non-Newtonian flow according to the effects produced under the action of a shear stress.

4.2.1 Definition of a newtonian fluid

Isaac Newton assumed that all materials have a viscosity that is independent of the shear rate at a constant temperature and pressure. In other words, the shear viscosity does not vary with shear rate and viscosity remains the same at different shear rates. Typical Newtonian fluids include water and thin motor oils. Newtonian fluids have a proportional relationship between shear stress, τ , and shear rate, $\dot{\gamma}$, as shown in Figure 4.7.

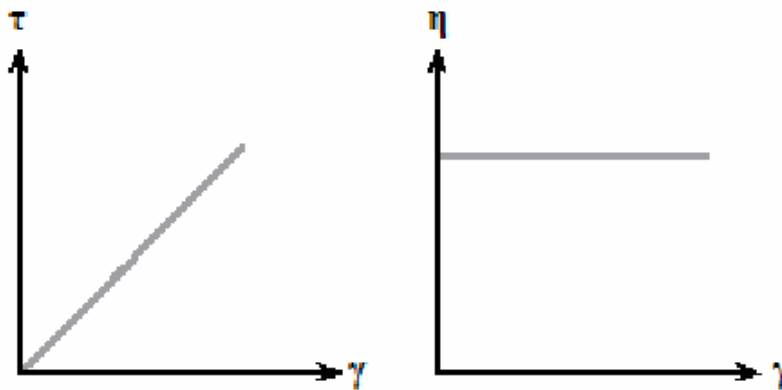


Figure 4.7 : Diagram for Newtonian behavior (Brookfield Engineering, 2005)

For a Newtonian fluid in simple shearing motion, it is also known that the normal stress components are identically zero.

4.2.2 Non-Newtonian flow behavior

These fluids have different viscosities at different shear rates. When the shear rate is varied, the shear stress does not vary in the same proportion. The viscosity of such fluids will therefore change as the shear rate is varied. This measured viscosity is called the apparent viscosity of the fluid. Such materials may be conveniently grouped into three general classes:

- (1) fluids for which the shear rate at any point is determined only by the value of the shear stress at that point at that instant; these fluids are variously known as ‘time independent’, ‘purely viscous’, ‘inelastic’ or ‘generalized Newtonian fluids (GNF)’,
- (2) more complex fluids for which the relation between shear stress and shear rate depends, in addition, upon the duration of shearing and their kinematic history; they are called ‘time-dependent fluids’, and finally,
- (3) substances exhibiting characteristics of both ideal fluids and elastic solids and showing partial elastic recovery, after deformation; these are categorized as ‘visco elastic fluids’ (Chhabra and Richardson, 2008).

4.2.2.1 Time-independent fluid behavior

In simple shear, the flow behavior of this class of materials may be described by a constitutive relation of the form in Equation 4.12.

$$\dot{\gamma}_{yx} = f(\tau_{yx}) \quad (4.12)$$

or its inverse form in Equation 4.13.

$$\tau_{yx} = f(\dot{\gamma}_{yx}) \quad (4.13)$$

These two equations imply that the value of the shear rate at any point within the sheared fluid is determined only by the current value of shear stress at that point or vice versa.

Depending upon the form of the function in Equation 4.12 or 4.13, these fluids may be further subdivided into three types: shear-thinning or pseudoplastic, viscoplastic and shear-thickening or dilatant.

Qualitative flow curves on linear scales for these three types of fluid behavior are shown in Figure 4.8. The linear relation typical of Newtonian fluids is also included.

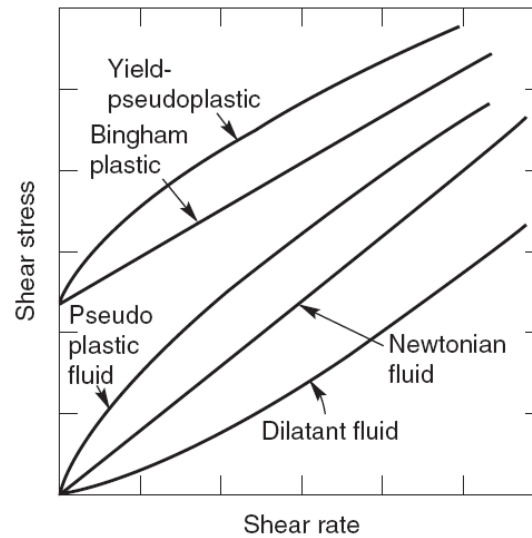


Figure 4.8 : Types of time-independent flow behavior

The most common type of time-independent non-Newtonian fluid behavior observed is pseudoplasticity or shear-thinning, characterized by an apparent viscosity which decreases with increasing shear rate. Both at very low and at very high shear rates, most shear-thinning polymer solutions and melts exhibit Newtonian behavior, in other words shear stress–shear rate plots become straight lines. The resulting values of the apparent viscosity at very low and high shear rates are known as the zero shear viscosity, μ_0 , and the infinite shear viscosity, μ_∞ , respectively. Thus, the apparent viscosity of a shear-thinning fluid decreases from μ_0 to μ_∞ with increasing shear rate. Typical examples of materials exhibiting pseudoplastic behavior include printing inks, polymer melts, polymer solutions, filled polymer systems.

Viscoplastic fluid behavior is characterized by the existence of a yield stress, τ_0 , which must be exceeded before the fluid will deform or flow. Conversely, such a material will deform elastically or flow like a rigid body when the externally applied stress is smaller than the yield stress. Once the magnitude of the external stress has exceeded the value of the yield stress, the flow curve may be linear or non-linear. A fluid with a linear flow curve for $|\tau_{yx}| > |\tau_0|$ is called a Bingham plastic fluid. It is characterized by a constant plastic viscosity with a yield stress. On the other hand, a substance possessing a yield stress as well as a non-linear flow curve on linear coordinates (for $|\tau_{yx}| > |\tau_0|$), is called yield-pseudoplastic fluid. Common examples

of viscoplastic fluid behavior include toothpaste, ketchup, blood, filled polymer systems.

Dilatant fluids are similar to pseudoplastic systems in that they show no yield stress but their apparent viscosity increases with increasing shear rate; thus these fluids are also called shear-thickening. This type of fluid behavior was originally observed in moderately concentrated suspensions like starch suspensions, wet sand, aqueous suspension of titanium dioxide.

4.2.2.2 Time-dependent fluid behavior

Apparent viscosities may depend not only on the rate of shear but also on the time for which the fluid has been subjected to shearing. Time-dependent fluid behavior may be further sub-divided into two categories: thixotropy and rheopexy or negative thixotropy.

When a material is sheared at a constant rate, its apparent viscosity (or the corresponding shear stress) decreases with the time of shearing that means this material exhibits thixotropy. A typical example of thixotropy behavior is shown in Figure 4.9.

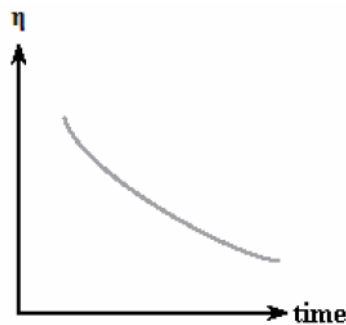


Figure 4.9 : Thixotropic fluid behavior (Shaw, 1992)

The relatively few fluids for which the apparent viscosity (or the corresponding shear stress) increases with time of shearing are said to display rheopexy or negative thixotropy. This kind of behavior is shown in Figure 4.10.

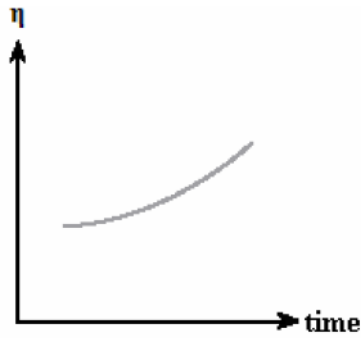


Figure 4.10 : Rheopectic fluid behavior (Shaw, 1992)

If the flow curve is measured in a single experiment in which the shear rate is steadily increased at a constant rate from zero to some maximum value and then decreased at the same rate to zero again, a hysteresis loop of the form shown in Figure 4.11 is obtained. The larger the enclosed area, stronger is the time-dependent behavior of the materials. Thus, hysteresis loop is not observed for time-independent fluids, that is, the enclosed area of the loop is zero.

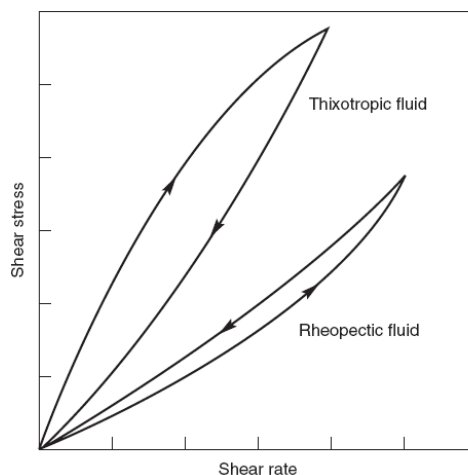


Figure 4.11 : Schematic shear stress–shear rate behavior for time-dependent fluid behavior

4.2.2.3 Viscoelastic fluid behavior

These fluids possess the added feature of elasticity apart from viscosity. These fluids exhibit process properties that lie in between those of viscous liquids and elastic solids. Filled polymer systems, polymer melts and polymer solutions exhibit this kind of flow behavior.

4.3 Rheological Models

There have been a number of rheological models proposed for representing the flow behavior of softened or molten polymers. The most known constitutive equations, which relate shear stress or apparent viscosity with shear rate, are presented below.

4.3.1 Ostwald-de Waele power law model

This is the most popular and simple model. This model is commonly used to describe the viscous behavior of polymeric materials, such as polyethylene, with shear rates greater than 2 or 3 decades. If the behavior at low shear rates needs to be fitted as well, the Bird-Carreau or Cross law will capture the plateau zone of the viscosity curve for low shear rates better than the power law (Polyflow, 2003).

The equation for this model is given in Equation 4.14 and 4.15 (Shenoy, 1999).

$$\tau = K \dot{\gamma}^n \quad (4.14)$$

$$\eta = K \dot{\gamma}^{n-1} \quad (4.15)$$

K reflects the consistency index of the polymer, with higher values representative of more viscous materials. n is the power-law index giving a measure of the pseudoplasticity. If the value of n is equal to one, the Equation 4.14 is identical to the Newton model. For a shear thinning material n is smaller than one and larger for shear thickening materials (Rheoplus Software, 2006).

4.3.2 Bird-Carreau law model

The Bird-Carreau law is commonly used when it is necessary to describe with Newtonian regions at low and at high shear rates and a shear thinning region at medium shear rates. (Rheoplus Software, 2006).

Equation for this model is given in Equation 4.16. In this equation, η_0 and η_∞ are the zero shear rate viscosity and infinite shear rate viscosity, respectively. For polymeric fluids, η_∞ can be taken zero. The relaxation time λ is considered to be the characteristic time available as the inverse of the shear rate at which the shear-thinning behavior begins. Where n is the power law index, is a measure of the shear thinning characteristics (Polyflow, 2003).

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) (1 + \lambda^2 \dot{\gamma}^2)^{\frac{n-1}{2}} \quad (4.16)$$

4.3.3 Cross law model

The Cross model describes the viscosity curve of a material with a zero shear viscosity, a constant viscosity at high shear rate values and a shear thinning region in between. It is similar to the Carreau evaluation. The Cross equation often fits well to polymer melts. The second Newtonian region cannot necessarily be observed for these materials (Rheoplus Software, 2006).

Equation for this model is given in Equation 4.17. In this equation, η_0 is the zero shear rate viscosity. The relaxation time λ is considered to be the characteristic time available as the inverse of the shear rate at which the shear-thinning behavior begins. m is the cross law index. For large shear rates, m is equal to 1 minus n (Polyflow, 2003).

$$\eta = \frac{\eta_0}{1 + (\lambda \dot{\gamma})^m} \quad (4.17)$$

It differs from the Bird-Carreau law primarily in the curvature of the viscosity curve in the vicinity of the transition between the plateau zone and the power law behavior. While the curvature in Bird-Carreau model is sudden, it is smooth in cross model (Polyflow, 2003).

4.3.4 Carreau-Yasuda law model

The Carreau-Yasuda equation describes the viscosity curve of a material with Newtonian regions at low and at high shear rates and a shear thinning region at medium shear rates (Rheoplus Software, 2006).

Equation for this model is given in Equation 4.18. The rotation is same with previous model. The Carreau-Yasuda law is a slight variation on the Bird-Carreau law (Equation 4.16). This model has an additonal index, a . It allows for control of the transition from the Newtonian plateau to the power-law region. A low value ($a < 1$) lengthens the transition, and a high value ($a > 1$) results in an abrupt transition (Polyflow, 2003).

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) (1 + \lambda^a \dot{\gamma}^a)^{\frac{n-1}{a}} \quad (4.18)$$

4.4 Other Relationships for Shear Viscosity Functions

4.4.1 Viscosity-Temperature relationships

An understanding of the mechanism of polymer flow processes in relation to the nature and composition of the material can be elucidated by a study of the temperature dependency of shear viscosity. The temperature sensitivity of the shear viscosity has a profound effect on the choice of processing conditions as well as on the quality of the end product. An increase in temperature sets up thermal motion of the molecules, resulting in their displacement based upon the available free motion and the overcoming of forces of intermolecular interactions. That's why viscosity decreases while temperature increases. Many attempts have been made to describe the viscosity-temperature dependence mathematically. Presently, there are two commonly used expressions to evaluate the temperature dependency of the viscosity. One is based on the absolute theory of rate processes, Arrhenius Eyring. The second expression is based on free-volume concepts, namely the equation proposed by Williams, Landel and Ferry (WLF).

4.4.1.1 Arrhenius-Eyring equation

Arrhenius-Eyring equation is the most widely used expression and define in Equation 4.19. It would provide a valid and useful means of predicting the viscosity-temperature dependence.

$$\eta = A_0 e^{E/RT} \quad (4.19)$$

Where η is the viscosity at temperature T , R is the gas constant, A_0 is the frequency term depending on the entropy of activation for flow, and E is taken to be the energy of activation for viscous flow. The activation energy E is said to be a measure of the height of a potential energy barrier associated with the force needed to produce elemental quantum steps in the movement of molecules (Barnes, 2000).

4.4.1.2 Williams, Landel and Ferry (WLF) equation

Equation of the Williams, Landel, Ferry (WLF) form is usually appropriate for melts of glassy polymers in the region of T_g to $T_g + 100$. WLF equation is demonstrated in Equation 4.20 where subscript r refers to conditions at some arbitrary reference

condition, often taken as T_g . C_1 and C_2 are constants. This equation describes the viscosity at temperature T in terms of viscosity at some reference temperature T_r . This equation is a direct result of the dependence of viscosity on free volume for glass forming materials (Macosko, 1994).

$$\log \frac{\eta_{T_r} \rho_r}{\eta_r T \rho} = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} = \log a_T \quad (4.20)$$

The WLF equation is used extensively to make master curves of viscoelastic data. The term a_T in equation 4.20 is called shift factor and used for that purpose.

The viscosity of a polymeric system decreases with increasing temperature due to the greater free volume available for molecular motion at the higher temperature. In the case of filled polymer systems, the free volume change is limited only to the polymer fraction of the composite. It is therefore expected that the filled polymer viscosity would be less temperature sensitive than the unfilled viscosity (Shenoy, 1999).

4.4.2 Viscosity-Pressure relationship

Viscosity generally increases with increasing pressure. The pressure reduces free volume. This restricts the molecular mobility. Thus viscosity increases. However, this effect becomes noticeable only at very high pressures (Shenoy, 1999).

5. VISCOELASTICITY

Two simple and easy to grasp concepts describing mechanical behavior of materials originated in the 17th century. One is the Hooke's law of solids, describing in Equation 5.1 where ε is deformation, σ_E is tensile stress and, E is elastic modulus of the solid. Another model is Newton's law of liquids, describing in Equation 5.2 where $\dot{\gamma}$ is rate of shear deformation, σ is shear stress and η viscosity of the liquid (Malkin et al, 2006)

$$\varepsilon = \frac{\sigma_E}{E} \quad (5.1)$$

$$\dot{\gamma} = \frac{\sigma}{\eta} \quad (5.2)$$

Both equations are the simplest rheological equations of state, or constitutive equations of material. These classical theories of linear elasticity and Newtonian fluids, though impressively well structured, do not adequately describe the response behavior of a large class of real materials. That is, a real material may exhibit, even if both strain and strain rate are infinitesimal, the combined response characteristics of the elastic solid and the viscous fluid, among other types of response behaviors. It is called as viscoelastic behavior (Buschow et al, 2001).

A viscoelastic material is characterized by a level of rigidity typical of an elastic solid, but, at the same time, it flows and dissipates energy by frictional losses just like a viscous fluid.

It is better to explain viscoelasticity by giving a few characteristics of a viscoelastic material and comparing with the classical types of material behavior of pure elasticity and perfect viscosity.

When a material is applied to a constant stress; strain response can instantly increase until it reaches a definite level and then stays constant that means it is pure elastic solid, or deformation can increase linearly with time which means it is perfect viscous liquid as seen in Figure 5.1.a respectively line H and line N. If the force is

taken away at the time t_0 , the deformation of liquid remains at the level reached before t_0 , at the point ϵ_t , and the deformation of solid instantly disappears.

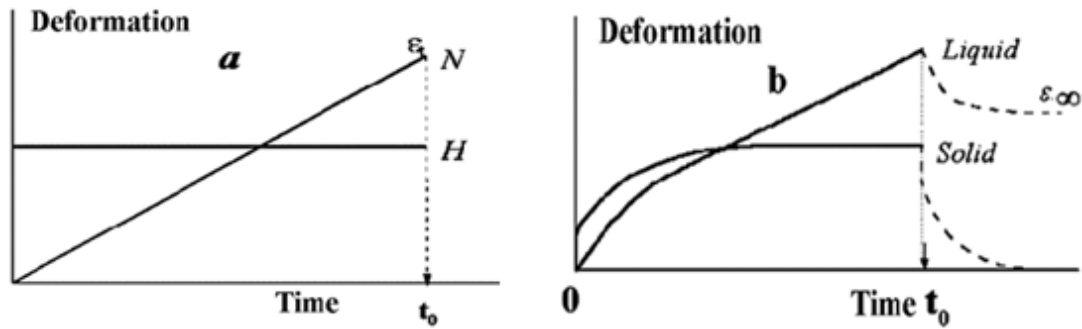


Figure 5.1 : Development of deformation and retardation in materials of different types (Malkin et al, 2006).

On the other hand, when a viscoelastic material is subjected to a constant stress, it does not hold a constant deformation (as would be the case for a pure elastic solid), but it continues to flow with time, for instance, it creeps. Immediately upon the removal of the load, the specimen is found to have taken an amount of residual strain. Following the removal of the load, a noticeable reduction in the amount of residual strain gradually takes place with the passage of time as seen in Figure 5.1.b. If this residual strain may disappear entirely in the course of time, material shows viscoelastic solid behavior else it is viscoelastic liquid (Malkin et al, 2006).

When a viscoelastic material is subjected to a sinusoidally oscillating stress, the resulting strain though sinusoidal, is neither exactly in phase with the stress ($\delta = 90^\circ$), as it would be for the case for a perfectly elastic solid, nor out of phase ($\delta = 0^\circ$), as it would be for a perfectly viscous fluid, it is somewhere between them as seen Figure 5.2. While loading and unloading a viscoelastic sample, some of the energy input is stored and recovered in each cycle and some of it is dissipated as heat (Macosko, 1994).

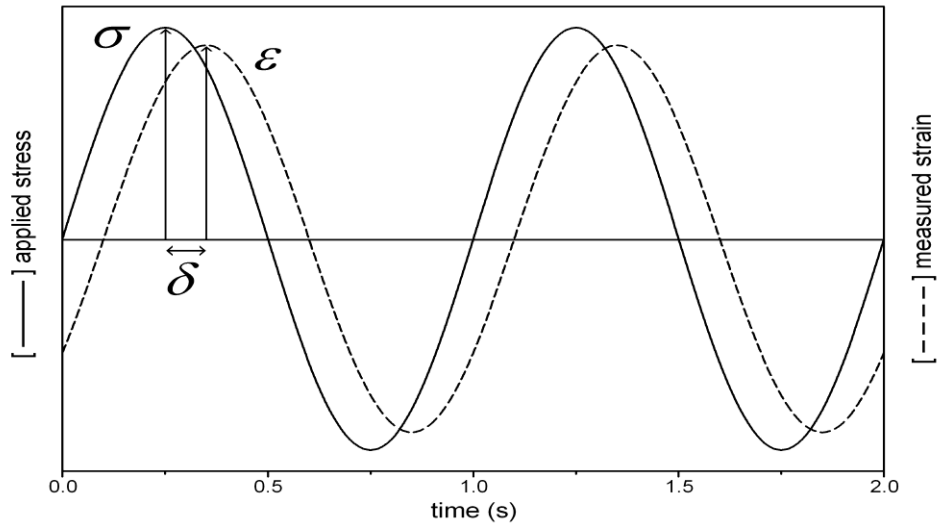


Figure 5.2 : Sinusoidally oscillating stress and strain with phase angle

5.1 Viscoelastic Response Behaviors

Two aspects of viscoelastic behavior can be considered, namely the creep response under constant stress and the stress relaxation response under constant strain.

5.1.1 Creep response

The creep response is mentioned earlier in connection with Figure 5.1. As a summary in creep, time dependent strain is observed while a constant stress is applied to the material. In the linear viscoelastic case, the total creep strain is proportional to the magnitude of the stress input. Accordingly, a creep compliance, $J(t)$ in Equation 5.3, which is a function of time only, may be defined, in the linear viscoelastic case. In the linear viscoelastic regime strain is linear with stress, strain versus time data at different τ_0 collapse into one $J(t)$ plot.

$$J(t, \gamma) = \frac{\gamma(t)}{\tau_0} \quad (5.3)$$

5.1.2 Creep and recovery

Considering the case in Figure 5.3 where the stress is applied at time zero and removed at time t_1 , in this duration between zero and t_1 material creeps. After t_1 , it recovers its a part of deformation. In Figure 5.3, γ_e is elastic part of the resulting strain, γ_d and γ_v are the delayed and viscous deformations, respectively.

