

CHAPTER II

LITERATURE REVIEW

2.1 Surfactant

The surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. The adsorption of surfactant at the solid-liquid interface plays an important role in many technological and industrial applications, such as detergency, mineral flotation, corrosion inhibition, dispersion of solids, oil recovery and so on. In a system with low surfactant concentration, the surfactant tends to adsorb at a surface or interface.

The molecular structure of a surfactant is called an amphipathic structure (Figure 2.1) because it consists of a lyophobic and a lyophilic group (a hydrophobic and a hydrophilic group, respectively in the case of aqueous solution). The surfactants should have an amphipathic structure in the solvent under the condition used for supporting the good surface activity in a particular system. The lyophobic group of surfactant is usually a long-chain hydrocarbon while the lyophilic group is an ionic or highly polar group.

The surfactant can be divided into 4 types. It depends on the nature of the hydrophilic group.

1. Anionic surfactant: The hydrophilic group consists of negative charge, for example, $\text{RC}_6\text{H}_4\text{SO}_3\text{Na}^+$ (alkylbenzene sulfonate).
2. Cationic surfactant: The hydrophilic group consists of positive charge, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of long chain alkyl amine).
3. Zwitterionic surfactant: The hydrophilic group may give both negative and positive charge, for example, $\text{RNH}_2^+\text{CH}_2\text{COO}^-$ (long-chain amino acid).
4. Nonionic surfactant: The hydrophilic group does not contain any ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid).

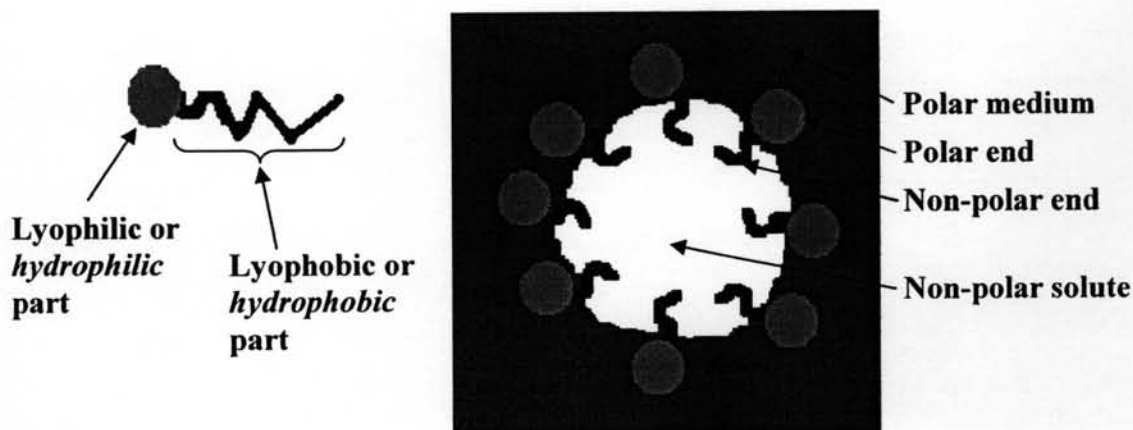


Figure 2.1 Molecular structure of a surfactant.

2.2 Ionic Surfactant Adsorption

The adsorption of surfactant have influenced from this factors:

1. The nature of the structural groups on solid surface (e.g. polar group, or nonpolar group).
2. The molecular structure of the surfactant (e.g. anionic, cationic, or nonionic surfactant).
3. The environment of the aqueous phase (e.g. pH, electrolyte content and temperature).

The point of zero charge (PZC) or the net surface charge of zero is the most critical parameter to manipulate the surfactant adsorption (Figure 2.2). The point of zero charge is specific for a substrate. It is known from the intersection of the electrophoretic mobility curve and the zero axis. When the solution pH is equal to PZC, the substrate surface has zero charge. At pH value below the PZC, the substrate surface exhibits a positive charge, while pH value above the PZC, the charge of the surface becomes negative. The PZC value can determine the type of surfactant adsorbed on the substrate surface. Anionic surfactants are adsorbed below PZC, while cationic surfactants are adsorbed above the PZC.

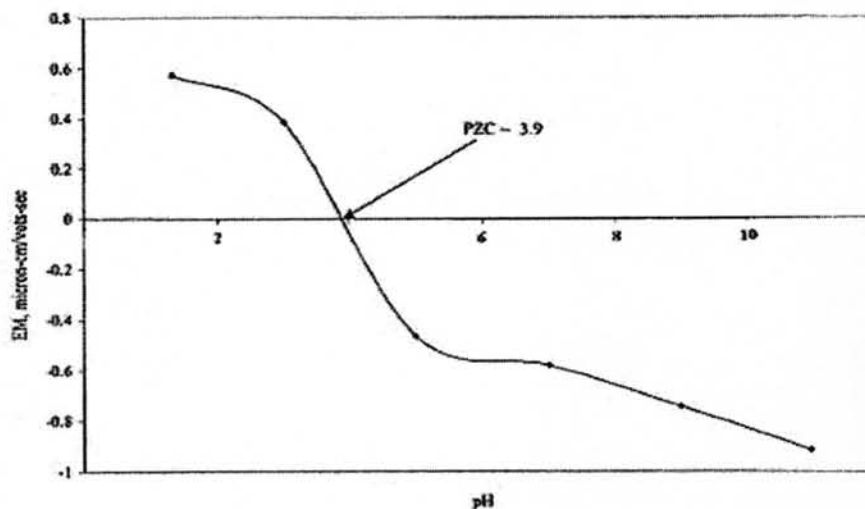


Figure 2.2 The point of zero charge on natural rubber surface (Bunsomsit *et al.*, 2002).

Figure 2.3 presents the typical isotherm of adsorption of surfactants on the solid-liquid interface in a rather wide range of concentration of surfactants going beyond the CMC. In general, a typical isotherm can be subdivided into four regions when plotted on a log-log scale. In region I, the adsorption obeys Henry's law, adsorption increases linearly with concentration and the slope of the curve is approximately one. Region I, occurs at low concentration of surfactant and monomers are electrostatically adsorbed to the substrate. Region II shows a sudden increase in the adsorption due to lateral interaction between the adsorbed monomer, resulting surface aggregation of the surfactants. Region III shows a slower rate of adsorption than region II. Region IV is the plateau region above the CMC. However, depending upon several factors the region IV may show a maximum. The four-regime adsorption isotherm mainly occurs by adsorption of ionic surfactant onto oppositely charged solid surface.

The explanations for the nature of adsorption curve in the first three regimes are well accepted. The sudden rise in adsorption in region II is due to formation of surface aggregate of the surfactant molecules on the solid surface. These surface aggregates are known as 'hemimicelles'. Because of the high surface charge, the head

of surfactant must necessarily be oriented with the charged head towards the surface and with tail striking out into the liquid. This type of adsorption is termed as 'head on' adsorption. Then the associative van der Waals force in the chains will be from hemimicelle.

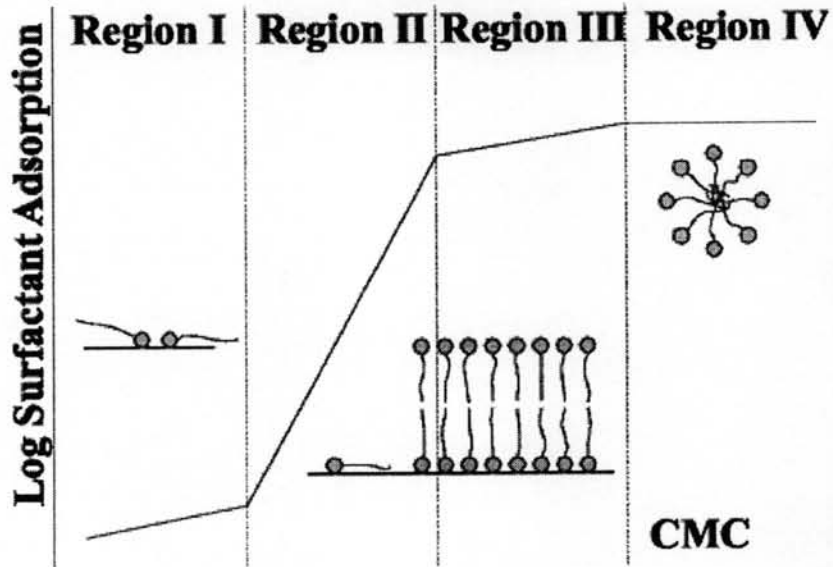


Figure 2.3 Typical adsorption isotherm of surfactants on a solid surface (Pongprayoon *et al.*, 2002).