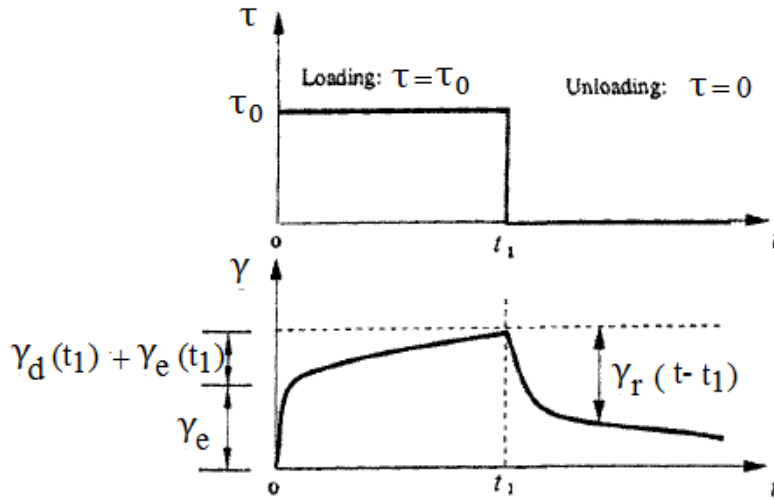


Figure 5.3 : Creep and recovery of a specimen (Haddad, 1995)

5.1.3 Stress relaxation

When a material is subjected initially to a step increase in strain as shown in Figure 5.4.a, the time-dependent stress response is observed. If this material is viscous liquid, the stress relaxes instantly to zero as soon as the strain becomes constant as seen in Figure 5.4.c. An elastic solid would show no relaxation as seen Figure 5.4.b. In a viscoelastic liquid stress relaxes to zero while for a viscoelastic solid it approaches an equilibrium stress as seen in Figure 5.4.d.

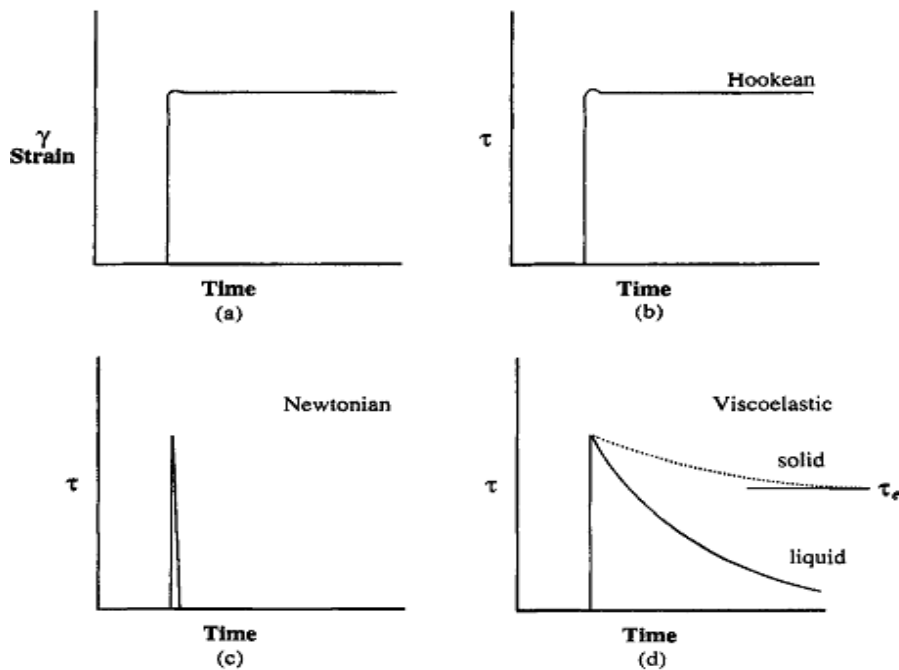


Figure 5.4 : Stress relaxations of materials (Macosko, 1994)

Relaxation of a material is generally given by relaxation modulus, which is define in Equation 5.4, so that strain dependent of relaxation can avoid. In other words, stress relaxation modulus is independent of strain at which values less than a critical strain value. This value as known linear viscoelastic region. Figure 5.4.a shows typical stress relaxation data for increasing strain magnitudes while Figure 5.4.b shows relaxation modulus at small strains fall in same curve.

$$G(t) = \frac{\tau(t)}{\gamma} \quad (5.4)$$

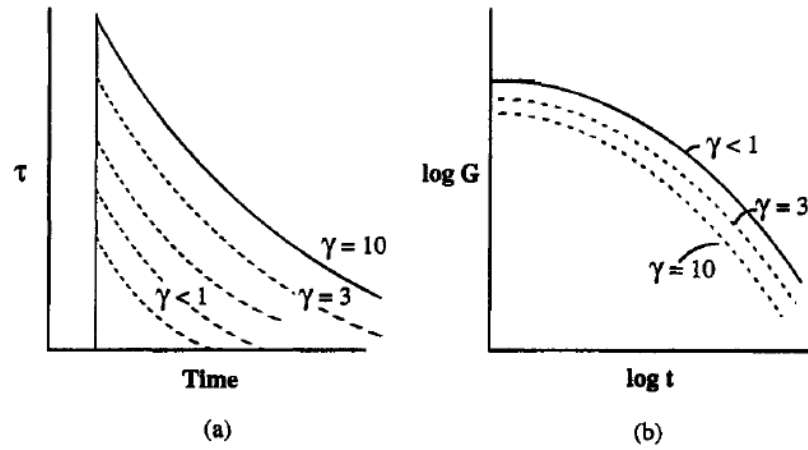


Figure 5.5 : Stress relaxation and relaxation modulus at different strain values (Macosko, 1994)

5.2 Viscoelastic Models

Hooken's spring and Newton's daspot are simple and basic model which are define the behavior of elastic solid and viscous liquid, respectively. Viscoelastic models are derived from these models by having variation of them.

5.2.1 Hooken's spring

A spring is a representation of a linear elastic element that obeys Hooke's law in Equation 5.5. The strain is proportional to the applied stress. In a simple shear deformation the constant of proportionality, G , is the elastic modulus.

$$\tau = G\gamma \quad (5.5)$$

5.2.2 Newton's dashpot

Similarly, linear viscous response can be modelled using a dashpot. A plunger moving through a very viscous Newtonian liquid physically represents this. The response of this model is described mathematically by the Equation 5.6.

$$\tau = \eta \dot{\gamma} \quad (5.6)$$

5.2.3 Maxwell model

If we connect a spring and a dashpot in series as shown Figure 5.6.a, we have the simplest representation of a viscoelastic liquid, and such a combination is called a Maxwell model.

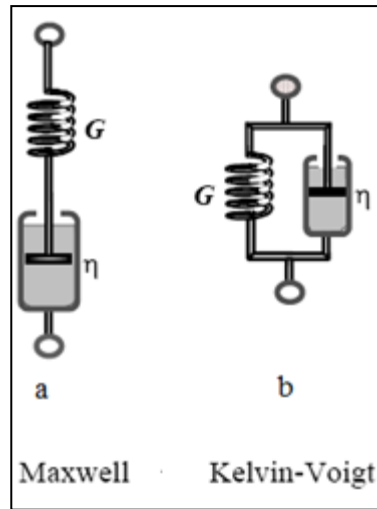


Figure 5.6 : The Maxwell and Kelvin-Voigt models

A creep test is performed on maxwell model, the behavior can be described by Equation 5.7.

$$\gamma = \tau \left(\frac{1}{G} + \frac{t}{\eta} \right) \quad (5.7)$$

It is characterised by an immediate elastic response, $\gamma = \tau/G$, at very short times and at very long times, when $t \gg \eta/G$, by simple viscous behavior, $\gamma = \tau t/\eta$. Here η/G is called the relaxation time.

5.2.4 Kelvin-Voigt model

If we combine the single elastic and viscous elements in parallel as shown Figure 5.6.b, we end up with the simplest representation of a viscoelastic solid, and this has been named after Kelvin-Voigt model.

If a creep test is performed on a Kelvin-Voigt model, the strain gradually builds up to a constant value as described by Equation 5.8.

$$\gamma = \frac{\tau}{G} \left(1 - e^{-\frac{t}{\tau}} \right) \quad (5.8)$$

Here τ is called the retardation time, since it characterises the retarded response of the model, and its value is again given by η/G . At very short times, the response is viscous, and $\gamma \sim \tau t/\eta$.

The Maxwell and Kelvin-Voigt models may be expanded to give either multiple Maxwell models, which are usually combined in parallel, or else multiple Kelvin-Voigt models, which are usually combined in series. However, if we combine a Maxwell model and a Kelvin-Voigt model in series as seen Figure 5.7, we obtain a Burgers model.

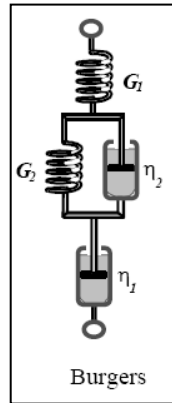


Figure 5.7 : Burgers model

5.2.5 Burgers model

If we now stress the Burgers model in a creep test, first, the unrestrained spring G_1 will instantaneously deform to its expected extent, while the isolated dashpot will start to deform at its expected rate. However, the spring in the Kelvin-Voigt element cannot immediately respond, being hindered by its dashpot. Nevertheless, it does

begin to deform, and eventually comes to its expected steady-state deformation. It is possible to show that the overall deformation can be written down in Equation 5.9.

$$\gamma = \left(\frac{1}{G_1} + \frac{1}{G_2} \left(1 - e^{-\frac{t}{\tau}} \right) + \frac{t}{\eta} \right) \quad (5.9)$$

6. THE EFFECT OF FILLERS ON RHEOLOGICAL PROPERTIES OF FILLED POLYMERS

6.1 Viscosity

In literature, there are some studies about the effect of fillers on rheological properties of filled polymers. Generally, increasing the amount of filler in a filled polymer increases shear stress and viscosity.

In order to describe the influence of particle loading and surface coating on the viscosity of particulate-filled compounds Yeh et al prepared calcium carbonate filled polypropylene composites. The viscosity appears to increase with increasing volume loading of calcium carbonate. The surface treatment of fillers, which presumably reduces the interaction between filler particles and the extent of agglomeration, results in major viscosity reductions (Yeh and Jyun, 1999).

The effects filler content and its surface treatment on the melt flow behavior of glass bead-filled PP composites are investigated. Viscosity increases obviously with the volume fraction of glass bead at lower shear rates, while the dependence of viscosity on filler fraction decreases with the increase of shear rates. As it is known that surface treatment helps to flow composite melts easily than including untreated filler composite melts. However, treated glass bead with silane filled composite has higher viscosity than unfilled composite when both composite are subjected to the same test condition. The increase of the resistance to flow and flow satiability for the former system is attributed to the improvement of the compatibility and interfacial adhesion between the filler due to the surface treatment of the glass beads (Ji-Zhao, 2001).

Note that the viscosity increase with filler addition depends on the properties of filler such as its particle size. The specific surface area of the calcite enormously increases as the average particle diameter becomes smaller than 600 nm. Due to the large contact area of the particles lead to a strong tendency to agglomeration. The agglomerated particles enhance the viscosity of the composites (Osman and Atallah, 2006).

With increasing filler volume fraction, the particles tend to agglomerate that can be disintegrated by shearing. Shearing can be applied before testing. Another way to prevent from agglomeration of the particles in the composite is coating the filler surface by a coating agent (The more common coating agent for calcite is stearic acid). By this way adhesion between the particles reduces. Particle-particle interaction weakens. Agglomeration of the particles can be obstructed. Thus, the effect of the agglomerated particles to viscosity is reduced (Osman and Atallah, 2005).

Melt viscosity of isotactic polypropylene filled with titanium dioxide nanoparticles of varying content from 5 to 30 % wt. and surface characteristics; uncoated (hydrophilic), silica (SiO_2) coated, and stearic acid coated are investigated by Dangtungee et al. Clearly, increasing the content of the nanoparticles increase the apparent shear viscosity of the melts. Viscosity of the silica coated titanium dioxide (hydrophilic) filled composite is highest. At any given content of the TiO_2 nanoparticles (hydrophobic), coating the TiO_2 nanoparticle surface with stearic acid reduced the apparent shear viscosity of the melt significantly (Dangtungee and Supaphol, 2008).

The reduction in the shear viscosity values of the isotactic polypropylene melts that has been filled with stearic acid coated TiO_2 nanoparticles should be a result of the lubricating effect of stearic acid that helps prevent the particles from aggregation and helps promote the distribution of the particles within the melts (Supaphol and Harnsiri, 2006).

On the contrary, the observed increase in the shear viscosity values of the isotactic polypropylene melts that has been filled with SiO_2 -coated TiO_2 nanoparticles could be a result of the ability of the iPP molecules to adsorb on the particle surface (Supaphol et al, 2007).

6.2 Dynamic Mechanical Behavior

The addition of a filler which interacts with the matrix restricts molecular mobility which can be measured using the dynamic mechanical analysis. Figure 6.1 shows the effect of particle size of glass beads on $\tan \delta$. Smaller beads with higher surface area available for interaction restrict molecular mobility (Wypych, 2000).

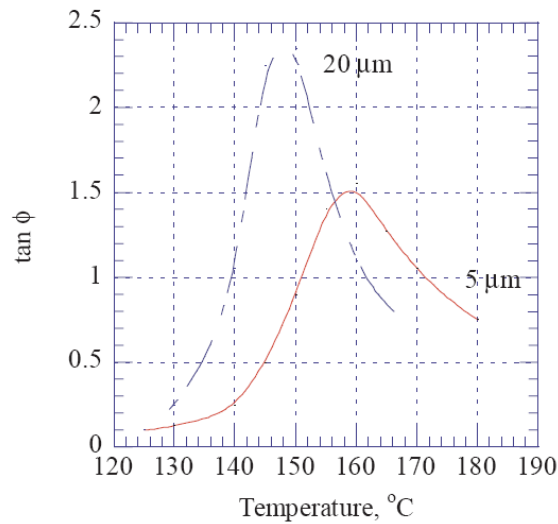


Figure 6.1 : Tan δ versus temperature for styrene-methacrylic acid copolymer filled with glass beads of different diameter (Bergeret and Alberola, 1996)

Figure 6.2 gives an example of how interaction affects dynamic mechanical properties. Two polymers were tested with various concentrations of alumina. Polystyrene was almost unaffected by various concentrations of filler. Sulfonated polystyrene interacts more strongly with its filler than polystyrene which contributes to increase in T_g (Cousin and Smith, 1994).

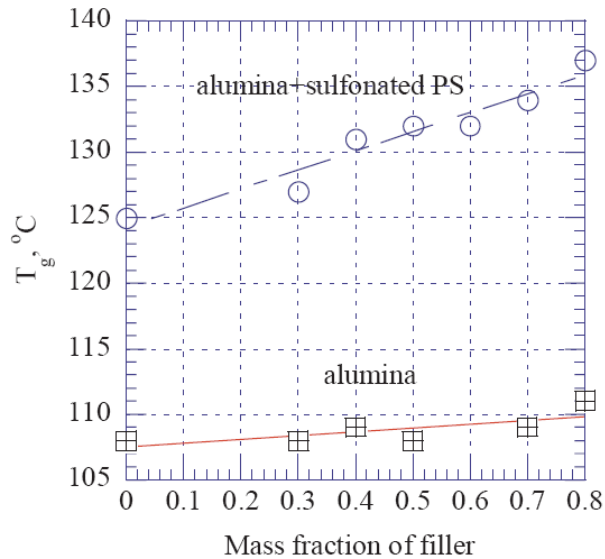


Figure 6.2 : T_g versus concentration of alumina (Cousin and Smith, 1994).

Hristov et al suggesting that because of restricting the macromolecules in amorphous phase by adding the filler is increased the T_g of composite. In the other

words, the addition of a rigid phase cuts down the mobility of the polymer chains, which results in a high in T_g value (Hristov and Vasileva, 2003)

Adding the filler in polymer does not always result in a higher temperature of glass transition. The experiment of Gutie'rrrez et al proves that in the case of PP-talc composites the T_g occurs at lower temperature. They explain this decreases that the talc acts as a nucleating agent, and this effect of the talc leads to a faster crystallisation of the PP. This crystallisation speed-up causes an amorphous phase with bigger mobility in the PP-talc composites, which results in a lower T_g value. If talc is treated with a coupling agent, the higher nucleating effect occurs. Thus treated talc filled PP composite has the glass transition at lower temperature than untreated talc filled PP composites (Gutie'rrrez et al, 1999).

The elastic modulus always increases with adding the rigid filler, because the filler is a stiffer material than the PP. Besides, the presence of talc produces a more rigid interface in the PP matrix. If the filler is a treated one, the interface will be stiffer. So, the treated filler filled composites, in spite of their lesser percentage of untreated filler, generally have a higher storage modulus than the untreated filler filled composites (Gutie'rrrez et al, 1999).

6.3 Viscoelasticity

Viscoelastic properties of filled polymer composites are important to determine the viscoelasticity of the composites. Thus, there are many study about viscoelasticity. Filler inclusions in polymer increase complex viscosity, the storage modulus and the loss modulus of the composites. Since particles exert strong restraints on the polymer chain relaxation. Moreover, filler addition increases the storage modulus more than the loss modulus, hence decrease the material damping. The crossover (liquid-like to solid-like) frequency shifts to lower values with increasing filler volume fraction (Osman and Atallah, 2005).

Increasing filler volume fraction, the particles tend to agglomerate. The presence of agglomerated particles increases the complex viscosity, the viscoelastic non-linearity, the storage and the loss modulus of the composites. Treated the filler with a surface modifier reduces its tendency to agglomerate as well as the adhesion between the particles and the polymer, leading to lower complex viscosity and modulus. Also

interfacial slippage reduces with increasing strain amplitude. In the other words, linear viscoelastic region narrows by coupling the filler such as treating calcite with stearic acid (Osman and Atallah, 2005).

Osman et al also investigate the effect of the particle size on viscoelastic properties of calcite filled HDPE. For this purpose, they compare nano sized calcite filled HDPE composite with micron size calcite filled HDPE composite. They explain that nanocomposite has bigger moduli (storage and loss moduli) and complex viscosity than microcomposite. The high moduli and complex viscosity of the nanocomposites are not a direct consequence of the particle size. But, the high moduli and complex viscosity of the nanocomposites is due to the presence of a large number of agglomerates and aggregates in these composites because of their higher surface areas (Osman and Atallah, 2006).

It is important to note that the linear region decreases as the filler loading increases for all composites regardless of surface treatment. For low volume fractions, the polymer entanglements predominate inside the polymer melt, which would sustain large shear strain deformation, and hence the linear plateau becomes wider. For high volume fractions, a filler network forms as a result of significant filler-filler interaction: however, the interparticle bonding forces are not strong enough to keep the structure intact beyond critical strains such that the linear region becomes narrower (Wang and Yu, 2000).

7. EXPERIMENTAL

7.1 Materials

The polypropylene random copolymer used is CarmelTech QB 79 P, supplied by Carmel Olefins Ltd (Europe). It has a melt flow index of 0.26 g/10 min (2.16 kg at 230 °C). Calcite, different particle size and surface properties, is supplied by Esen Mikronize, Turkey. The density of calcite is 2.7 g/cm³. Calcite grades are listed in Table 7.1. Particle size distribution of calcites are given in App. F.

Table 7.1 : Commercial calcite grades and their properties

code	Commercial Grades	Average Particle Size [μm]	Surface Modification
C-s-ut	A-1	1.85-1.97	untreated
C-s-t	400-E	1.85-1.97	treated with stearic acid
C-m-ut	A-3	2.7-3.3	untreated
C-m-t	KA-2S	2.7-3.3	treated with stearic acid
C-b-ut	A-5	4.7-5.3	untreated
C-b-t	KA-5	4.7-5.3	treated with stearic acid
C-vb-ut	A-30	7.8-10.3	untreated

7.2 Equipments

7.2.1 Thermokinetic mixer

Thermokinetic mixer (TKM) is used to mix calcite and PP-R. It is equipped with a 150 gr chamber and co-rotating blades. TKM can be operated with at shaft speed of 4500 rpm. In pre-mixing mode, the shaft speed is less than 4500 rpm and this speed is not constant. TKM has not a heating unit and a temperature control system. Polymers melt by friction.

7.2.2 Extruder

A twin screw extruder (TSE) is also used to mix calcite with PP-R. It has co-rotating screws. Screw diameter and L/D ratio are 35 mm and 52, respectively. The operation temperature of extruder is 220-230 °C.

7.2.3 Press machine

The composite is pressed to 1-1.5 mm thick plaques between polytetrafluoroethylene covered two steel plates at temperature 180 °C by a press machine under 80 bar for two minutes. Then, cooling the plaque to room temperature for two minutes with the same press machine which has a cold press section under the same pressure.

7.3 Sample Preparation

Composites containing different mass fractions (5-50 wt %) calcite filled PP-R are prepared by using TSE and/or TKM.

The mixing conditions are chosen to minimize polymer degradation and achieve optimal homogenization of the filler. For this purpose, six different mixing method is applied.

In the first preparation method, the polymer granuls are first put in the chamber of TKM and it is operated for 32 seconds. Then required amount of calcite is added in the chamber and it is operated for 15 seconds. By this way, only 30 wt % C-s-ut-coded calcite filled PP-R composite is obtained.

In the second preparation method, granuls and the required amount of calcite are added together in the chamber of TKM. Then mixer is operated for 22 seconds to have composite. According to this method, 10 wt % C-m-t-coded calcite filled PP-R and 30 wt % C-s-ut-coded calcite filled PP-R composites are prepared.

In the third method, polymer granuls, required amount of c-b-t-coded calcite and various amonut (1, 2 and 5 wt %) of 1 wt % antioxidant filled PP-R are put in the chamber of TKM. Then, it is operated for 22 seconds to obtain 5 wt % C-b-t-coded calcite filled PP-R composites.

In the fourth method, again the PP-R and required amout of calcite are added together in the chamber of TKM. But in this method, pre-mixing time is 12 seconds while it is 5 second in first three methods. The total time is changed from 22 seconds to 29 seconds to achieve optimal filler dispersion in PP-R matrix. According to this method, 20 and 40 wt % C-b-t-coded calcite filled PP-R composites are prepared.

In the fifth method, treated calcite (which are coded as C-s-t, C-m-t, C-b-t) filled PP-R composites are prepared in TSE. Then, composite granuls are added to TKM. It is

operated for 12 second pre-mixing time and totally 22 seconds. According to this method, 5-50 wt % calcite (which are coded as C-s-t, C-m-t and C-b-t) filled PP-R composites are prepared.