2.3 Technique of Admicellar Polymerization

Admicellar polymerization is a fine-coating technique that leads to the formation of ultrathin polymer films on charged surface by using surfactant bilayers film as a reaction template. The four main steps of this process are consisted of surfactant adsorption onto the surface of solid particles, adsolubilization of monomers into admicelles, polymerization, and washing of outside layer of surfactant.

Step I: Admicellar Formation.

The formation of an admicelle is occurred by the adsorption of a surfactant bilayer at the solid/aqueous solution interface.

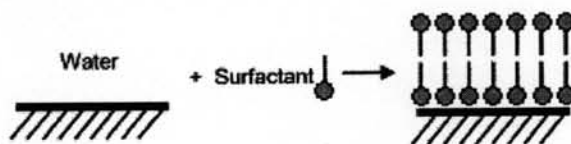


Figure 2.4 Schematic of admicellar formation (Xin Wei *et al.*, 2003).

Step II: Monomer Adsolubilization.

The process of hydrophobic monomer preferably adsolubilize into the hydrophobic interior of admicelle. There can occur either after the formation of the admicelle or concurrently with surfactant adsorption.

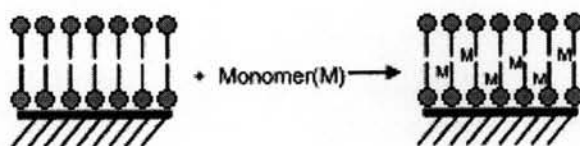


Figure 2.5 Schematic of monomer adsolubilization (Xin Wei *et al.*, 2003).

Step III: Polymer Formation.

The polymerization is occurred when concentrated monomers at the surfactant bilayers are reacted with a water-soluble initiator. Generally, the water-soluble initiators are started in the aqueous phase as in the case of emulsion polymerization.

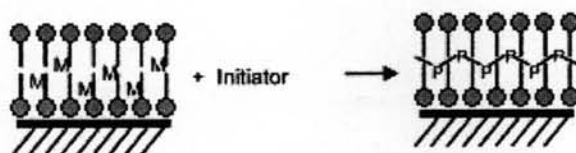


Figure 2.6 Schematic of polymer formation (Xin Wei *et al.*, 2003).

Step IV: Washing or Solvent Removal.

After the polymerization reaction is complete, the upper layer of surfactant can be removed by washing to expose the layer of polymer on the substrate surface. Thus, the ultra thin films of polymer are obtained.

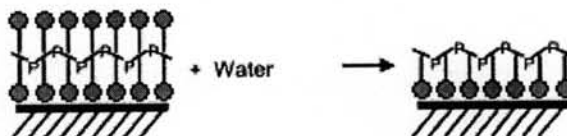


Figure 2.7 Schematic of washing or solvent removal (Xin Wei *et al.*, 2003).

There are some studied researches and reviews involved the behavior of surfactant adsorption of the solid substrate and the admicellar polymerization technique from various different substrate, surfactant, monomer and condition, which are briefly showed as follows:

Paria and Khilar (2004) reviewed the experimental studies of surfactant adsorption at the hydrophilic solid-water interface. There are some important conclusions in adsorption of ionic surfactant which are following:

- The kinetics and equilibrium adsorption of surfactants at the solid-liquid interface depend on the nature of surfactants and the nature of the solid surface. If the surfactant and the adsorbent is very fast and the equilibrium time is also less.
- Generally, the adsorption of ionic surfactants onto oppositely charged solid surface show four-region isotherm.
- The region IV of the adsorption isotherm is commonly a plateau region above the CMC.
- The influences of different parameters such as molecular structure, temperature, salt concentration are very important in adsorption.
- The order of rate of adsorption is cationic > anionic \approx non-ionic
- The hemimicellar aggregation numbers at region II and III decreases with the decreasing chain length of the surfactants. The steric hindrance due to

the position of the functional group in the surfactant leading to decrease the hemi-micellar aggregation number.