In the first five methods, composite melts called bulk form is obtained after TKM operation. Then it is taken to the press machine.

In the sixth method, calcite and PP-R are mixed in TSE and composite granules are obtained. These granules are directly press twice under same press conditions which is applied in first five method. According to this method, 5-50 wt % calcite (which are coded as C-s-t, C-s-ut, C-b-ut and C-vb-ut) filled PP-R composites are prepared.

Disks 25 mm in diameter and rectangle in 40x10 mm are stamped out of the plaques of composites for the rheological measurements and dynamic mechanical analysis, respectively.

7.4 Test Methods

7.4.1 Rheological Tests

The rheological properties are measured using a stress and strain-controlled rheometer (MCR 301-Physica, Stuttgart, Germany) equipped with an electrically heated thermostating unit (P-ETD350) and its hood (H-ETD400) which helps test environment reaches thermal equilibrium. A photo of MCR 301 rotational rheometre is shown in Figure 7.1. The experiments are carried out with plate and plate geometry. One of the plate is stationary and it heats test enviroment. The other plate is dynamic. The dynamic plate diameter is 25 mm. The gap between the plates is standart at all measurement as 1 mm. The specimens are put on the stationary plate, then dynamic plate is squeezed until the gap between the plates is 1 mm. The specimen around the dynamic plate is trimmed to prevent calculation errors. The specimen is allowed to fully relax after squeezing in the rheometer (monitored by measuring the normal force) before starting the measurement. It takes approximately two minutes for all specimen. The two minutes of duration is standart and applied to all specimens. Assuming that specimen may contain agglomerates, preshearing all the specimens at a shear rate of 1 s^{-1} for sixty seconds to destroy many of the agglomerates. Preshearing is even applied to the neat PP-R to obtain the same test condition for all specimen. After the preshearing normal force is not zero. To set the

normal force zero, very small deformation applied to the specimens for sixty seconds. All these are pre-test labouing before the main tests. The following are the details of the individual tests performed.



Figure 7.1 : A photo of rotational rheometre MCR 301

7.4.1.1 Flow curve test

This test is performed to define how shear stress and shear viscosity change with respect to shear rate. Shear rate, the independent variable, is swept from 0.01 to 150 s^{-1} .

7.4.1.2 Amplitude sweep test

The strain controlled experiments included dynamic strain amplitude, γ_0 , sweep. Strain amplitude logarithmically increasing from 0.01 to 100 % at a fixed angular frequency 10 rad/s. This test helps to define linear viscoelastic region.

7.4.1.3 Frequency sweep test

Dynamic moduli and complex viscosity are measured by sweeping the frequency from 0.01 to 100 rad/s at a constant amplitude, which is in linear viscoelastic regime. The strain amplitude is 1 % for all composites.

All these tests above mentioned are performed at 230 $^{\circ}\text{C}$. In additon neat PP-R and 20 % calcite filled PP-R are tested at 210 and 260 $^{\circ}\text{C}$ to examine temperature effect.

Fresh spicemen is used for each test.

7.4.2 Dynamic mechanical analysis

Dynamic mechanical analyse is carried out by means of a Perkin Elmer Pyris Diamond dynamic mechanical analyser. Test pieces of thickness approximately 1mm, width 10 mm and length 40 mm are prepared. Measurements are performed at frequency of 1 Hz and the temperature program is run from -50 to 150 °C, at a heating rate of 3 °C /min under a flow of liquid nitrogen. The viscoelastic properties such as the elastic modulus (E'), viscous modulus (E''), damping factor ($\tan\delta=E''/E'$) are recorded as a function of temperature.

7.4.3 Light microscopy

To evaluate quality of compound and to see dispersion of calcite particle in polymer matrix, light microscopy observations are performed by Unitron MEC2 light microscop. Depending on the average particle size of calcite, observations are generally performed at 1000x mode.

8. RESULTS AND DISCUSSION

8.1 Sample Preparation Methods

8.1.1 First method

Viscosity curves of 30 wt % C-s-ut-coded calcite filled PP-R composites prepared by first and second preparation methods are given in Figure 8.1. The viscosity of the composite which is prepared according to first preparation method is lower than the viscosity of the composite which is prepared according to second preparation method. Because more shearing is applied to composite in the first method. It is well known that more shearing causes decrease in viscosity. The composites which is prepared according to the first method behaves like a Newtonian fluid while the other shows shear thinning behavior.

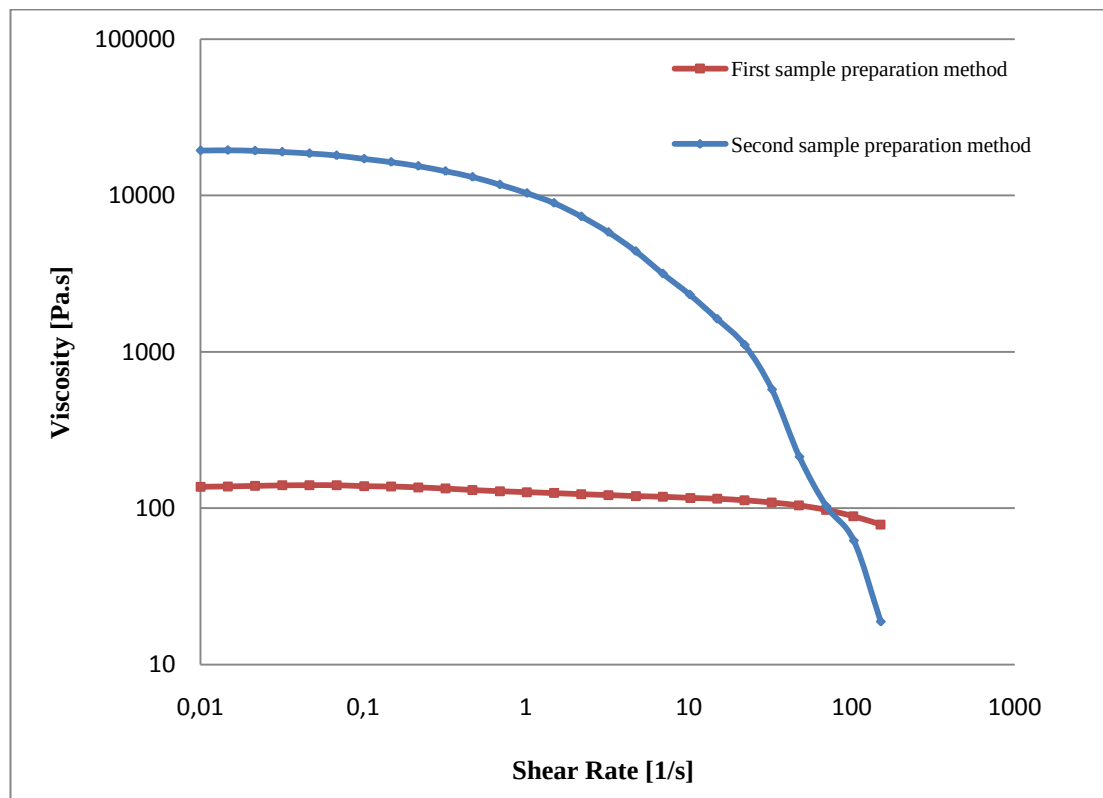


Figure 8.1 : Viscosity curves of 30 % C-s-ut-coded calcite filled PP-R composites prepared by the first and second methods

Light microscopy observation of composites which are prepared by first and second methods are given in Figure 8.2. Although the smallest particle sized calcite (1.85-1.97 μm) is used for composite preparation, agglomeration occurred. The particle size of calcite is determined between 17.7-25.6 μm for agglomerated particles. Scratches are seen from two images. They formed due to polytetrafluoroethylene covered steel plates during pressing samples. Well dispersed composites could be prepared by second method.

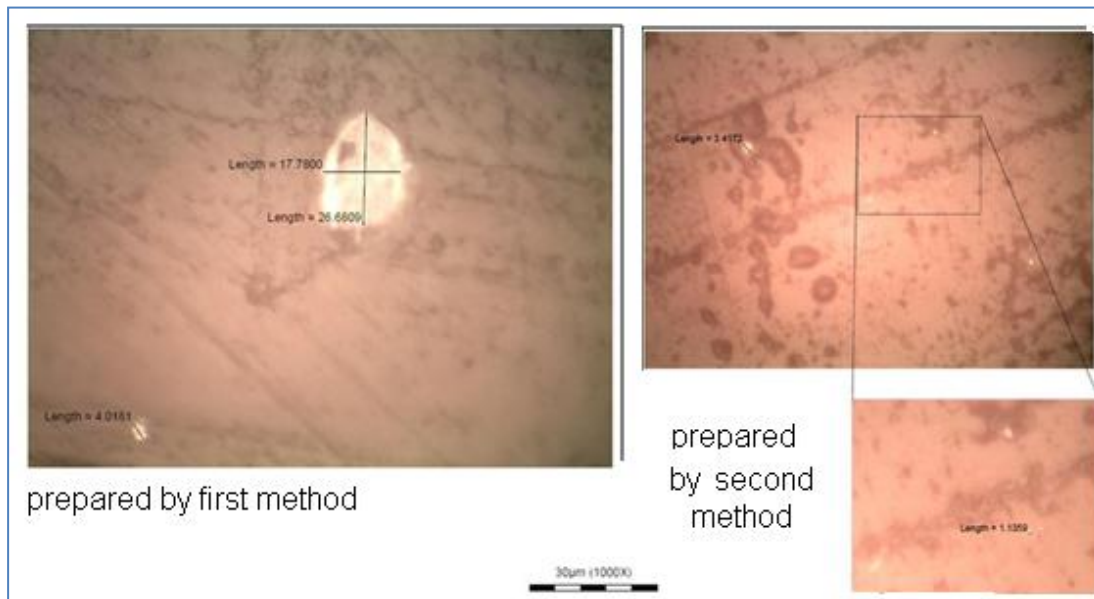


Figure 8.2 : Light microscopy images of composites which are obtained by different sample preparation methods

8.1.2 Second method

Seven different parts of a plaque of 10 wt % C-m-t-coded calcite filled PP-R which is prepared by using second sample preparation method are tested for viscosity measurement. Since there are local degraded parts on the plaque and they are seen yellow, test results which are given in Figure 8.3, are not consistent. First four test and seventh test are performed by using the white part of the plaque. Fifth test is performed by using yellow part of the plaque while the sixth test is performed by using more yellow part. When the sample is yellower, its viscosity is lower. In other words yellow parts are degraded parts. It means that second method causes local degradation of composites. For this reason it is not convenient for preparing composites.

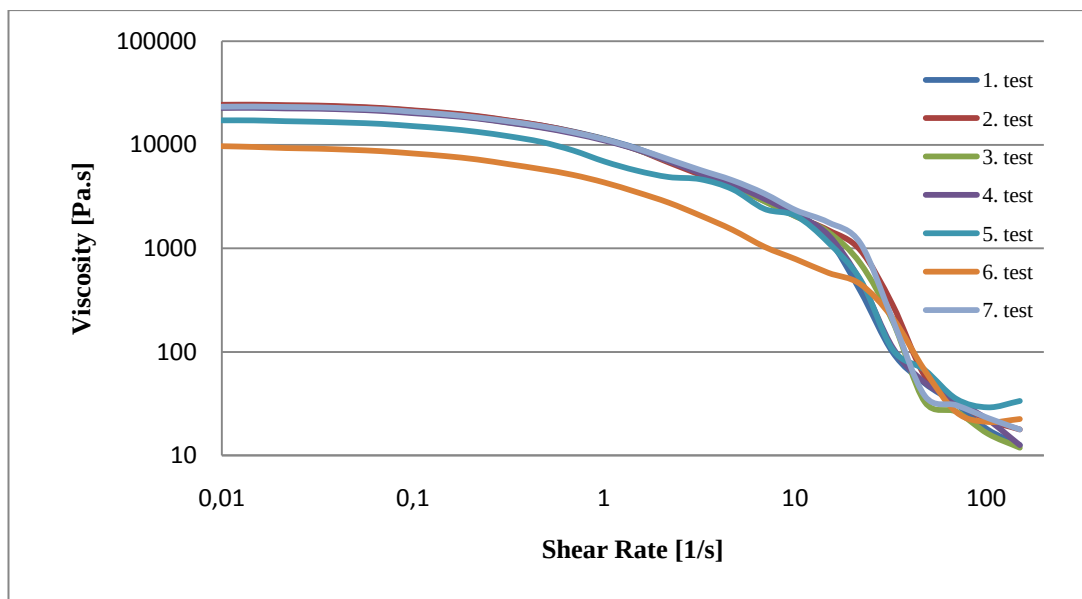


Figure 8.3 : Viscosity curve of 10 wt % C-m-t-coded calcite filled PP-R

8.1.3 Third method

To prevent degradation of polymer during mixing, varying amounts (1-5 wt %) of 1 wt % antioxidant filled PP-R is added in 5 wt % C-b-t-coded calcite filled PP-R composites. The antioxidant-free sample is tested from white part of the plaque. Samples which consist of different amounts of antioxidant are performed from their yellow part. The results are compared with that of the antioxidant-free samples. It is seen from Figure 8.4 that adding antioxidant does not prevent degradation of polymer.

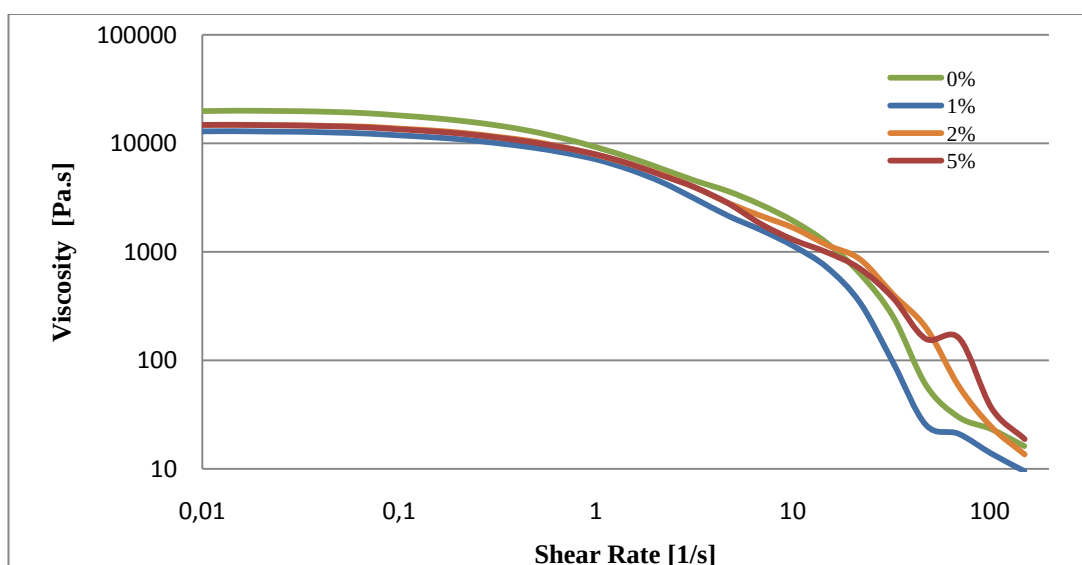


Figure 8.4 : Effect of antioxidant amount on the viscosity of 5 wt % C-b-t-coded calcite filled PP-R

8.1.4 Fourth method

40 wt % C-b-t-coded calcite filled PP-R composites are worked by changing the total mixing time. Table 8.1 shows that well mixed composite can be achieved by 29 s of mixing time. But this period of time also causes local degradation of PP-R. Shorter total mixing time does not cause degradation. However these shorter mixing time is not enough to achieve optimal homogenization of the filler.

Table 8.1 : Change of compounding situtaion with total mixing time

Sample	Total Mixing Time [s]	Situtation
Neat PP-R	22	---
40 % C-b-t-coded calcite filled PP-R	22	unmixed
40 % C-b-t-coded calcite filled PP-R	24	not exactly mixed
40 % C-b-t-coded calcite filled PP-R	26	exactly mixed (has yellow parts)
40 % C-b-t-coded calcite filled PP-R	29	well mixed (has yellow parts)

Figure 8.5 shows that increasing the mixing time decreases the viscosity.

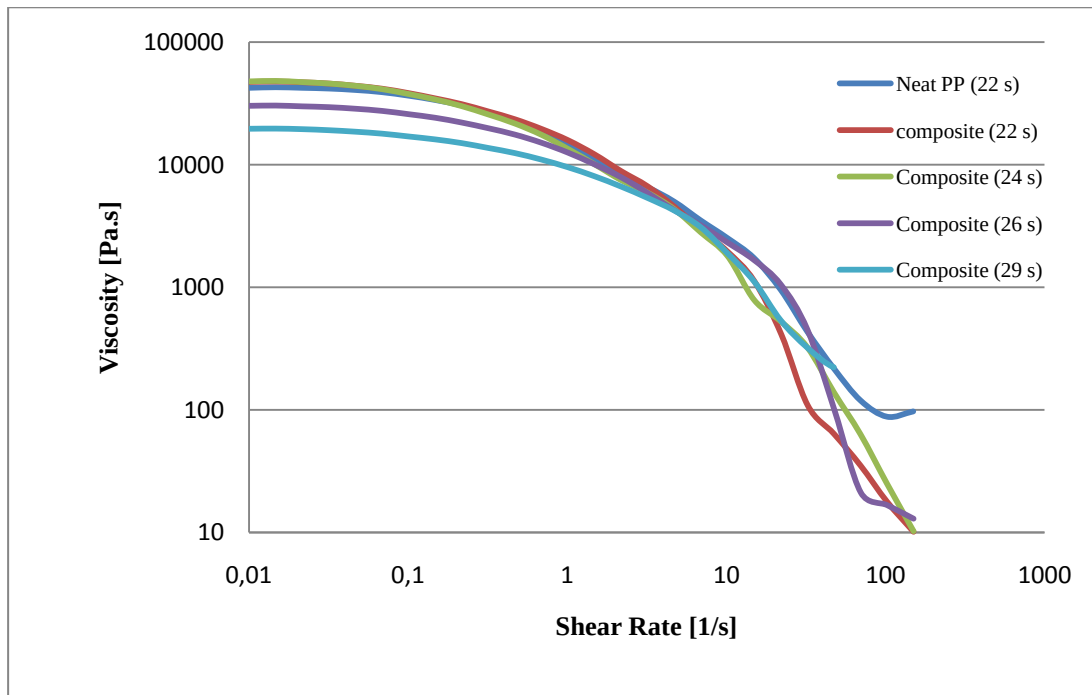


Figure 8.5 : Effect of total mixing time on viscosity of 40 wt % C-b-t-coded calcite filled PP-R

The obtained results from the first fourth methods show that changing the pre-mixing and total mixing time or adding antioxidant to composite can not prevent degradation of PP-R in TKM. For this reason, it is decided to use TSE to obtain well-mixed composite.

8.1.5 Fifth method

It is obvious that the choice of the mixing equipment used in the compounding operation has an effect on the rheological properties of the prepared filled systems. This is due to the differences in the mixing mechanisms, the degree of the shear stress and stress patterns developed in different equipments.

In the first four preparation methods, composites are prepared by using TKM. But in the fifth preparation method, composites in granule form are prepared in TSE. TKM is only used to melt the granules.

Identical compositions (20 wt %) of C-b-t-coded calcite filled PP-R systems are prepared by fifth method and fourth method with different total mixing time, 22, 32 and 42 s. The results are shown in Figure 8.6.

The samples are designated using the abbreviation. For example A method (a) where A indicates the number of the method and a indicates the mixing time. In order to determine repeatability, two different samples are prepared by fourth preparation method for 22 s mixing and the results are compared to each other. The difference between the viscosities of the samples coded as Fourth method (22s)-1 and Fourth method (22s)-2 are not consistent despite of having prepared in same condition. This results show that TKM results are not reliable. Also the samples coded as Fourth method (42 s) has lower viscosity value than the sample coded as Fourth method (32 s).

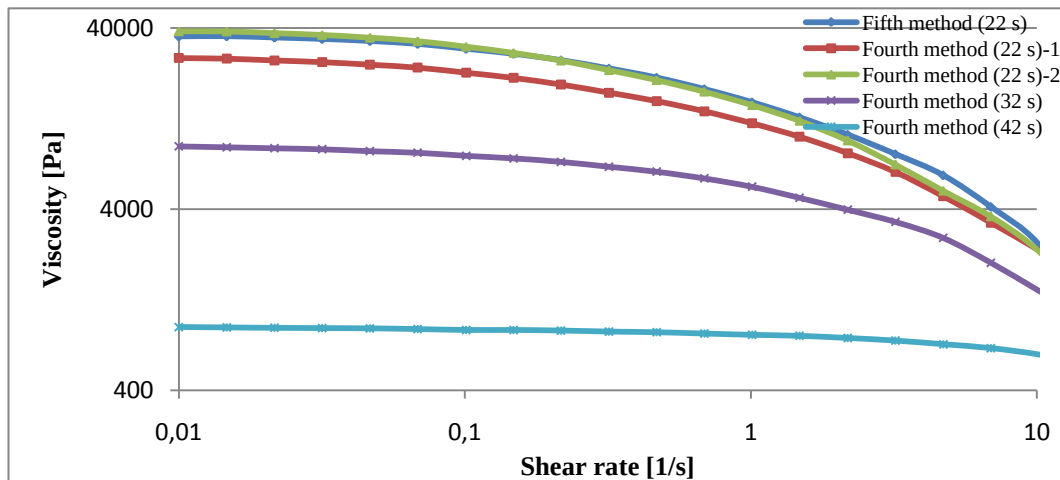


Figure 8.6 : Effect of sample preparation methods on viscosity of 20 wt % C-b-t-coded calcite filled PP-R composites

The test result of oxygen induction time (OIT) and melt flow index (MFI) of 20 wt % C-b-t-coded calcite filled PP-R which are obtained by different sample preparation methods are listed in Table 8.2. It is well known that processing on polymers reduces their viscosities. In other words, MFI of polymers increases by processing. It is also well known that degraded polymers need less oxygen than non or less degraded polymers. Increasing the mixing time reduces the oxygen induction time. That means oxidative degradation occurs due to having long mixing time. OIT and MFI results show that the differences in viscosities in Figure 8.6 could be attributable to considerable oxidative degradation of the PP-R during mixing from the long residence time. On the other hand, composite which is prepared by fifth preparation method has more oxygen induction time. This shows that it contains less or non degraded polymer. According to these results, it is concluded that for this study the use of TSE in composite preparation is more effective way than that of mixer. Additionally, there are no yellow parts on plaques which are prepared by fifth method. So, C-s-t, C-m-t and C-b-t coded calcites filled PP-R composites are prepared by fifth preparation method. Zero shear stresses and viscosities of these calcites and neat PP-R are given in Table 8.3.