- The adsorption of ionic surfactant on similarly charged solid surface enhanced in presence of electrolyte.
- The maximum amount adsorbed at the plateau for ionic surfactant decreases with increasing temperature
- The magnitude of adsorption at the saturation decreases by increasing the chain length of the hydrophilic group. The rate of adsorption increases by increasing the chain length of the hydrophilic group.
- If the adsorbate molecules are adsorbed by strong electrostatic attraction/and long time then it takes long time to desorb from the surface.

Wu *et al.* (1987) used the admicellar polymerization for forming ultrathin polymer film on a solid surface. The styrene, sodium dodecyl sulfate (SDS) and alumina were used as the monomer, the surfactant and the solid substrate, respectively. The experiments illustrated that admicellar polymerization consisted of three steps which are including admicelle formation, monomer adsolubilization and polymer formation. They also found that the several nanometer thick of ultrathin polystyrene film was formed on alumina surface.

Funkhouser *et al.* (1995) coated the polypyrrole on alumina surface by using SDS surfactant. The polypyrrole is a one type of conductive polymer that used in electrical conductivity application e.g. sensor, electrode, etc. They found the reverse result of SDS adsorption when adding the pyrrole and salt. The present of pyrrole results in decreasing the SDS adsorption. But added salt is vice versa result.

The problem of non-bonding interaction between reinforcing silica and polymer affects their compatibility, especially rubber compound. Weddell *et al.* (1996) improve those problem using admicellar polymerization to modify the silica surface by coating it with polymers. There are many types of polymers and copolymers were used for coating, the result showed that the modified silica can improve mechanical properties of rubber compounds and improve cure time. The

different chemical substance and the reaction condition result in different properties of modified silica.

In 2002, thin film polystyrene coating on cotton using linear alkylbenzene (LAS) as the surfactant by admicellar polymerization of was investigated by Pongprayoon *et al.*. The result showed that the high pH results in low adsorption of LAS, and the increase of salt concentration causes an increase of LAS adsorption.

Bunsomsit *et al.* (2002) studied admicellar polymerization process of polypyrrole coated on natural rubber latex using sodium dodecyl sulfate (SDS) as the surfactant and sodium sulphate (Na_2SO_4) as the initiator. They found that the increase of salt concentration results to increase SDS adsorption and pyrrole adsolubilization. The increase of pyrrole concentration causes a decrease of SDS adsorption at equilibrium. They also found the conductivity of the polypyrrole coated NR latex film prepared by admicellar polymerization without salt was the lowest. With salt addition, the conductivity of the film improved significantly.

Arayawongkul (2002) characterized the polystyrene produced by admicellar polymerization using cetyltrimethylammonium bromide (CTAB) as the surfactant, AIBN as an initiator (insoluble initiator) and using tetrahydrofuran (THF) for extracting the polystyrene from the surface of modified silica. She found that the extent of the polystyrene film and amount of polystyrene forming on silica particles increase with increasing CTAB adsorption and styrene adsolubilization.

Srinarang (2004) investigated the admicellar polymerization of polystyrene on natural rubber particles using hexadecyltrimethylammonium bromide (CTAB) as the surfactant and 2,2'-azobis(2-methylpropionamide) (V50) as the soluble initiator. The suitable pH, time of surfactant adsorption, CTAB concentration and styrene concentration were studied. She found that the suitable pH was chosen at higher than 3.3 to achieve the adsorption of the cationic surfactant CTAB. The present of salt resulted in increasing CTAB adsorption and styrene adsolubilization, moreover it also improved the amount, orientation and packing of CTAB. Time of 15 h was sufficient for surfactant adsorption. She also found that the higher initial styrene concentration resulted in the higher equilibrium styrene concentration and the higher the styrene adsolubilization.

Nontasorn *et al.* (2005) modified the silica surface by using admicellar polymerization in a continuous stirred-tank reactor system (CSTR) to improve the compatibility between the silica and rubber. The ingredient was comprised of precipitated silica, cetyltrimethylammonium bromide (CTAB) cationic surfactant, styrene and isoprene comonomers, and 2,2'-azobisisobutyronitrile initiator. The result showed that the modified silica reduced T_{90} cure times and improved modulus, abrasion resistance, and compression set. The optimum conditions for surface modification of silica by the admicellar polymerization process were 5 g comonomer loading per kg silica and a 30 min reaction time. In comparison with the modified silica using a batch process, the modified silica obtained from the CSTR process was found to be superior in the performance of rubber compound.