Table 8.2 : OIT and MFI results of 20 % C-b-t-coded calcite filled of PP-R which are obtained by different sample preparation methods

Sample	OIT [min]	MFI [gr/10dk] [230°C-2.16kg]
Fifth method (22 s)	78.11	0.39
Fourth method-1(22 s)	70.44	0.52
Fourth method-2(22 s)	69.47	0.52
Fourth method (32 s)	56.65	1.44
Fourth method (42 s)	35.96	14.98

When the results given in Table 8.3 are examined; contrary to literature, increasing the calcite content does not increase the viscosity of the composites, even decreases the viscosity. This inconsistent situation is lead to be realized another disadvantage of the TKM. During mixing, despite of operating TKM in short time (pre-mixing time: 12 s, total mixing time: 22 s), PP-R burns and degrades because of an excessive temperature rise in calcite. The more amount of calcite, the more degradation occurs in PP-R. That's why 50 % calcite filled PP-R has low viscosity. In other words, the increase in viscosity due to calcite inclusion can be considered as a positive effect, and the increase in degradation due to calcite inclusion can be evaluated a negative

effect. However, negative effect increases more than positive effect. So calcite inclusion decreases the viscosity.

Table 8.3 : Zero shear stresses and viscosities of calcite filled PP-R

Calcite Content [%]	C-s-t		C-m-t		C-b-t	
	Shear stress [Pa]	Zero shear viscosity [Pa.s]	Shear stress [Pa]	Zero shear viscosity [Pa.s]	Shear stress [Pa]	Zero shear viscosity [Pa.s]
0	331	33104	331	33104	331	33104
5	357	35747	333	33317	336	33629
10	374	37406	344	34443	354	35373
20	369	36855	360	35964	370	37038
30	312	31238	403	40276	369	36938
40	354	35437	324	32384	451	45103
50	276	27605	340	34009	393	39325

8.1.6 Sixth method

In the sixth method, composite granules which are prepared in TSE are directly pressed to form plaques as indicated in Section 7.2. All rheological tests and dynamic mechanical analyses are performed by using the samples which are prepared according to sixth preparation method.

8.2 Viscosity

8.2.1 Effect of calcite inclusion

Shear viscosity of neat PP-R and 1.85-1.97 μm untreated C-s-ut-coded calcite filled PP-R samples of various filler contents as a function of shear rate is shown in Figure 8.7. Apparently, neat PP-R and relatively low filler loadings (about 5-30 wt %) composites exhibit the typical shear thinning behavior, with a plateau region observed at low shear rates ($< \text{about } 0.1 \text{ s}^{-1}$) and a shear thinning region at higher shear rates ($> \text{about } 0.1 \text{ s}^{-1}$). At relatively higher filler loadings ($> 30 \text{ wt } \%$) however, the compounds exhibit shear thinning behavior as well, but without the presence of a plateau region at low shear rates. The other composites filled with larger particle sized calcites (which are coded as C-b-ut and C-vb-ut) also exhibit similar behavior. All results are given in App. A. The similar results are reported in literature. Yeh et al. studied shear yield behavior of calcite filled PP-R and obtained very similar results (Yeh and Jyun, 1999).

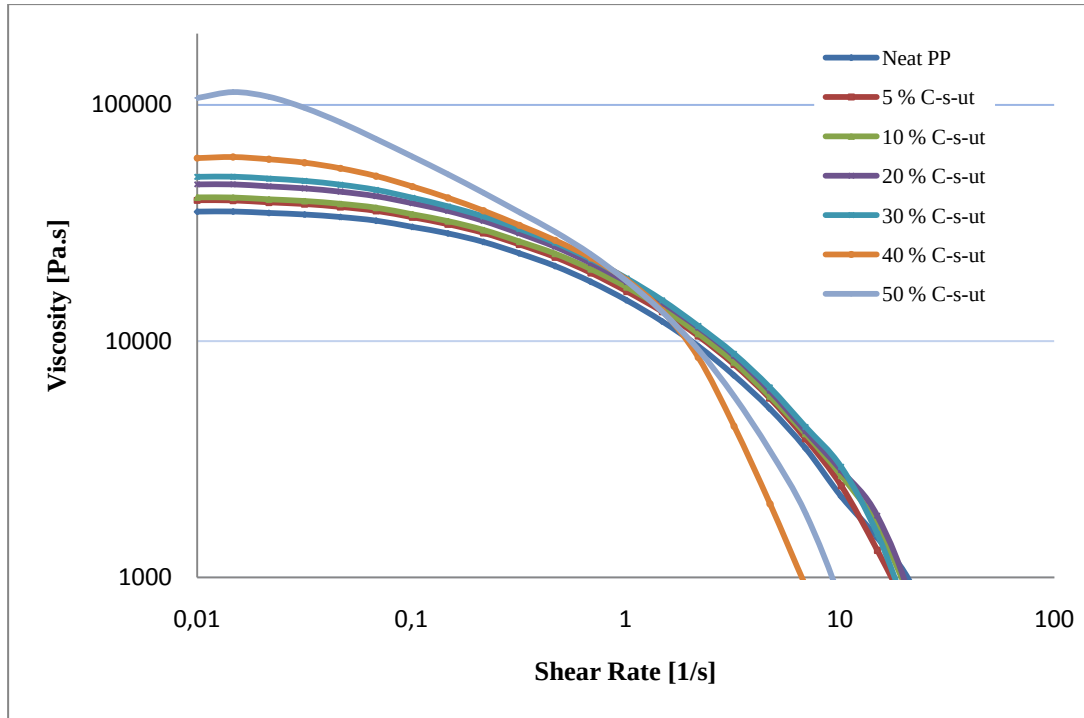


Figure 8.7 : Shear viscosity of neat PP-R and C-s-ut-coded calcite filled PP-R samples of various filler contents as a function of shear rate

Figure 8.8 shows the melt flow curves of the composites at 230°C. It can be seen that shear stress increases with increasing shear rate between the shear rates of 10^{-2} - 1 s^{-1} . Shear stress starts to fall down after shear rate is 1 s^{-1} . This is because of edge failure at high shear rates.

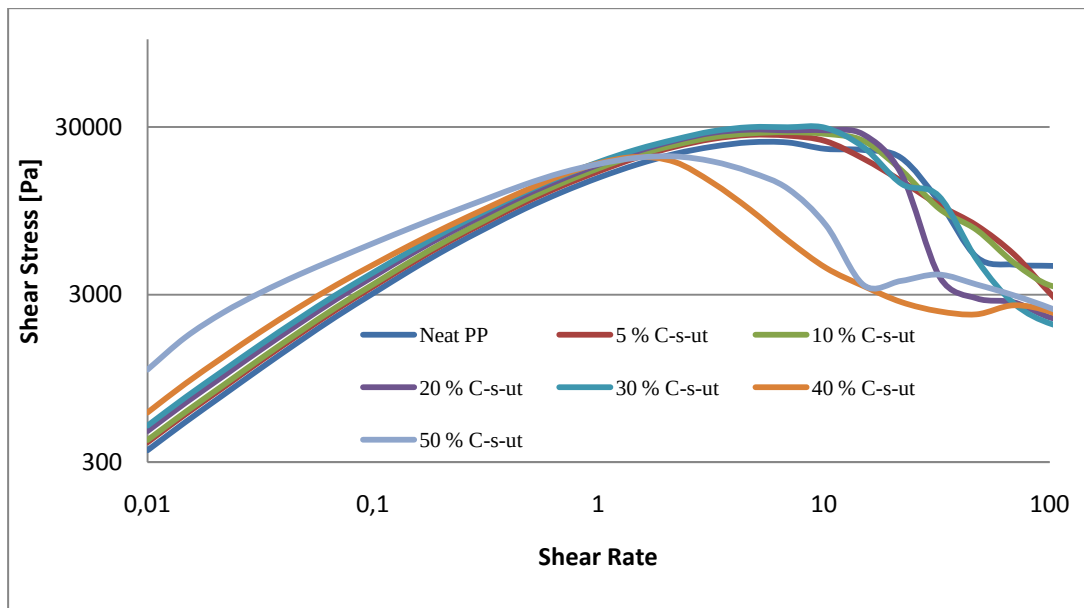


Figure 8.8 : Flow curves of various content of C-s-ut-coded calcite filled PP-R at 230 °C

It can be seen from Figure 8.8 that yield stress increases with increasing the calcite concentration in PP-R matrix. At any stress below yield stress, there is no flow. Various particle size of calcite filled PP-R composites show the similar behavior in Figure 8.8. Flow curve of these composites are presented in App. B.

8.2.2 Effect of particle size

The zero shear viscosity values at a shear rate of 0.01 s^{-1} of neat PP-R and PP-R/calcite samples filled with various particle sizes are shown in Figure 8.9 as a function of calcite content. Apparently, zero shear viscosity values increase with increasing the filler content. In more concentrated systems, strong interactions between filler particles give rise to much larger energy dissipation, resulting in much stronger viscosity enhancement. This may be the reason for the profound increase in zero shear viscosity values at high filler loadings observed for the PP-R/calcite compounds. The similar results were obtained by Supaphol et al (Supaphol and Harnsiri, 2006).

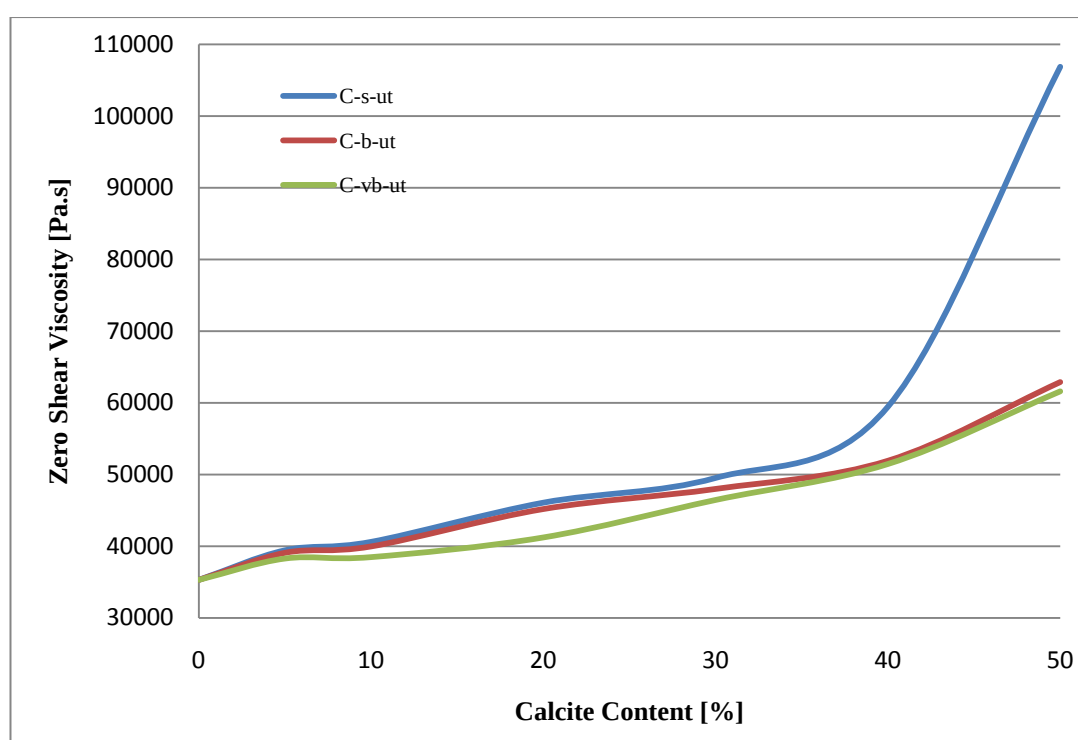


Figure 8.9 : Zero shear viscosity of neat PP-R and calcite/PP-R compounds as a function of calcite content

Another results obtained from data shown in Figure 8.9 is that, among samples loaded with untreated calcite at high filler loadings (> approximately 30 wt %),

1.85-1.97 μm untreated C-s-ut-coded calcite filled PP-R samples exhibit the highest zero shear viscosity values. The smaller particles has larger the surface area. That's why smaller particle sized calcite has rise to a greater possibility of the formation of interparticular structure. This may be due to the strong interparticular interactions, the enhancement of the shear viscosity for the samples filled with calcite particles are apperent.

8.2.3 Effect of surface treatment

Shear viscosities of neat PP-R and 1.85-1.97 μm treated C-s-t-coded calcite filled PP-R samples are shown in Figure 8.10. The composites filled with stearic acid treated calcite particles exhibites a similar behavior to those filled with untreated ones as seen in Figure 8.7. Interestingly at low shear rates, the shear viscosity of PP-R filled with treated calcite particles does not seem to vary much with variation in the filler content, suggesting that interparticular structure does not form for these treated particles.

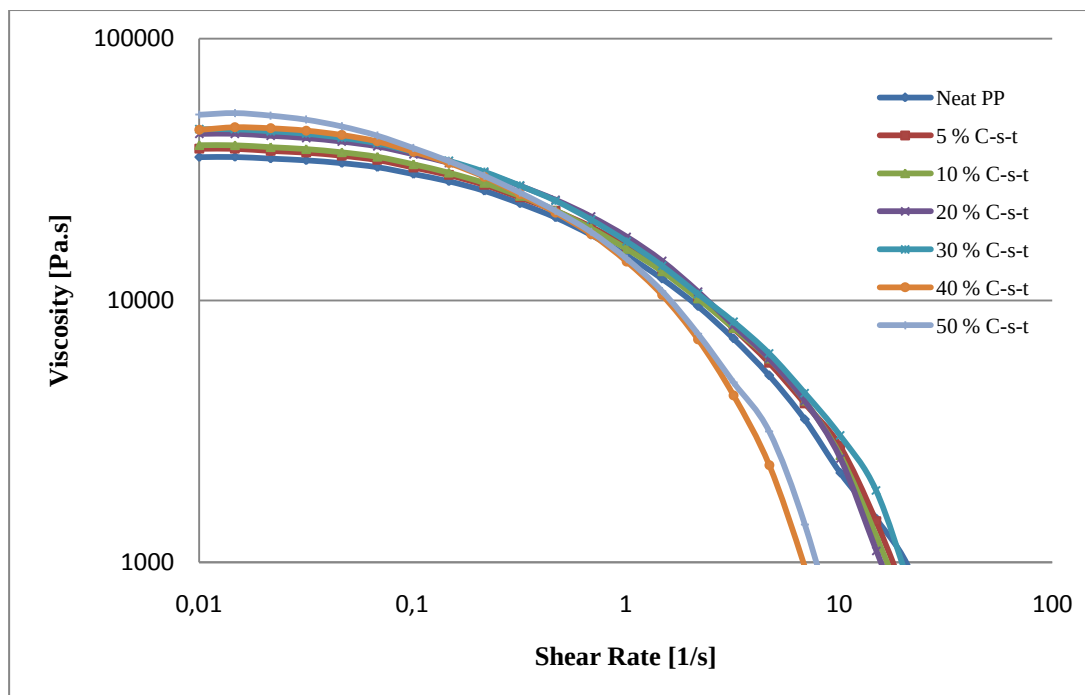


Figure 8.10 : Shear viscosity of neat PP-R and C-s-t-coded calcite filled PP-R samples of various filler contents as a function of shear rate

Zero shear viscosity values of treated calcite, which is coded as C-s-t and untreated calcite, which is coded as C-s-ut filled PP-R composites are illustrated in Figure 8.11. Zero shear viscosities of PP-R filled with treated calcite, which is coded as C-s-

t particles are lower than those of PP-R filled with untreated calcite, which is coded as C-s-ut particles, especially when the calcite inclusion exceeds 10 wt%. The reason is that when the surface of calcite particles are treated with stearic acid, the effective area of the particles reduce. So, interparticular interactions decrease. Also agglomeration may reduce. Thus viscosity decreases. There have been many investigation on effects of surface modification on the shear viscosity. Recently, Kwang et all implied that surface treatment of calcite is effective in lowering the viscosity of calcite filled PP-R composites (Kwang et all, 2004).

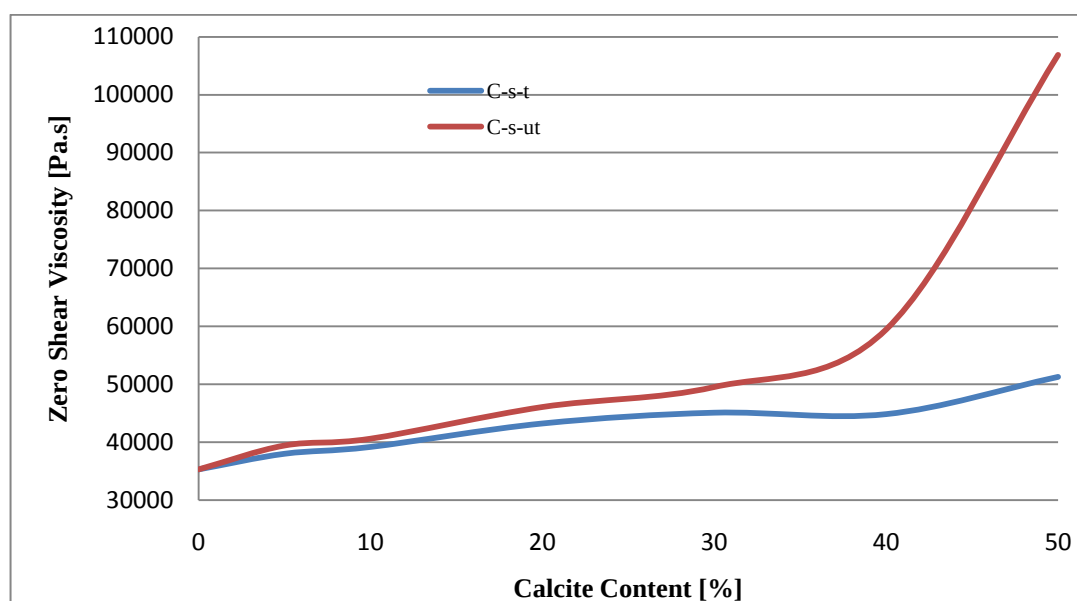


Figure 8.11 : Zero shear viscosity as a function of calcite content for neat PP-R and PP-R filled with 1.85-1.97 μm calcite (C-s-t versus C-s-ut) particles of varying type of surface.

Some of the researchers report strong influence of the particle size on viscosity of polymer melts, while the some other authors find that the viscosity of polymer melt is independent of particle size. Osman et all reported that higher viscosity of nanocomposites is not direct consequence of the particle size, but it is due to the precence of more agglomerates (Osman and Atallah, 2005). In Figures 8.12 and 8.13, viscosity curves of 5 wt % and 50 wt % calcite filled PP-R composites are shown as, respectively. The effect of particle size on viscosity is distinct only at 50 wt % calcite inclusion and it becomes less dominant at higher shear rates. Viscosity curves of 10 - 40 wt % of calcite filled PP-R composites are presented in App. C. For higher shear rates, $>20 \text{ s}^{-1}$, viscosity values are not reliable. Since edge failure occurs at high shear rates, the viscosity should be measured by capillary rheometre.

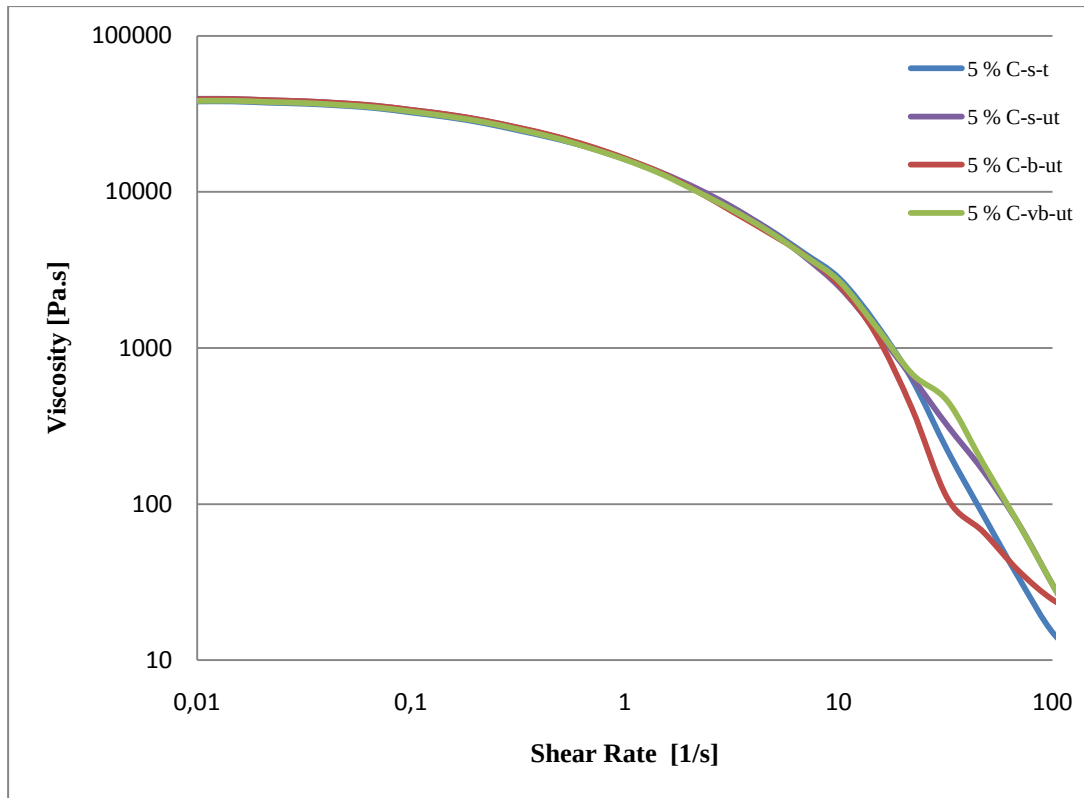


Figure 8.12 : Shear viscosity of 5 wt % calcite filled PP-R samples as a function of shear rate

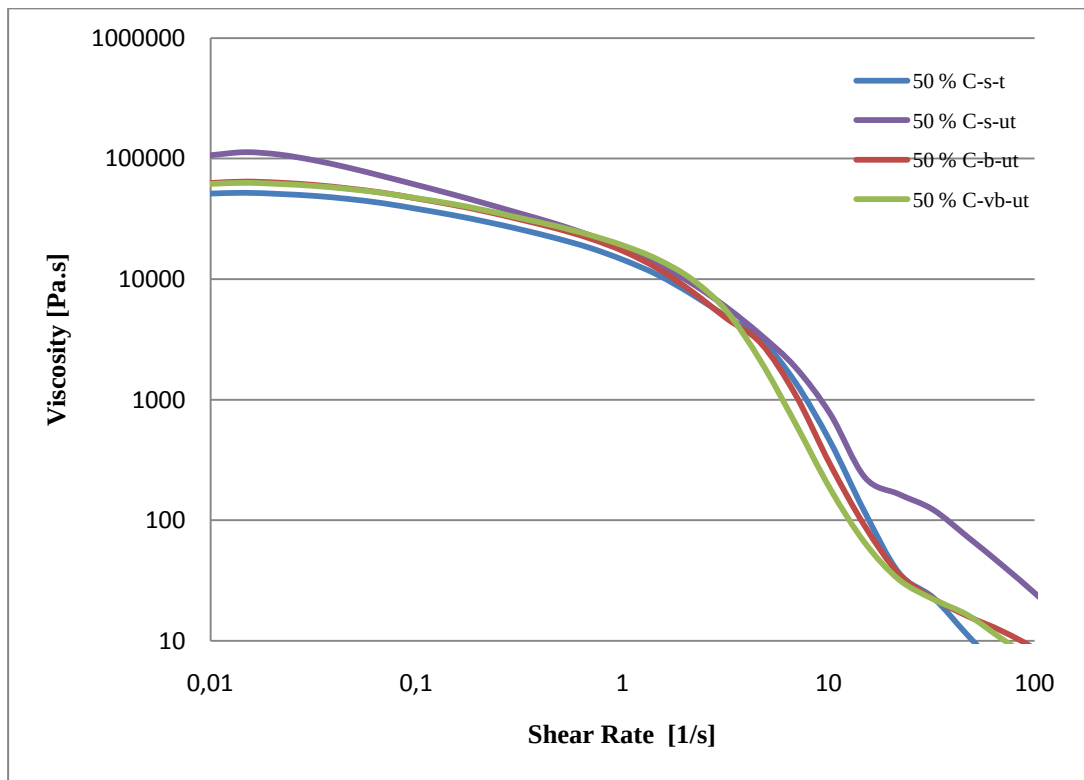


Figure 8.13 : Shear viscosity of 50 wt % calcite filled PP-R samples as a function of shear rate

8.2.4 Effect of temperature

Effect of the temperature on viscosity of neat PP-R is shown in Figure 8.14. As expected, viscosity of PP-R decreases with increasing temperature, because an increase in temperature causes thermal motion of the molecules. Molecules overcome forces of intermolecular interactions. This result in their displacement based upon the available free motion. The composites filled with C-s-ut, C-b-ut and C-vb-ut coded calcites and treated calcite, which is coded C-s-t also show similar behavior. The obtained results are given in App. D.