The surface modified calcium carbonate (CaCO_3) particles by admicellar polymerization to be used as filler for isotactic polypropylene was investigated by Rungruang *et al.* (2006). The sodium dodecyl sulfate (SDS) and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) were used as the surfactant template and the thermal initiator, respectively. Non-isothermal crystallization was studied and indicated that surface treatment of CaCO_3 particles reduced the ability for CaCO_3 particles to nucleate the isotactic PP matrix. The behavior of these coated particles in an isotactic PP matrix was compared to that of uncoated and stearic acid-coated ones. The composites made with stearic acid-coated and admicellar-treated CaCO_3 particles had lower tensile strength, Young's modulus and flexural strength, but higher impact strength.

In 2006, Preechasup *et al.* studied the admicellar polymerization of styrene coated on natural rubber using two different types of surfactants (SDS and CTAB) and optimum conditions with ratio of styrene to initiator at 1:0.04. Under aging condition, the modulus, tensile strength and thermal mechanical property can be improved caused by increment of the compatibility between two components.

2.4 Polymer Rheology

The rheological study of elastomers using capillary rheometer is importance in predicting and comprehending their processing characteristics. Both the viscous and elastic properties of elastomer can be analyzed and correlated with the flow behavior. The viscous flow is related to the output rate, whereas the elastic behavior corresponds to the dimensional stability (Bhowmick *et al.*, 2004). The main advantage of the capillary rheometer for measuring rubber viscosity is the wide range of shear rate which can be applied to the rubber specimen. The apparent values of shear stress, shear rate and shear viscosity were calculated using the derivation of the Poiseuille law for capillary flow as equation follows:

$$\text{Apparent shear stress (Pa);} \quad \tau = Fr/2\pi R^2L = Pr10^6/2L = K(\dot{\gamma})^n \quad (1)$$

$$\text{Apparent shear rate (s}^{-1}\text{);} \quad \dot{\gamma} = 4R^2V/r^3 \quad (2)$$

$$\text{Apparent shear viscosity (Pa*s);} \quad \eta = \tau/\dot{\gamma} = K(\dot{\gamma})^{n-1} \quad (3)$$

where;

F	=	force (N)
R	=	piston radius (mm)
r	=	capillary radius (mm)
L	=	capillary length (mm)
P	=	pressure (MPa)
V	=	piston downward speed (mm/sec)
K	=	consistency index (Pa*s ⁿ)
n	=	power law index

The capillary instruments are very valuable for steady-shear investigations at very high shear rates for examining the flow behavior of polymer melt. The appropriate range of deformation (strain) or load (stress) would have been used in obtaining the relevant parameter for a given process as shown in Figure 2.9. The example of relationship between shear stress and shear viscosity of PP/EPDM blends at any blending composition is shown in Figure 2.10.

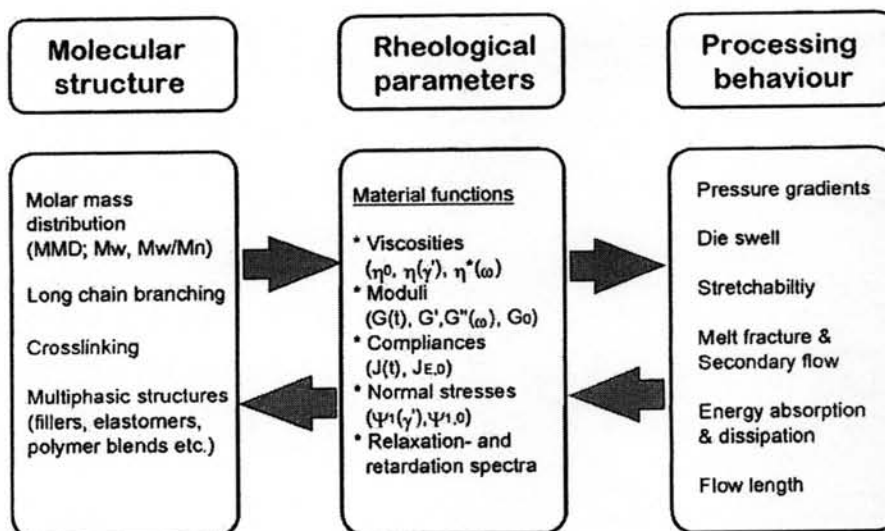


Figure 2.8 Rheological parameters acting as a link between molecular structure and processing behavior (Gahleitner, 2001).