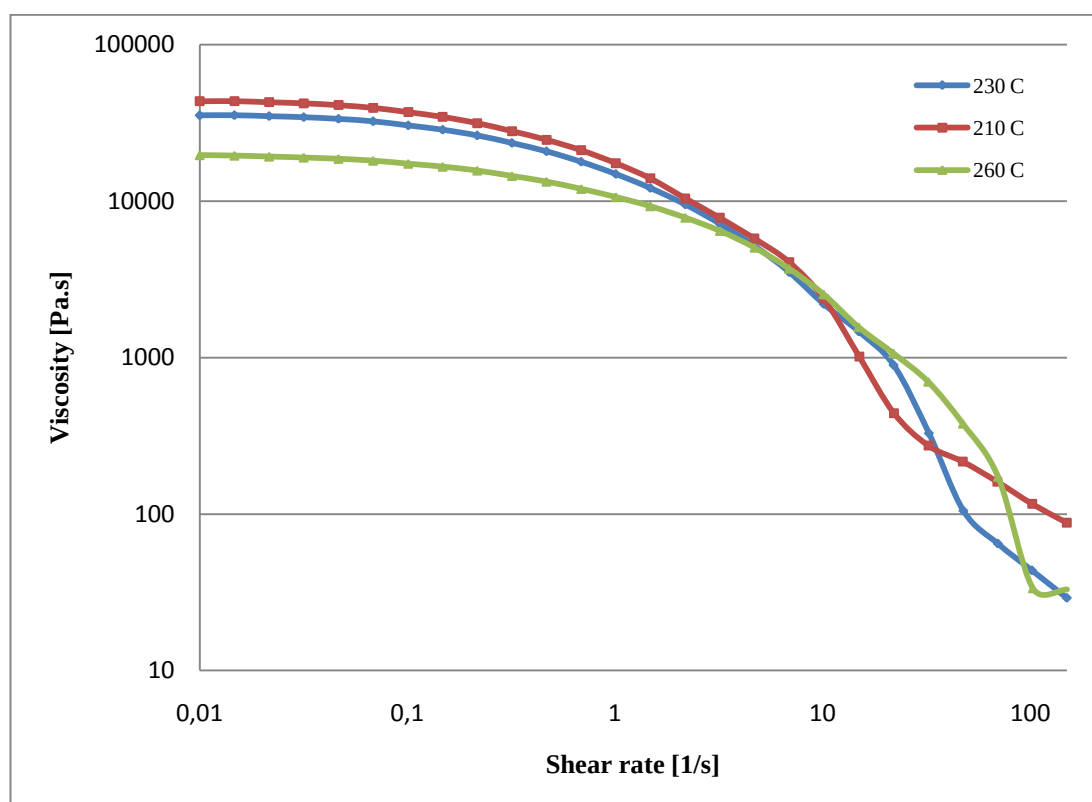


Figure 8.14 : Viscosity curves of neat PP-R at different temperatures

According to Arrhenius-Eyring equation, the activation energy which is a measure of the height of a potential energy barrier associated with the force needed to produce quantum steps in the movement of molecules, is calculated for neat PP-R and 20 % various particle sized calcite filled PP-R. The results are given in Table 8.4. Adding calcite causes the increase in activation energy, because calcite restricts polymer molecules movement. It is important to note that surface treated calcite which is coded as C-s-t filled PP-R has a bigger activation energy than untreated calcite, which is as coded as C-s-ut filled PP-R composite, because surface treatment causes

stronger interaction between particle and polymer matrix. Thus, movement of treated calcite filled PP-R molecules need more energy barrier to flow. Effect of particle size on activation energy is not distinct. However, at present little basic study has been performed to determine the temperature effect on filled systems that can define the activation energies of filled systems. Further study is required to understand the details.

Table 8.4 : Activation energy of filled PP-R

Samples		Activation Energy (kJ/mol)
Neat PP-R		34.6
Neat PP-R from Litterateur (Shenoy, 1999)		33.5-41.9
20 % Calcite Filled PP-R	C-s-t	40.0
	C-s-ut	36.5
	C-b-ut	36.5
	C-vb-ut	35.4

8.3 Dynamical Mechanical Behavior

8.3.1 Effect of calcite inclusion

Dynamic mechanical analysis is often used to study relaxations in polymers. The analysis of elastic modulus, viscous modulus and $\tan \delta$ curves is useful in ascertaining the performance of the material under stress and temperature.

The temperature dependence of elastic modulus for neat PP-R and C-s-t-coded calcite filled PP-R composites is shown in Figure 8.15. Elastic modulus of C-s-t-coded calcite filled PP-R composites increases with increasing calcite content. As it is reported by Gutie'rrez et al, the elastic modulus always increases with increasing filler content, because the calcite is a stiffer material than the polypropylene (Gutie'rrez et al, 1999). Besides, the presence of calcite produces a more rigid interface in the PP-R matrix.

Damping, $\tan \delta$, is an important parameter characterizing viscoelasticity of polymeric materials. It can be seen in Figure 8.16 that $\tan \delta$ increases with increasing temperature. It indicates that the decrease of the stored elastic energy of the composite is greater than the viscous dissipation energy of the composite with increasing temperature.

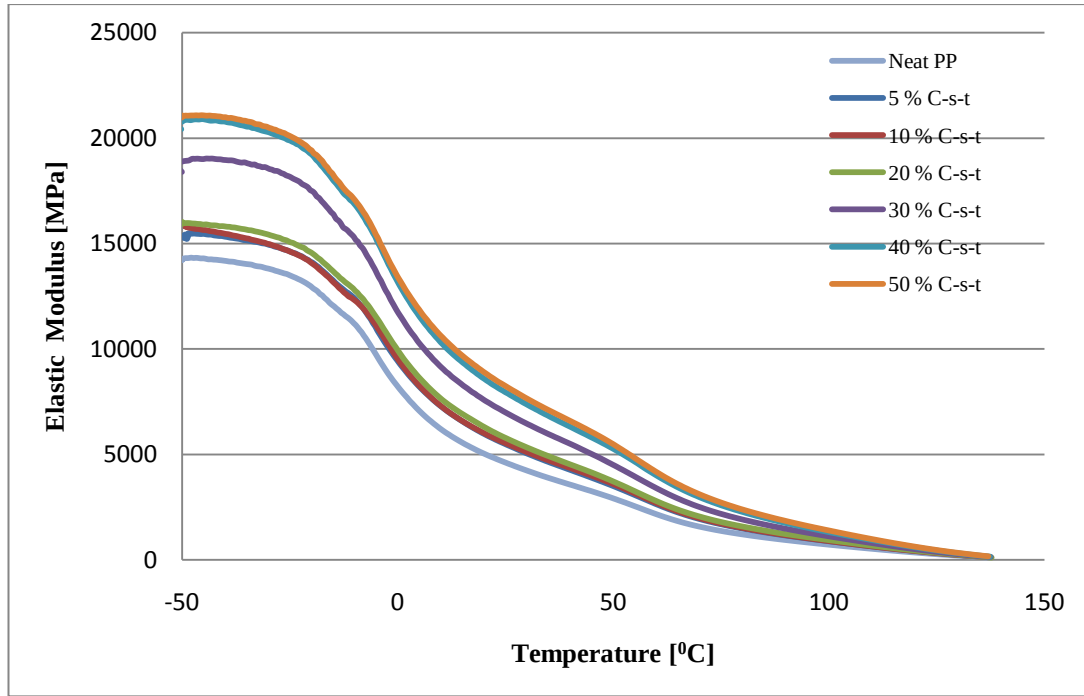


Figure 8.15 : Elastic modulus versus temperature graph of C-s-t-coded calcite filled PP-R composite

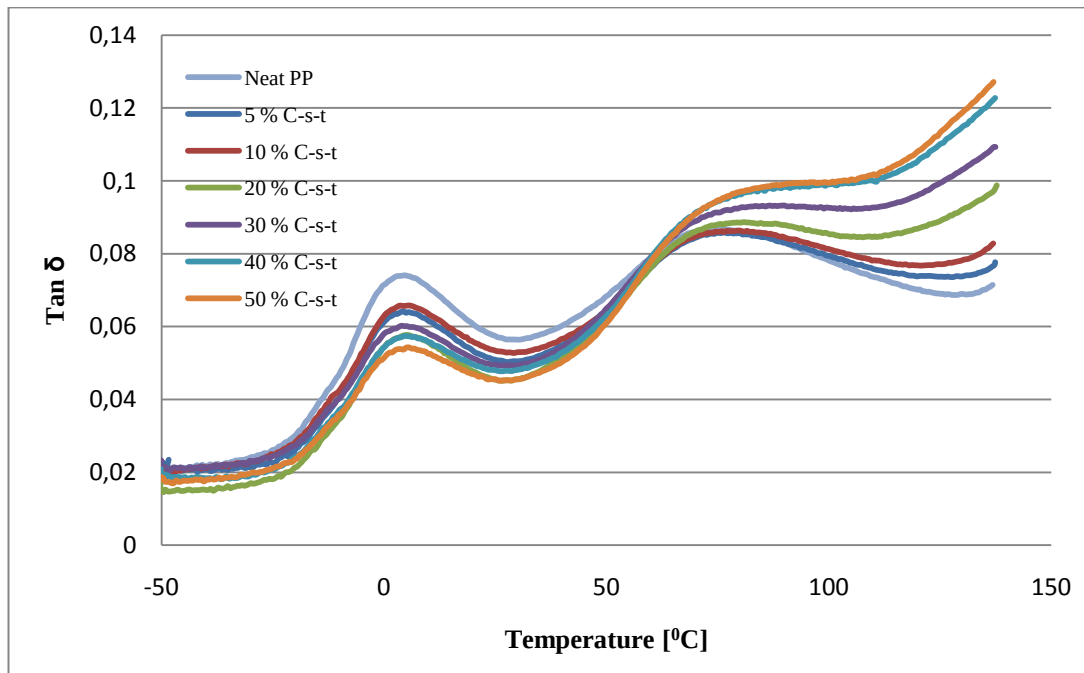


Figure 8.16 : Damping factor versus Temperature graph of C-s-t-coded calcite filled PP-R composites

In the analyzed temperature range, between -50-150 °C, the $\tan \delta$ curve of the neat PP-R and filled PP-R composites are characterized with two relaxations located in the vicinity of 10 °C (β - transition) and 80 °C (α -transition). The α -transition is related to the relaxation of restricted PP-R amorphous chains in the crystalline phase.

The first transition is related to unrestricted amorphous PP-R chains and the temperature of the β -maximum is taken as the glass transition temperature, T_g .

The intensity of the β -transition is bigger for the PP-R than that of the PP-R-calcite composites. Gutie'rrrez et al justify this behavior in two relevant reasons (Gutie'rrrez et al, 1999). Firstly, the glass transition occurs in the amorphous phase of the PP-R, so the greater the amount of polypropylene in the samples, the higher the intensity of the glass transition observed. Secondly, the addition of a rigid phase cuts down the mobility of the polymer chains, which results in a lower value of the transition intensity.

The glass transition temperature of the composites are higher than that of the neat PP-R. The addition of a calcite cuts down the mobility of the polymer chains, which results in a high in T_g value. In literature, Cousin et al found the similar result by adding alumina into sulfonated polystyrene (Cousin and Smith, 1994).

8.3.2 Effect of particle size

Elastic modulus of various particle sized untreated calcite filled PP-R composites are shown in Figure 8.17. Effect of particle size on elastic modulus is dominant at low temperatures. Wypych reported that smaller particles with higher surface area available for stronger interaction which restrict molecular mobility (Wypych, 2000). So, smaller particle sized calcite filled PP-R composite has bigger elastic modulus. But experimental results of this study are not convenient with report of Wypych.

Damping factor, $\tan \delta$, of untreated calcite filled PP-R composites is shown in Figure 8.18. Small particle sized calcite cuts down the mobility of the polymer chains more than that of big particle sized calcite. That's why T_g of the smaller particle sized calcite filled PP-R is higher than larger particle sized calcite filled PP-R due to restricting the macromolecules in amorphous phase by more interparticular interactions. Wypych proved this situation by studying on styrene-methacrylic acid copolymer filled with various particle sized glass beads (Wypych, 2000). The similar trend can not be determined for the samples prepared in this study (Figure 8.18). This may be because of not occurring interparticle bonding in PP-R.

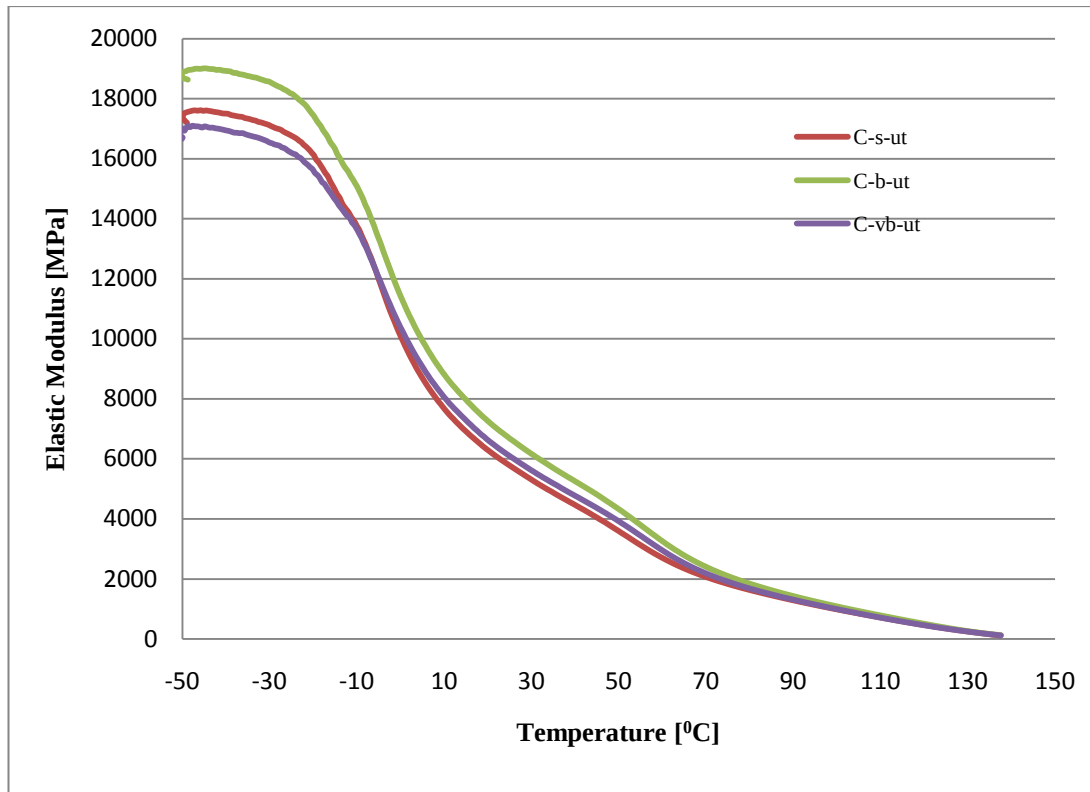


Figure 8.17 : Elastic modulus versus temperature graph of 20 % calcite filled PP-R composites

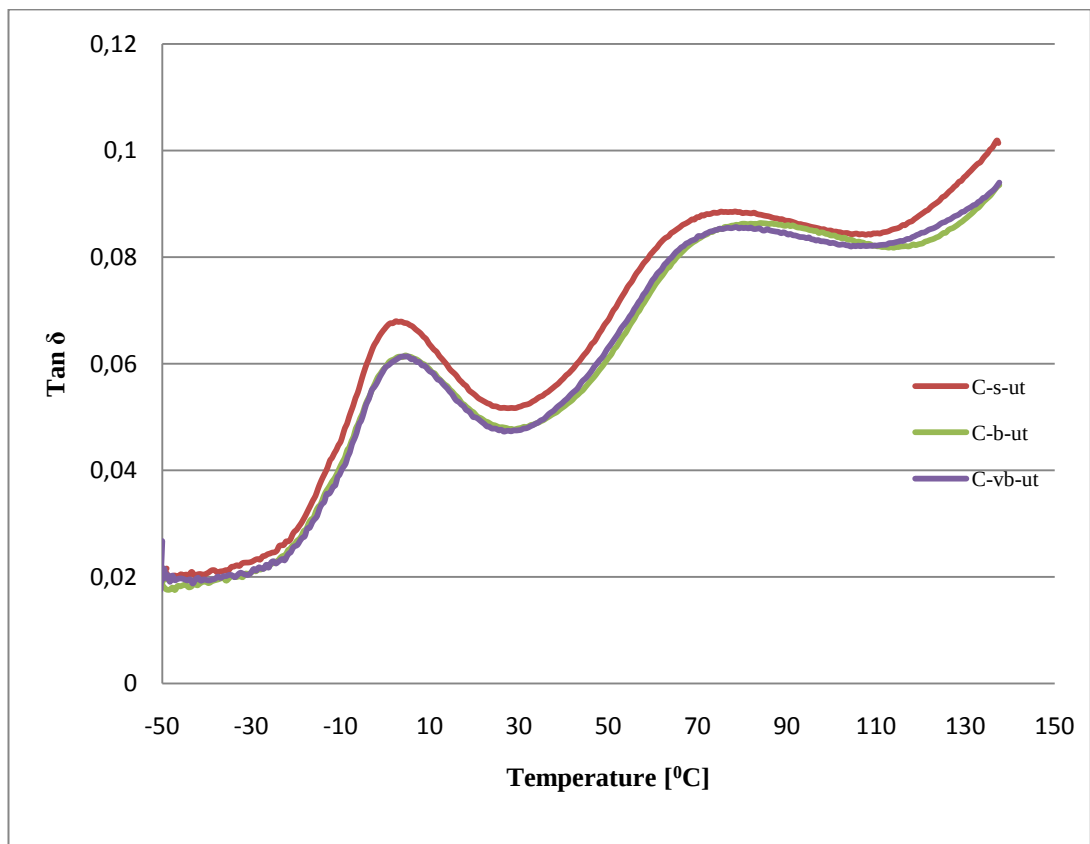


Figure 8.18 : Tan δ versus temperature graph of 20 % calcite filled PP-R composites

8.3.3 Effect of surface treatment

Comparison of elastic modulus of treated calcite, which is coded as C-s-t and untreated calcite, which is coded as C-s-ut filled PP-R composites are illustrated in Figure 8.19. It is obviously seen that elastic modulus of treated calcite, which is coded as C-s-t filled PP-R composite is lower than that of untreated calcite which is coded as C-s-ut filled PP-R composite at low temperatures, because surface modification reduces the particle-particle interaction.

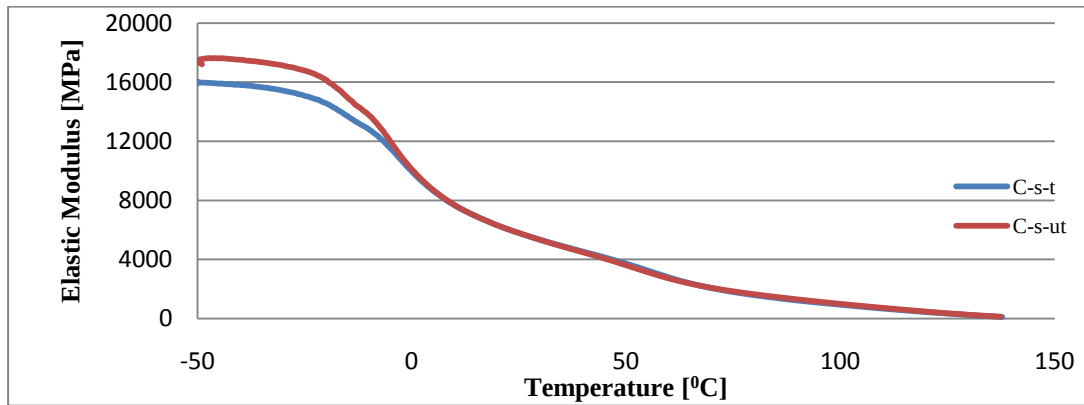


Figure 8.19 : Elastic modulus versus temperature graph of 20 % treated and untreated calcite filled PP-R composites

Comparison of $\tan \delta$ of treated calcite, which is coded as C-s-t and untreated calcite, which is coded as C-s-ut filled PP-R composites are illustrated in Figure 8.20. It is obviously seen that T_g of the untreated calcite, which is coded as C-s-ut filled PP-R composites is lower than that of treated calcite, which is coded as C-s-t filled PP-R composites. This is not expected result. Generally, surface treated particle does not cut down the mobility of the polymer chain as untreated does.

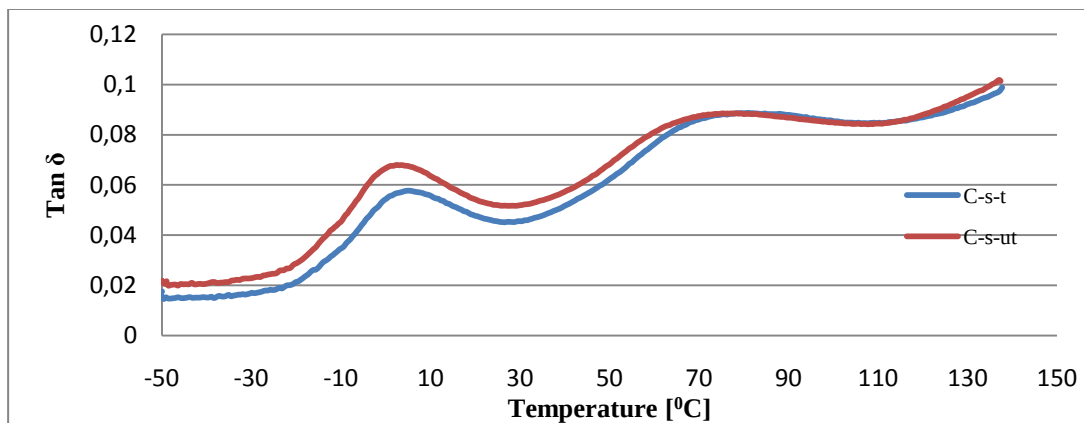


Figure 8.20 : $\tan \delta$ versus temperature graph 20 % treated and untreated calcite filled PP-R composites

8.4 Viscoelasticity

In Figure 8.21, the complex viscosity of c-s-t-coded calcite filled PP-R composites is shown as a function of angular frequency. While increasing calcite content, complex viscosity of filled PP-R increases. Similar behavior is also determined for the composites prepared with untreated calcites (App. E). Consistent results exist in literature (Kwang et al, 2004).

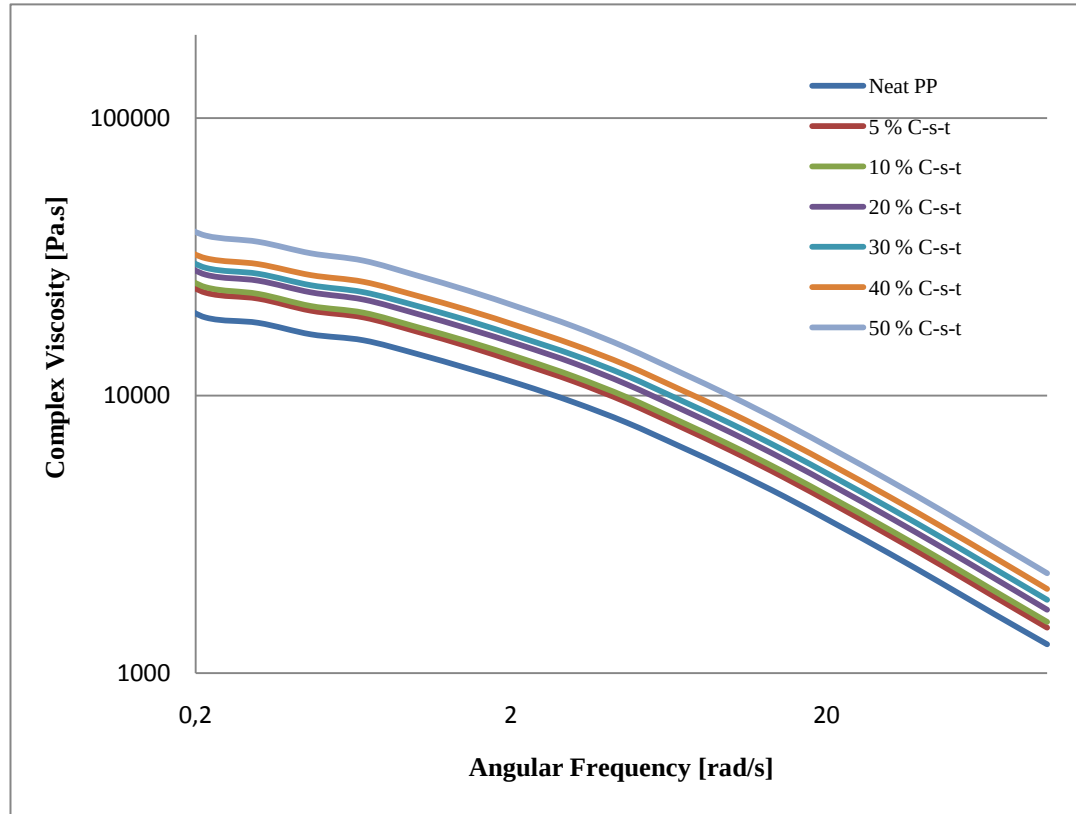


Figure 8.21 : Complex viscosity of C-s-t-coded calcite filled PP-R

In Figure 8.22, the values of G' (storage modulus) of the different type of calcite filled PP-R composites are given as a function of calcite content at two different frequencies, 1.47 rad/s (for small frequency) and 100 rad/s (for high frequency). Supaphol et al are reported that when increasing the calcite content, the increase in G' should be more pronounced at low frequencies than the increase in G' at high frequencies (Supaphol and Harnsiri, 2006). Because high frequency can damage the interparticular interaction. Interparticular interactions becomes less dominant at higher frequencies. It can be seen from Figure 8.22 that the increase in G' with calcite inclusion is much less pronounced at low frequencies than at high

frequencies. The absence of the interparticular interactions could be a reason for such observation. Storage modulus of untreated calcite, which is coded as C-s-ut filled PP-R composites increases sharply after exceeding the calcite content 40 wt % at both frequencies. But the increase in G' with calcite inclusion after 40 wt % is again much less pronounced at low frequencies than at high frequencies. This increase is probably because of agglomeration of calcite particles.

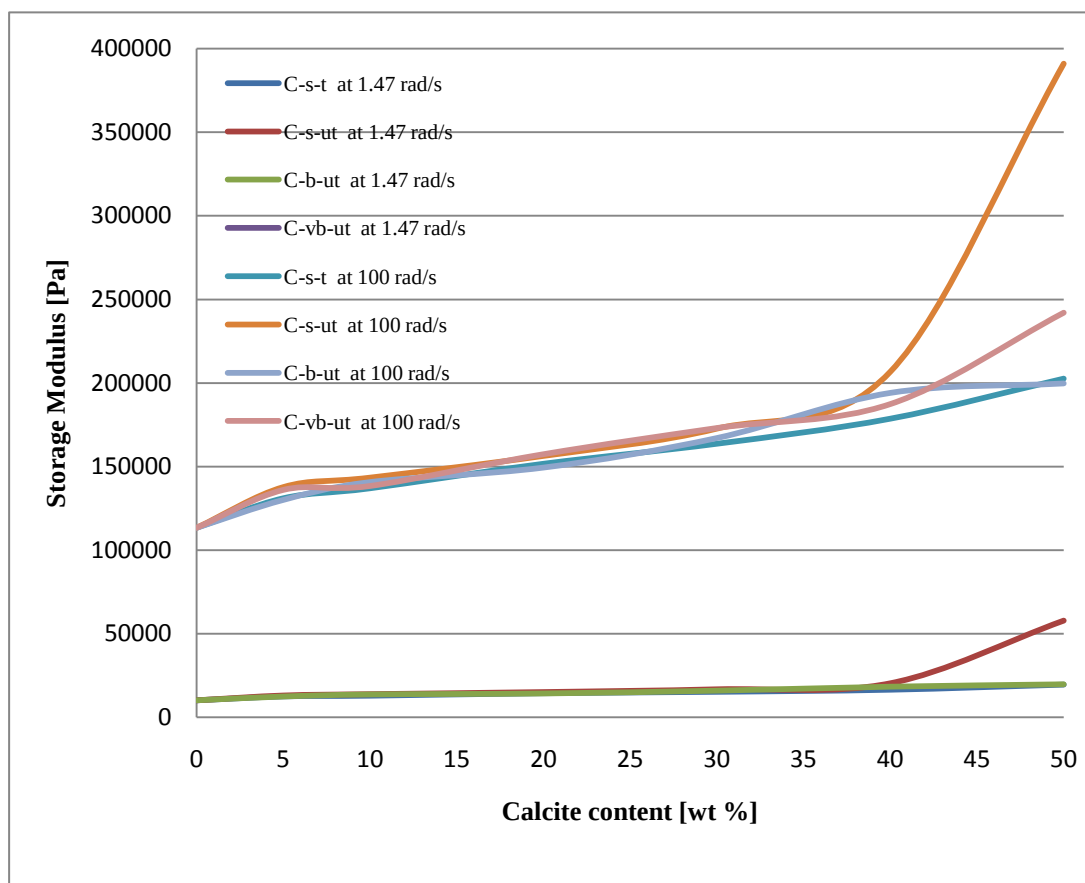


Figure 8.22 : Storage modulus of neat PP-R and calcite/PP-R compounds as a function of calcite content at 1.47 rad/s and 100 rad/s

Storage modulus represents the elastic response of a material which relates to the potential energy stored by the material during deformation. The value of the storage modulus represents the stiffness of the material. On the contrary, loss modulus represents the viscous response of the material. The value of the loss modulus signifies the dissipation of energy in the form of heat during deformation. According to Figure 8.23 both the storage and the loss modulus of the composites increase with increasing calcite content. Osman et al. found the same results for composites based on high density polyethylene (Osman and Atallah, 2005).

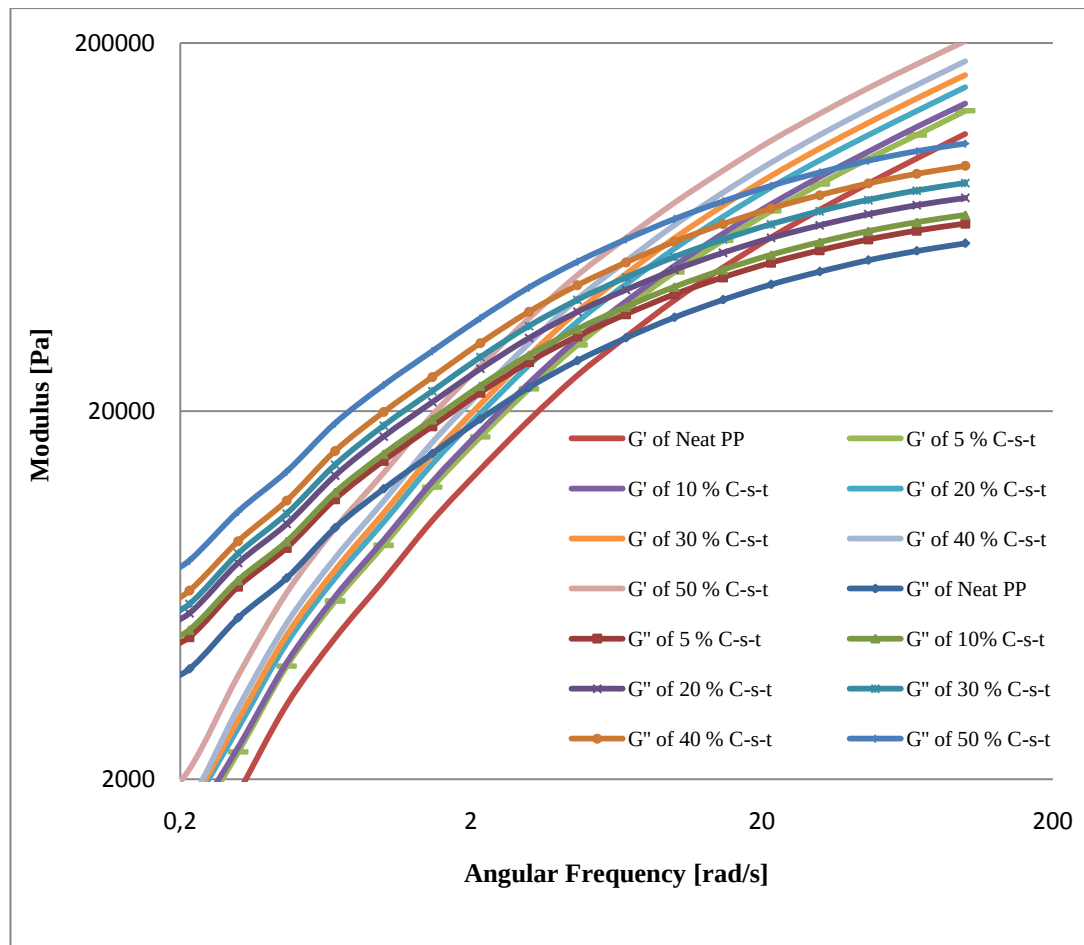


Figure 8.23 : Storage and Loss modulus of various content of C-s-t-coded calcite filled PP-R

As it is seen from Figure 8.23, both modulus of the composites also increase with increasing angular frequency. In low frequency region loss modulus is larger than storage modulus, demonstrating the viscous nature of samples. However, the storage modulus increases more than the loss modulus, so that with increasing angular frequency two modulus cross each other. The frequency at which the modulus cross each other called as crossover frequency. This characteristic frequency marks as viscous to rubbery response. Crossover frequency is approximately equal to the inverse of the fluid's characteristic relaxation time, roughly the longest relaxation time. In Table 8.5 crossover frequencies of PP-R and calcite filled PP-R composites are listed. Normally, increasing calcite content causes crossover frequencies shifted to lower values as it is described before by Osman et al (Osman and Atallah, 2005). But experimental results which are shown in Table 8.5 are not consistent with literature.

Table 8.5 : Crossover frequencies of varying amount and type of calcite filled PP-R composites

Calcite Content [wt %]	Crossover Frequencies [rad/s]			
	C-s-t	C-s-ut	C-b-ut	C-vb-ut
0	6.63	6.63	6.63	6.63
5	5.76	5.99	5.78	5.69
10	5.97	5.76	5.63	5.64
20	5.95	5.76	5.85	5.96
30	6.26	5.91	5.97	6.05
40	6.58	6.17	6.47	6.44
50	6.57	3.05	6.52	6.69

In Figure 8.24 linear viscoelastic region of treated calcite, which is coded as C-s-t filled PP-R composites is given as a function of calcite content. It is interesting to note that the linear viscoelastic (LVE) region narrows as the filler loading increases. As it is explained by Wang et al; for lower calcite content, the polymer entanglements predominate inside the polymer melt, which would sustain large shear strain deformation, and hence the linear region becomes wider (Wang and Yu, 2000). For high calcite content, filler networks can form as a result of filler-filler interaction. But interparticle bonding forces are not strong enough to keep the structure intact beyond critical strains such that linear region becomes narrower. The values of LVE regions are given in Table 8.6 for all composites.

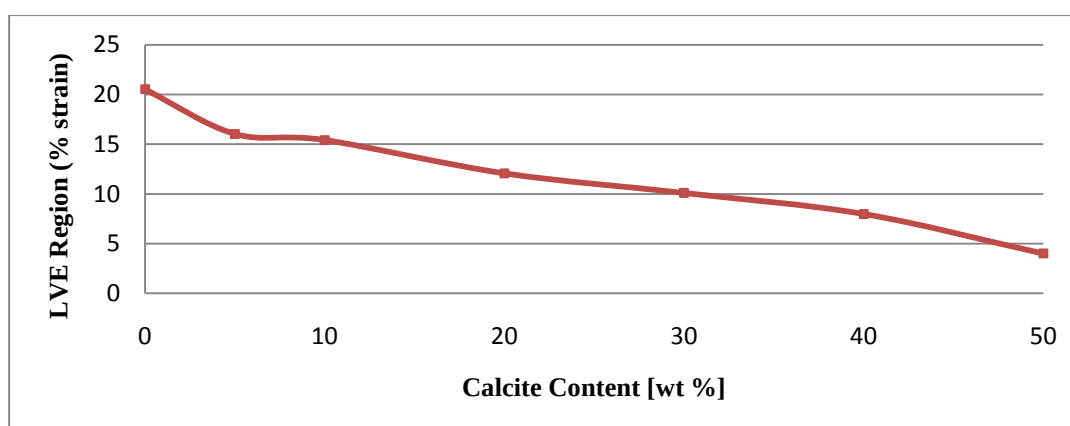


Figure 8.24 : LVE regions of C-s-t-coded calcite filled PP-R

As it is seen from Table 8.6, effects of particle size and surface treatment on LVE region are not clear. Despite of expecting that surface treatment causes the LVE region narrower due to reducing the interparticular interactions. The surface area of calcite increases with decreasing its particle size. Increasing surface area causes to

form more interparticle bonds in PP-R matrix. These bonds can sustain large shear strain deformation, and hence the linear region becomes wider if the calcite used in PP matrix is smaller. Experimental results are not compatible with each others.

Table 8.6 : LVE regions of varying amount and type of calcite filled PP-R composites

Calcite Content [wt%]	LVE Regions [strain %]			
	C-s-t	C-s-ut	C-b-ut	C-vb-ut
0	20.5	20.5	20.5	20.5
5	16.0	18.9	15.4	14.7
10	15.4	15.4	15.6	14.6
20	12.1	12.1	11.9	11.8
30	10.1	9.8	10.2	10.4
40	8.0	8.0	8.5	8.3
50	4.0	2.6	4.4	4.5

9. CONCLUSION

In this thesis, the optimization of preparation method for calcite/PP-R composites is achieved by using TKM and/or TSE. The mixing conditions are chosen to minimize polymer degradation and achieve optimal homogenization of the filler. For this purpose, six different mixing methods are applied. It is determined that sixth preparation method is the best way to compound calcite and PP-R. According to this method granules of composites which are prepared in TSE, are directly compressed twice in press machine to obtain plaque.

Filler content of the composites affect its rheological properties and viscoelastic behavior of the composites. It is determined that while the calcite content increases, viscosity of the composite increases. By increasing calcite content, shear thinning behavior also increases.

Particle size affects shear viscosity for only composites prepared with 50 % calcite addition. However, in more concentrated systems, it is obviously examined that the smaller particle sized calcite filled PP-R composite has the highest zero shear viscosity. This increase is due to the stronger interactions between filler particles. According to the results of oscillation test, the increase in G' with calcite inclusion is much less pronounced at low frequencies than at high frequencies. It is realized that the absence of the interparticular interactions could be a reason for such behavior. Agglomeration of smaller particle sized calcite particles probably causes increase in viscosity. The obtained results indicate that the higher modulus and viscosity of the composites are not direct consequence of the particle size. Agglomeration of calcite particles may cause viscosity and modulus increase.

Surface treatment on calcite particles decreases the viscosity of the composites resulting of reducing interparticular interactions and agglomeration.

The effect of temperature on viscosity is investigated by using Arrhenius-Eyring equation for neat PP-R and the composites filled by 20 wt % calcite. Adding calcite causes to increase in activation energy due to being restricted PP-R molecules movement by calcite. Moreover, surface treated calcite, which is coded as C-s-t filled

PP-R has a bigger activation energy than untreated calcite, which is coded as C-s-ut filled PP-R composite, because surface treatment causes stronger interaction between particle and polymer matrix. Thus, movement of treated calcite filled PP-R molecules need more energy barrier to flow. Effect of particle size on activation energy is not determined.

The presence of calcite in PP-R matrix produces a more rigid interface in the PP-R matrix. Thus, elastic modulus of composites increase by calcite inclusion.

Restricting the macromolecules in amorphous phase of PP-R matrix by adding the calcite causes to increase the T_g of composite and to decrease the intensity of the glass transition pick. Effect of particle size and surface treatment on dynamic mechanical behavior results are found unexpectedly. T_g of the untreated calcite filled PP-R composites is lower than that of treated calcite filled PP-R composite. Smaller particle sized calcite filled PP-R composite has the lower elastic modulus.

The storage and loss modulus of calcite filled PP-R composites are both found to increase with increasing calcite content and frequency. The increase in storage modulus is greater than loss modulus. The storage and loss modulus cross each other at a crossover frequency. Behavior of the composites changes from liquid-like to solid-like response at crossover frequency. It is not understood why crossover frequency is not shifted lower values by increasing calcite content. It is probably the reason of not occurring particle network.

The linear viscoelastic region becomes narrower while increasing the content of the calcite in PP-R, since the interparticle bonding forces are not strong enough to keep the structure intact beyond critical strains.

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APPENDICES

APPENDIX A : Shear viscosity of neat PP-R and various particle sized calcite filled PP-R samples of various filler content as a function of shear rate

APPENDIX B : Flow curves of various content of different particles sized calcite filled PP-R composites at 230 °C

APPENDIX C : Shear viscosities of 10-40 wt % calcite filled PP-R samples as a function of shear rate

APPENDIX D : Effect of temperature on viscosities of various calcite filled PP-R composites

APPENDIX E : Complex viscosities of various particle sized untreated calcite filled PP-R composites

APPENDIX F : Particle size of commercial calcite grades

APPENDIX A

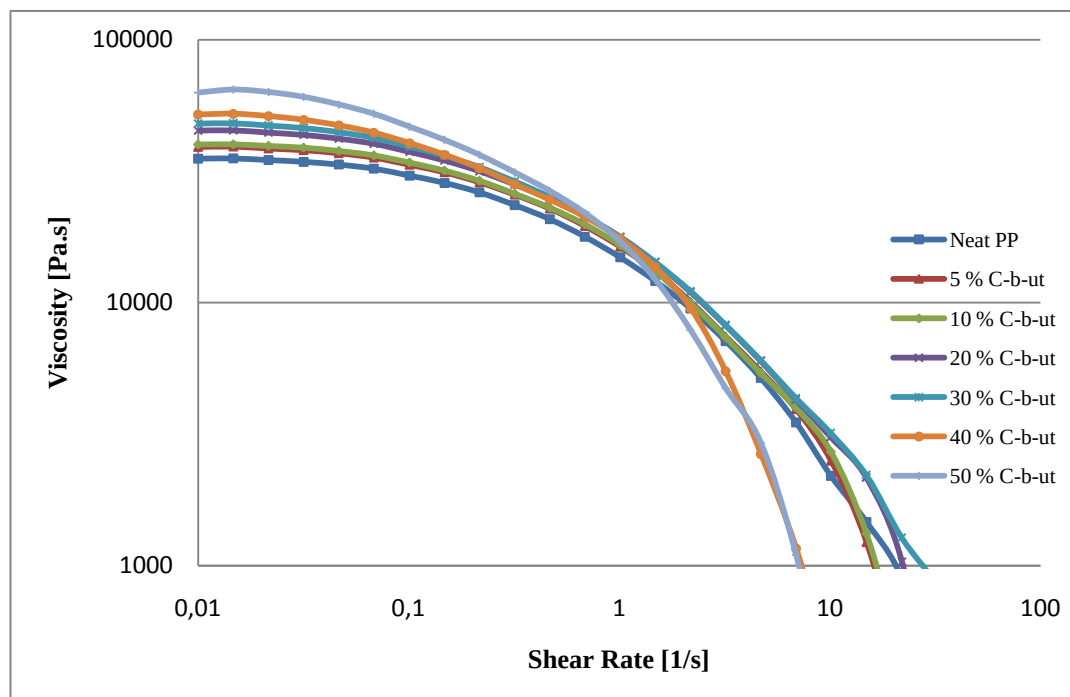


Figure A.1 : Shear viscosity of neat PP-R and C-b-ut-coded calcite filled PP-R samples of various filler contents as a function of shear rate

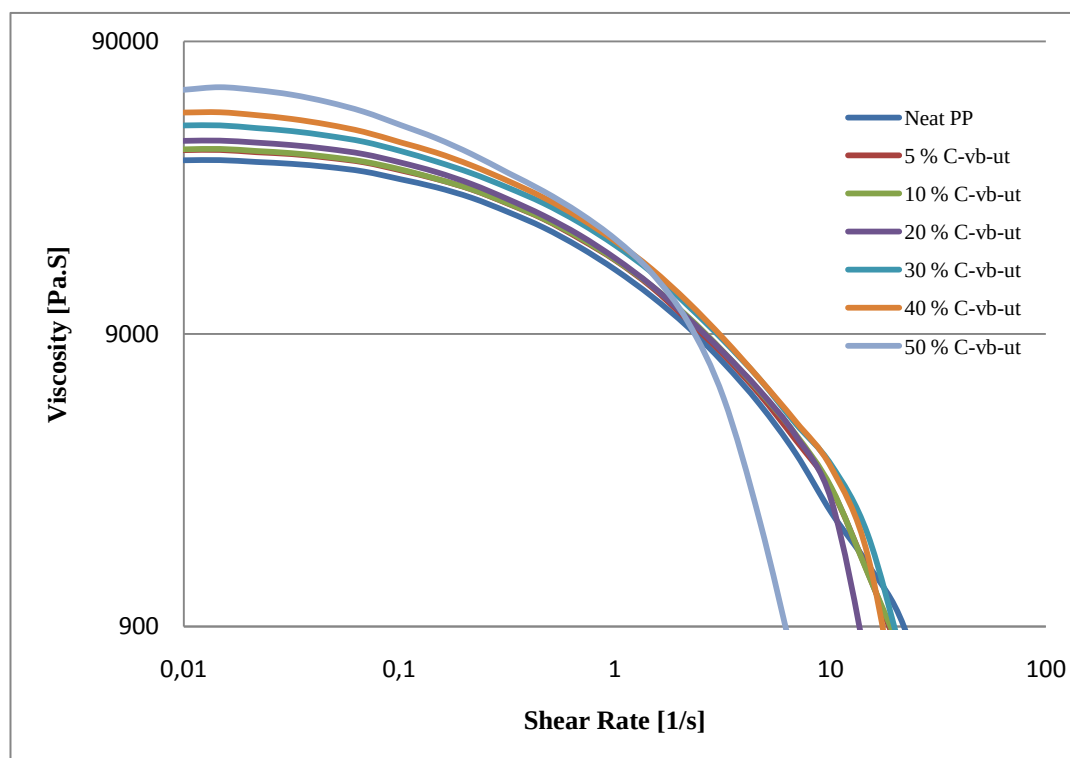


Figure A.2 : Shear viscosity of neat PP-R and C-vb-ut-coded calcite filled PP-R samples of various filler contents as a function of shear rate

APPENDIX B

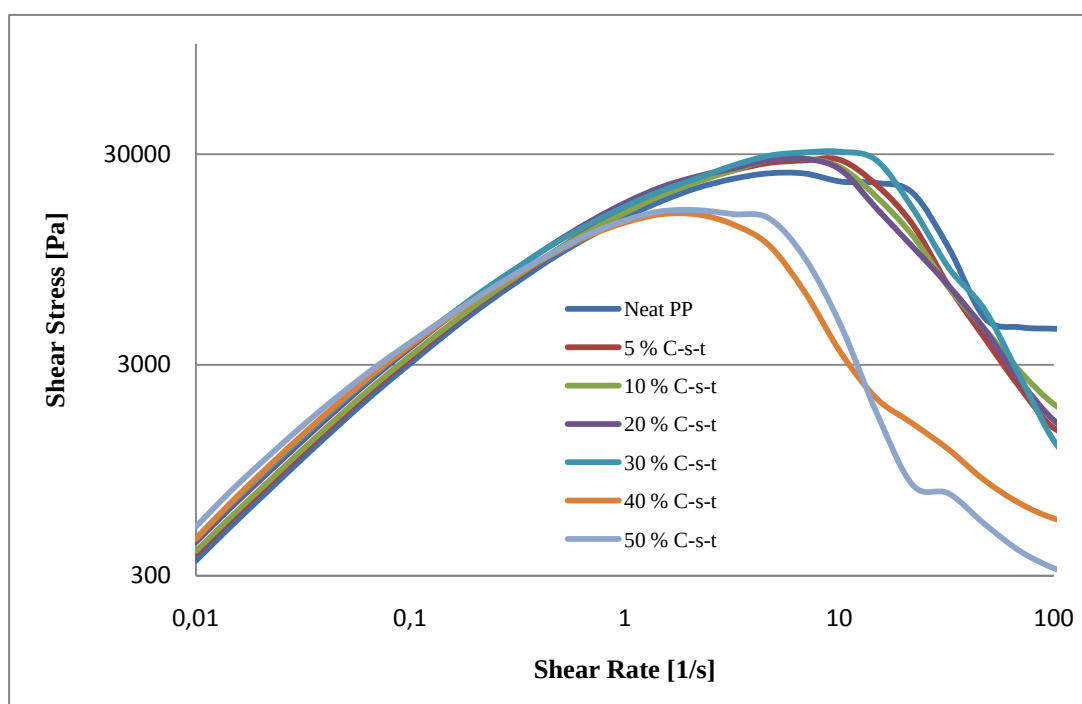


Figure B.1 : Flow curves of various content of C-s-t-coded calcite filled PP-R at 230 °C

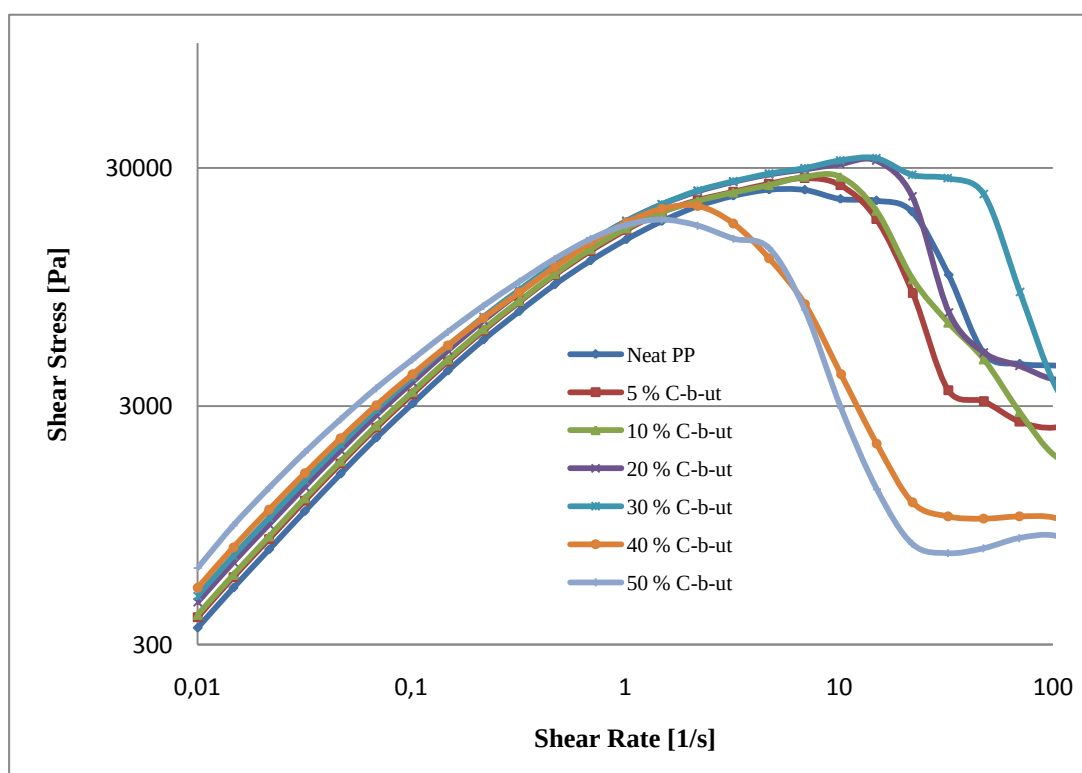


Figure B.2 : Flow curves of various content of C-b-ut-coded calcite filled PP-R at 230 °C

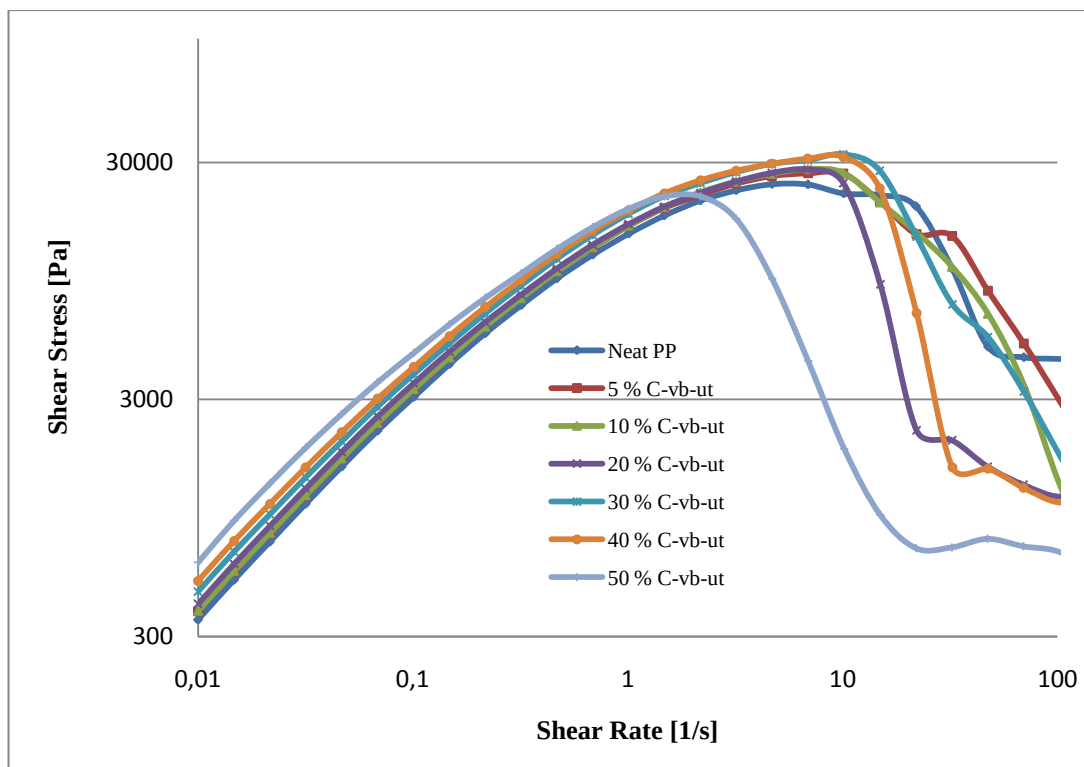


Figure B.3 : Flow curves of various content of C-vb-ut-coded calcite filled PP-R at 230 °C

APPENDIX C

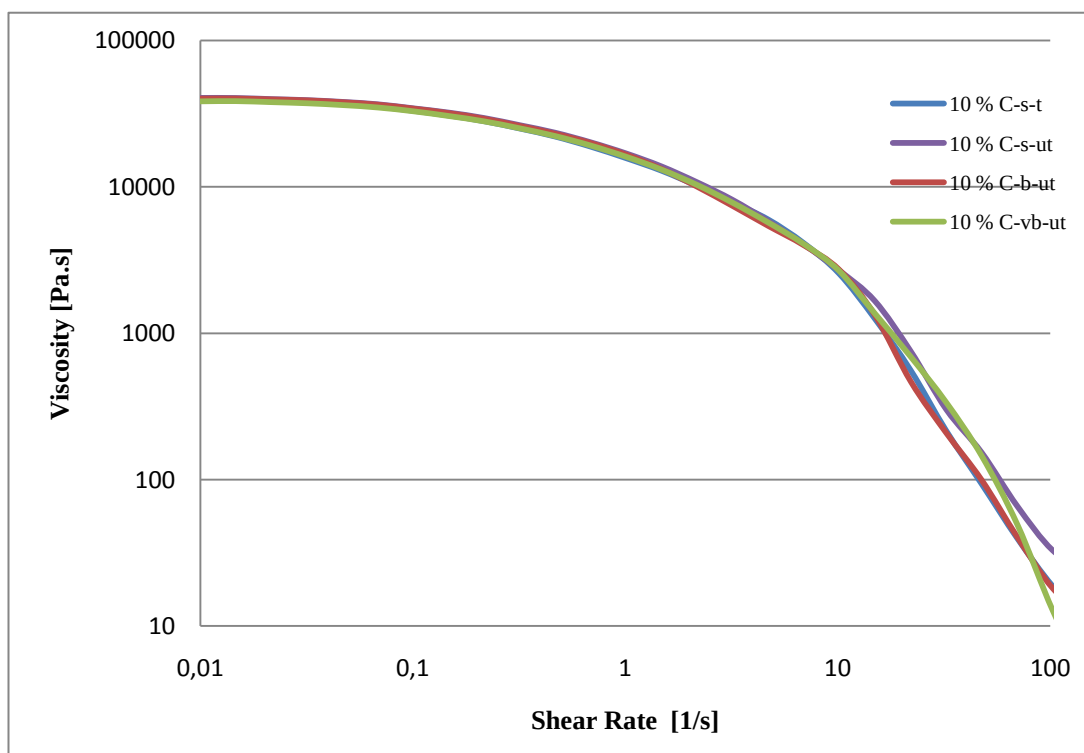


Figure C.1 : Shear viscosity of 10 wt % calcite filled PP-R samples as a function of shear rate

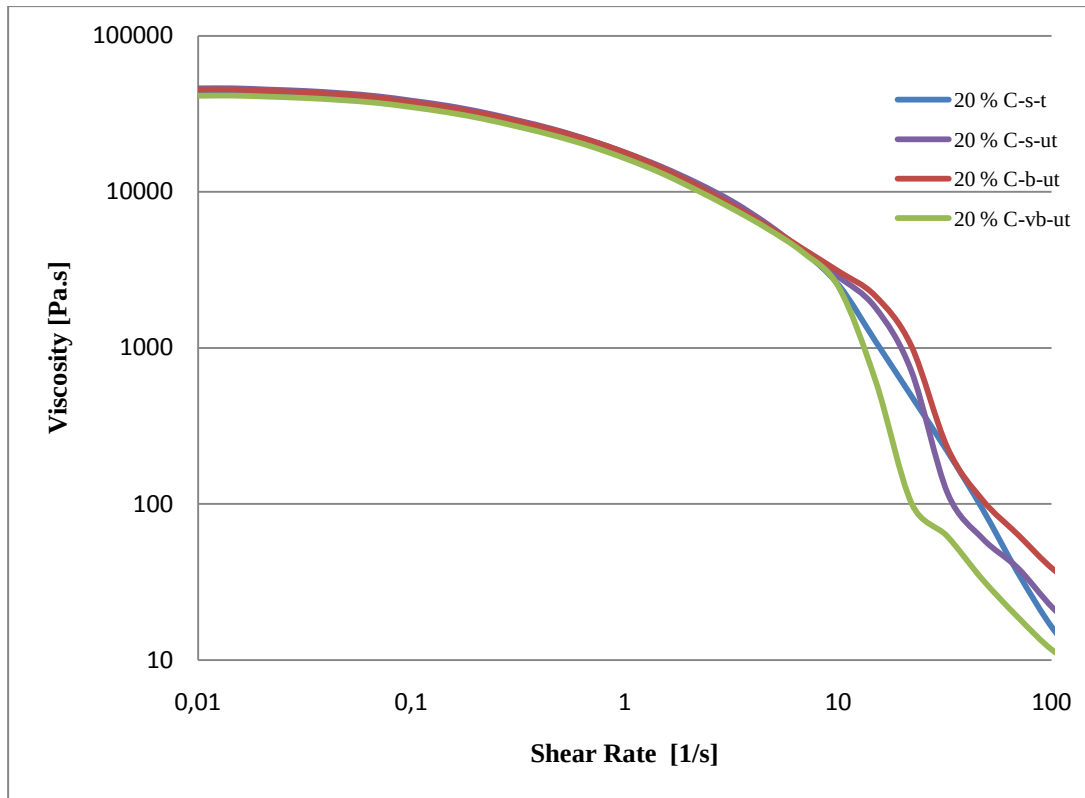


Figure C.2 : Shear viscosity of 20 wt % calcite filled PP-R samples as a function of shear rate

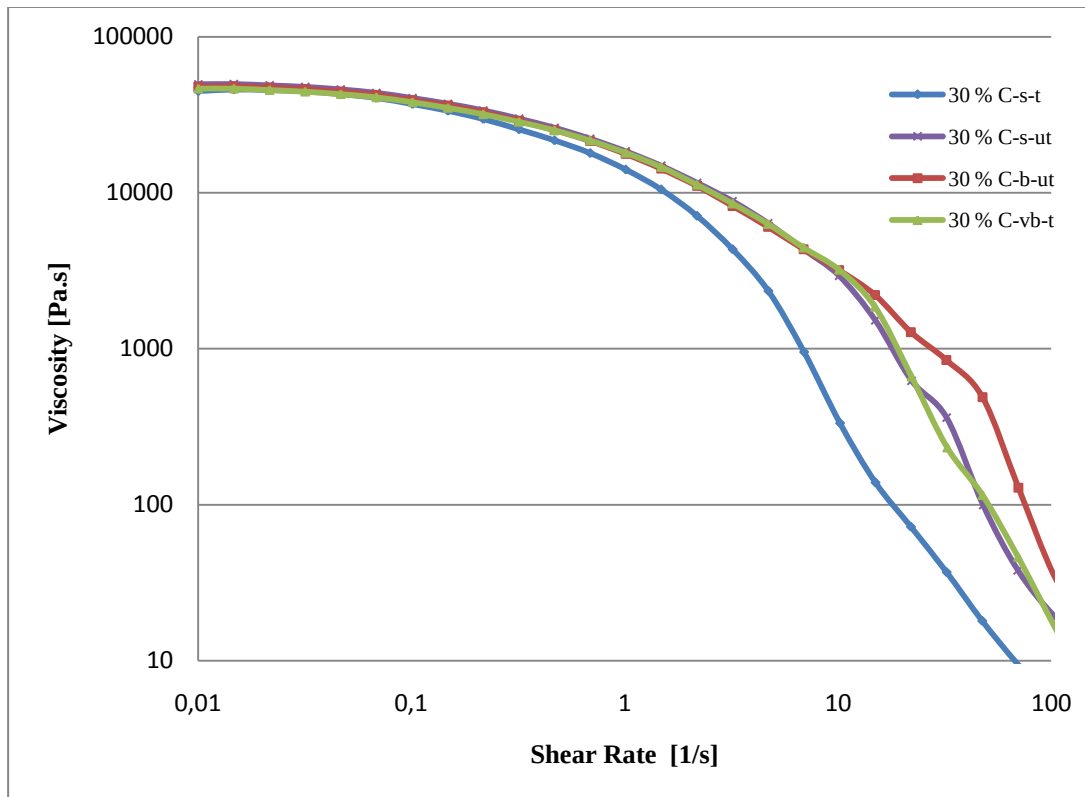


Figure C.3 : Shear viscosity of 30 wt % calcite filled PP-R samples as a function of shear rate

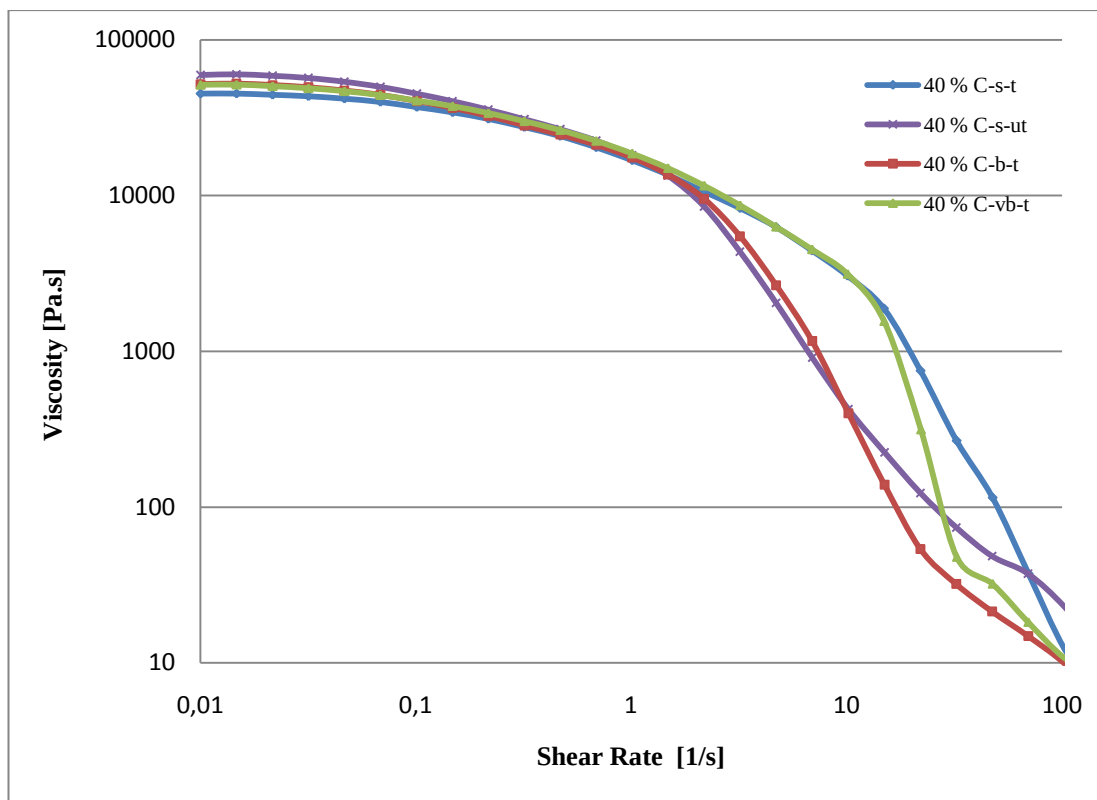


Figure C.4 : Shear viscosity of 40 wt % calcite filled PP-R samples as a function of shear rate

APPENDIX D

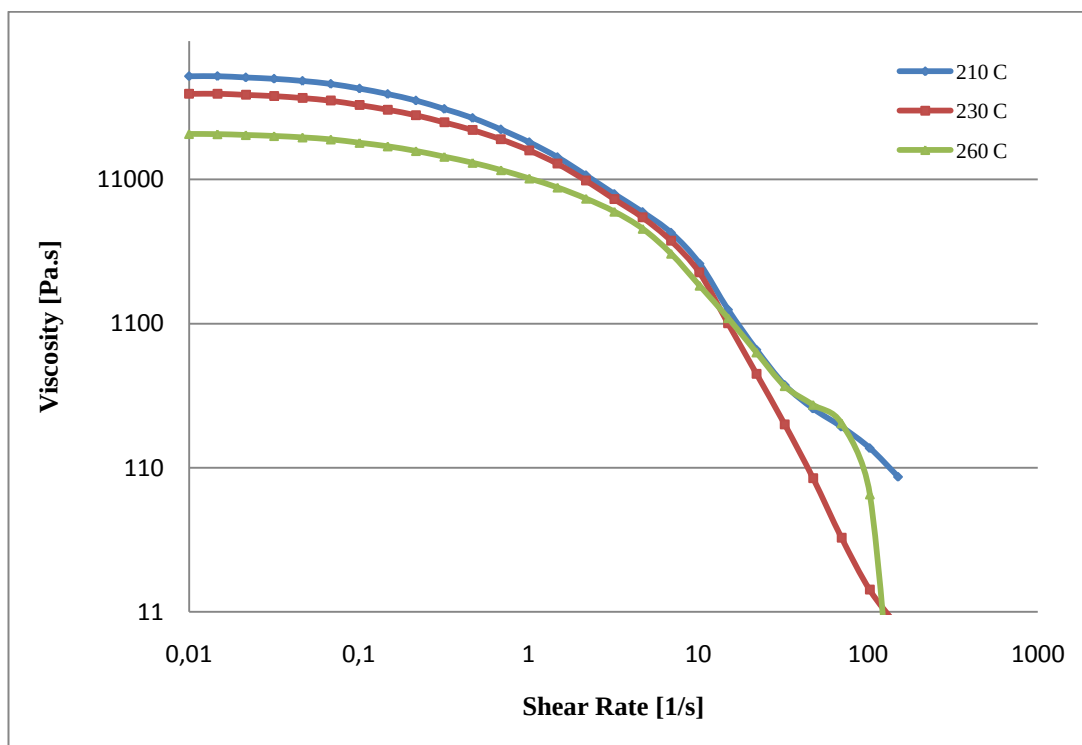


Figure D.1 : Viscosity curves of 20 wt % C-s-t-coded calcite filled PP-R composites at different temperatures

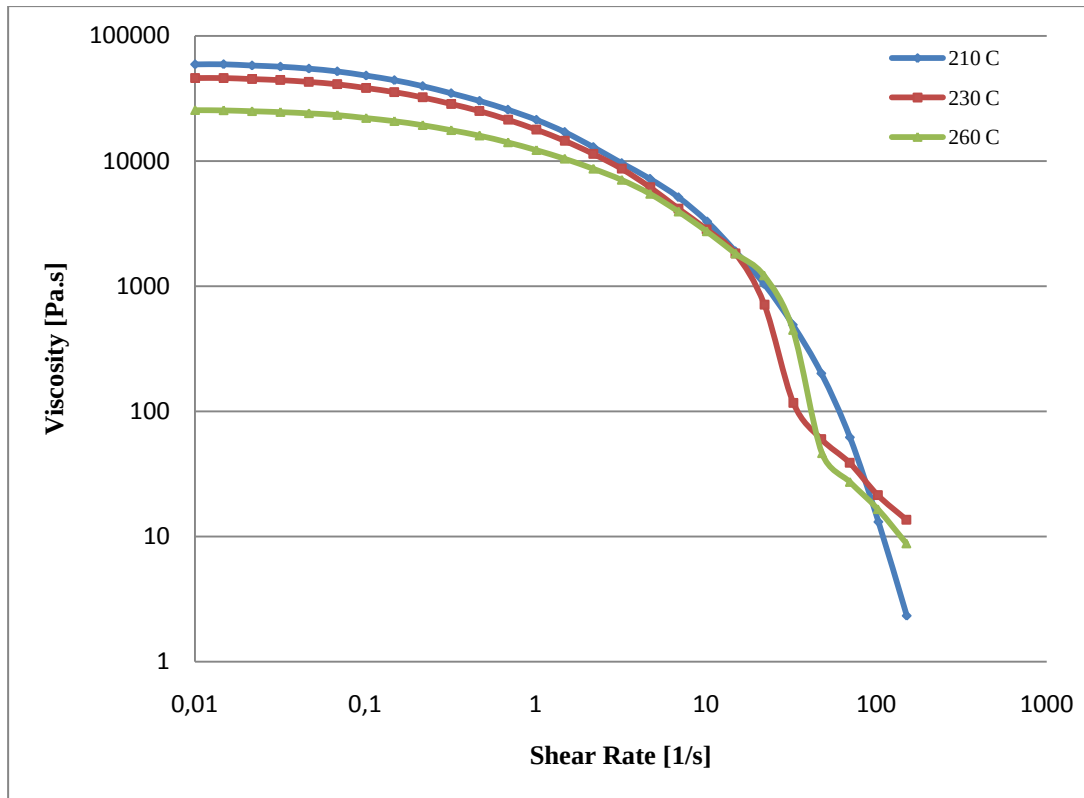


Figure D.2 : Viscosity curves of 20 wt % C-s-ut-coded calcite filled PP-R composites at different temperatures

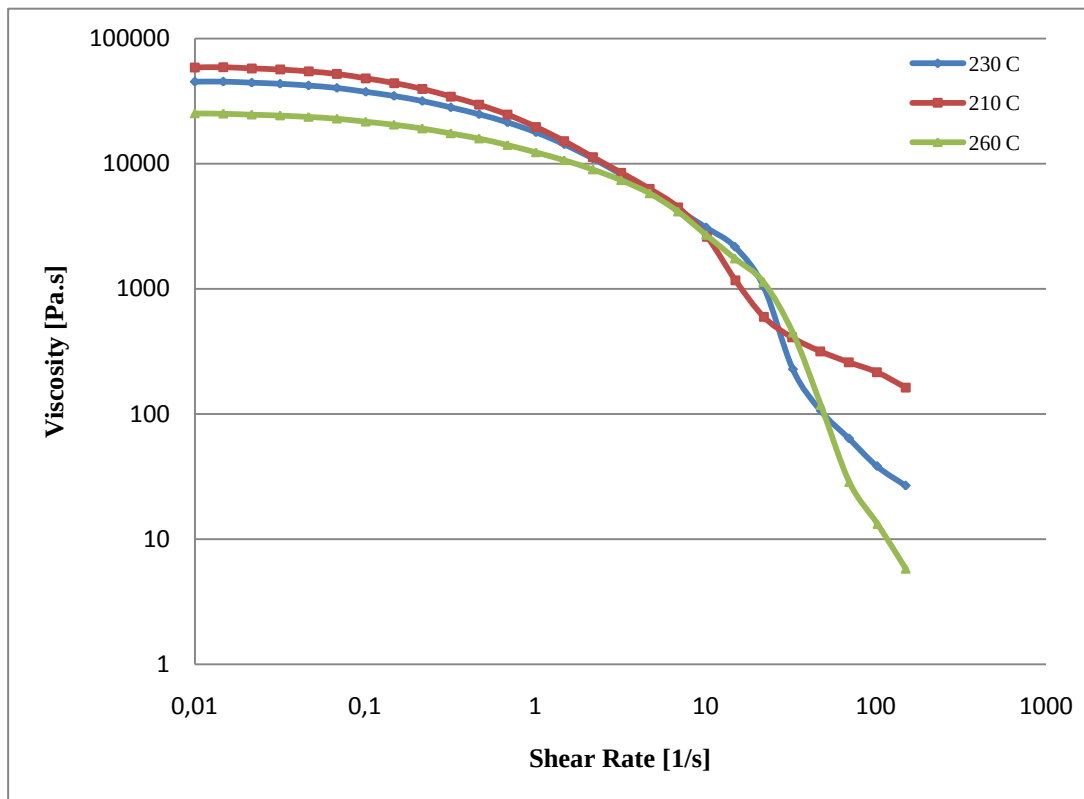


Figure D.3 : Viscosity curves of 20 wt % C-b-ut-coded calcite filled PP-R composites at different temperatures

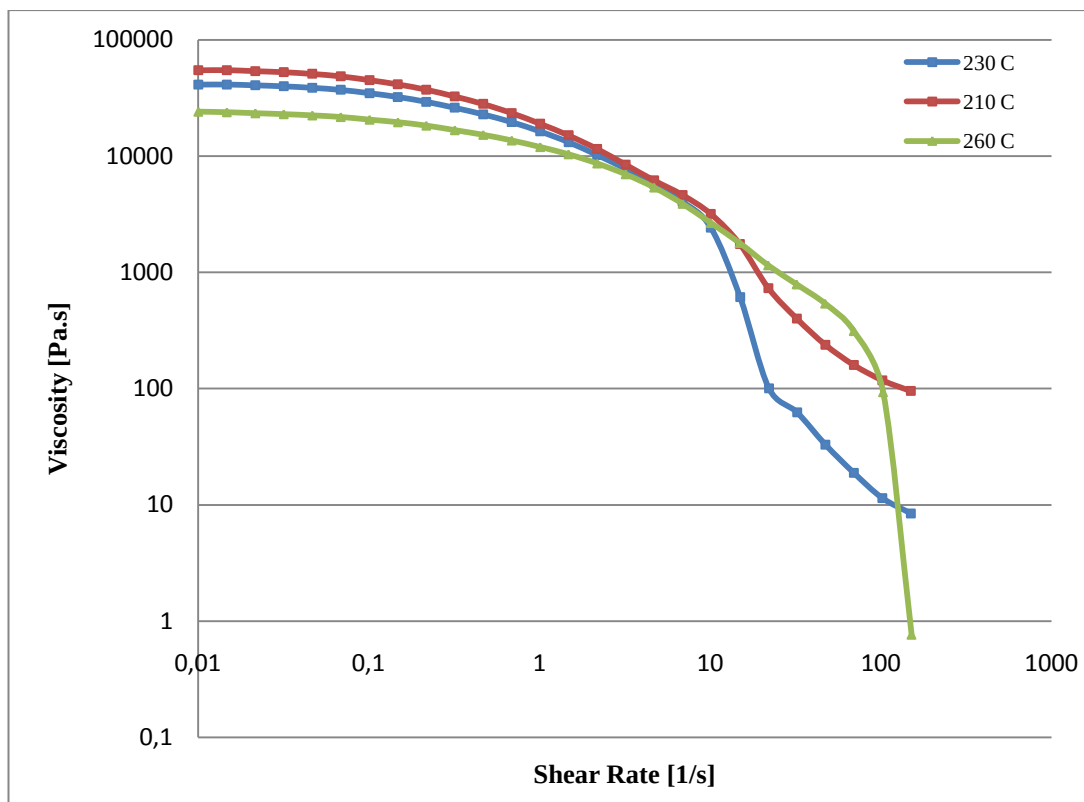


Figure D.4 : Viscosity curves of 20 wt % C-vb-ut-coded calcite filled PP-R composites at different temperatures

APPENDIX E

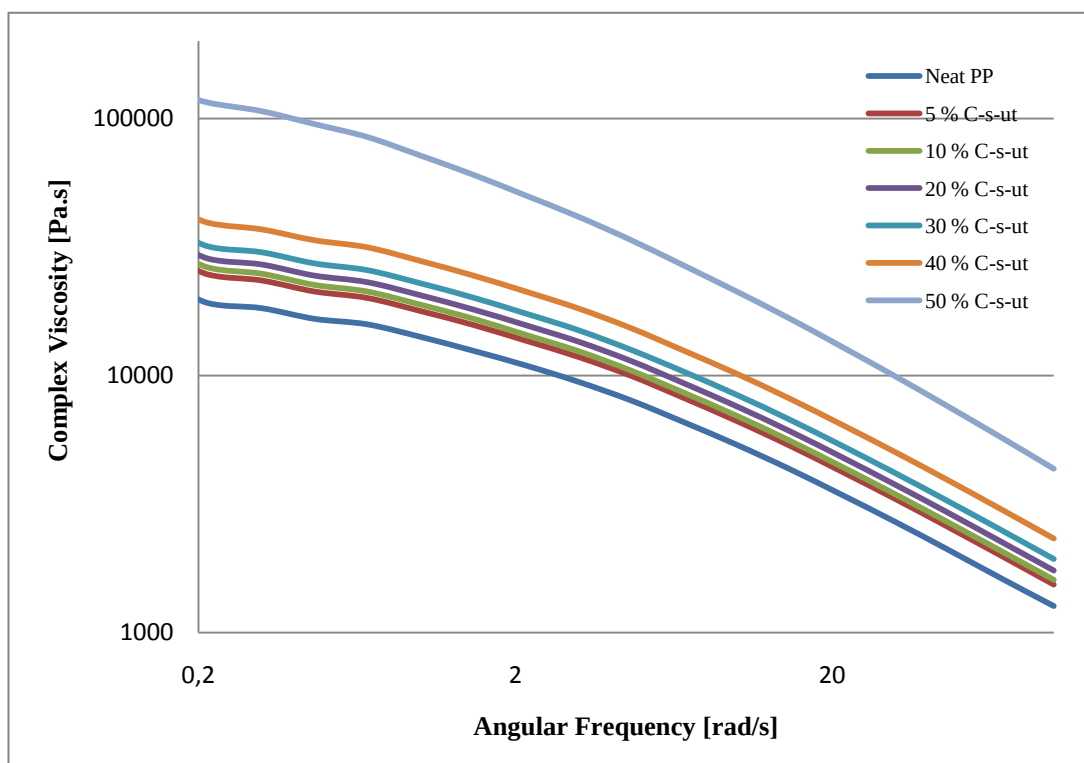


Figure E.1 : Complex viscosity of C-s-ut-coded calcite filled PP-R

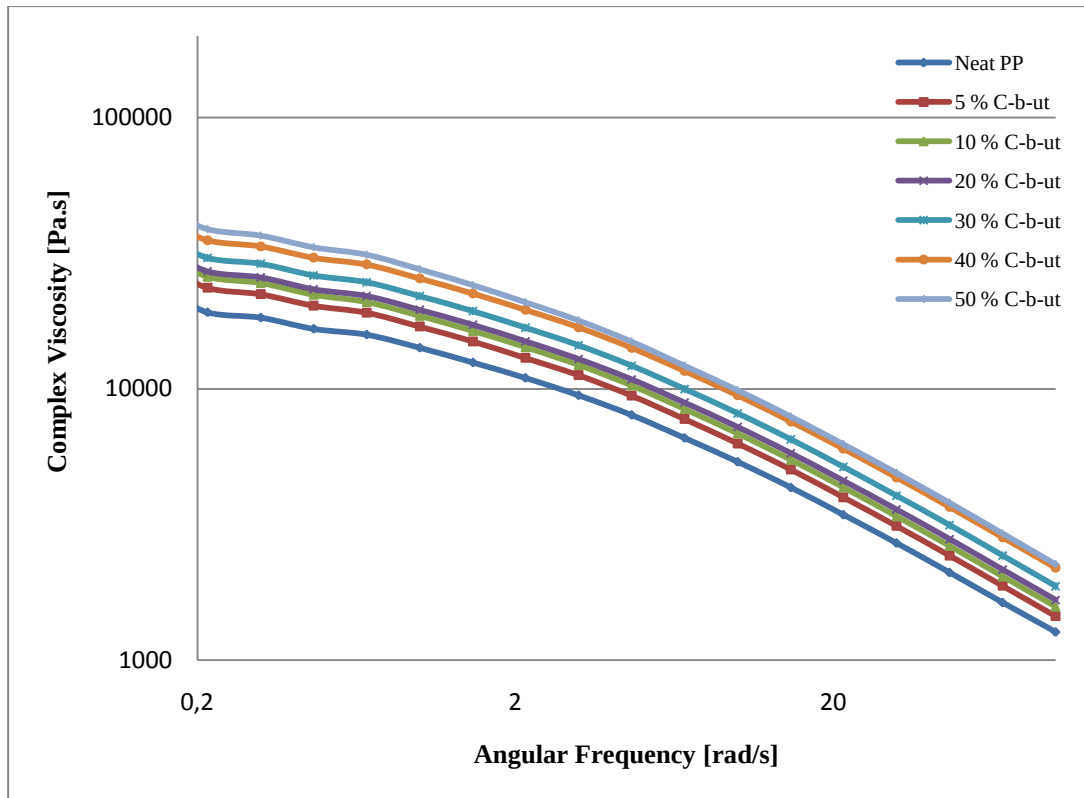


Figure E.2 : Complex viscosity of C-b-ut-coded calcite filled PP-R

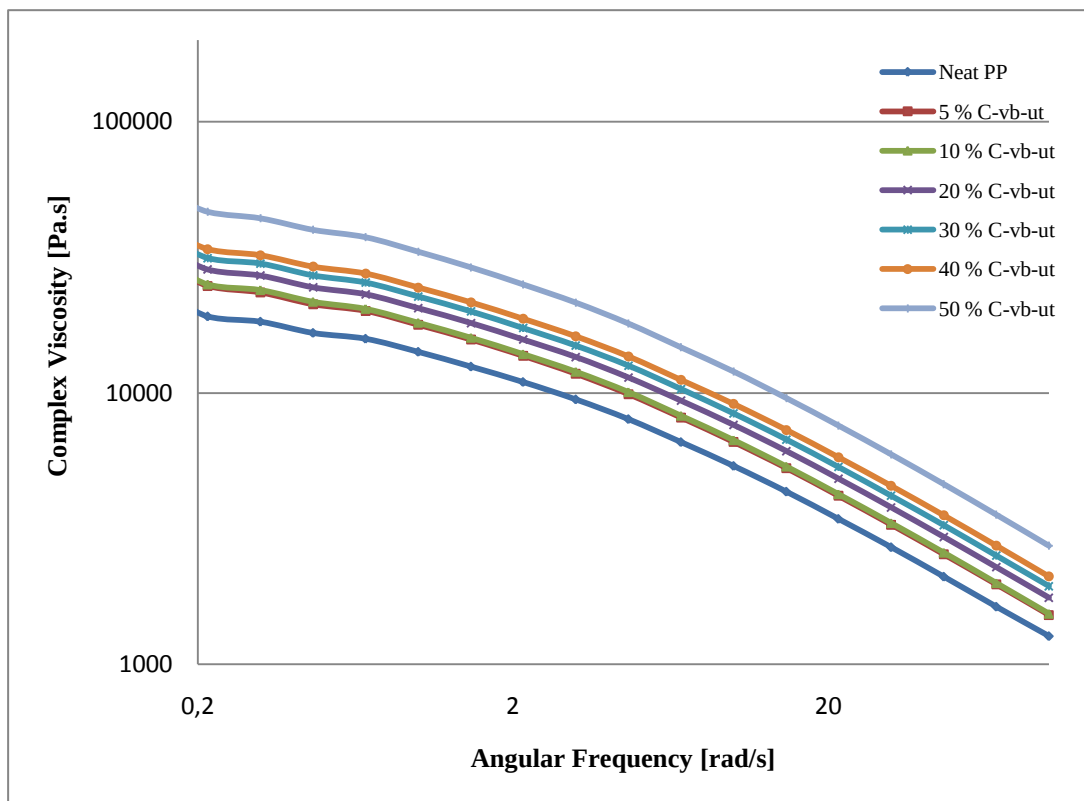


Figure E.3 : Complex viscosity of C-vb-ut-coded calcite filled PP-R

APPENDIX F

Table F.1 : Particle size distribution of commercial calcite grades

codes	Calcite Grades	Average Particle Size [μm]	The Biggest Particle Size [μm]	Under 2 μm [%]	Surface Type
C-s-ut	A-1	1.85-1.97	7.3-8.6	53-60	untreated
C-s-t	400-E	1.85-1.97	7.3-8.6	53-60	treated
C-m-ut	A-3	2.7-3.3	12.5-15.6	36-43	untreated
C-m-t	KA-2S	2.7-3.3	12.5-15.6	36-43	treated
C-b-ut	A-5	4.7-5.3	20-25	29-35	untreated
C-b-t	KA-5	4.7-5.3	20-25	29-35	treated
C-vb-ut	A-30	7.8-10.3	47-60	28.5-25	untreated

CURRICULUM VITA

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