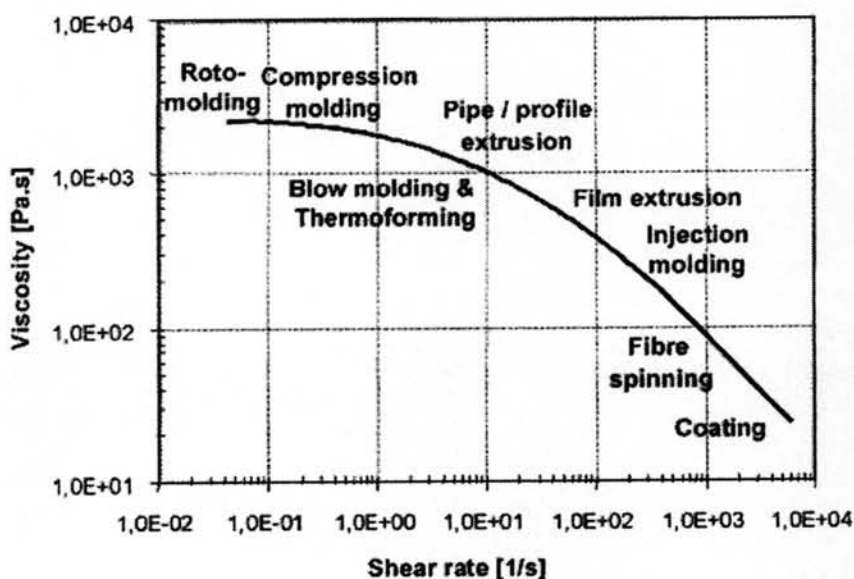


Figure 2.9 Typical viscosity curve of a polyolefin with indication of the shear rate regions of different conversion techniques (Gahleitner, 2001).

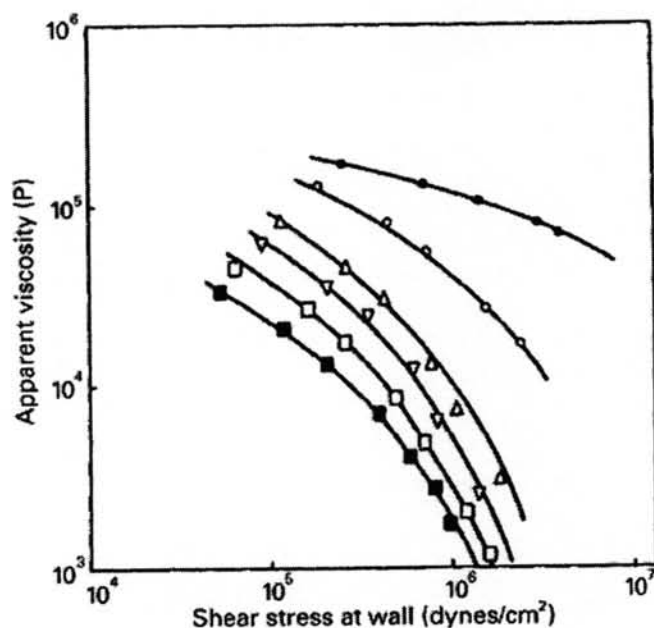


Figure 2.10 Capillary rheology of PP/EPDM-blends (200°C) based on a PP-homopolymer (■) and EPDM (●); blends with 20 wt.% (□), 40 wt.% (▽), 60 wt.% (△) and 80 wt.% (○) of EPDM (Gahleitner, 2001).

A large number of rheological behavior studies have been reported by several workers concerning the melt flow behavior of elastomers and their blends as follows

In 1997, Thomas *et al.* studied the melt rheological behavior of NR/PMMA blend system with and without the addition of compatibilizer. They found that the viscosity of the blend increased as the amount of NR increased. In the case of solution cast samples the melt viscosity increased as the percentage of graft copolymer increased and the blend became more sensitive to temperature in the presence of graft copolymers. And also, addition of compatibilizer was found to reduce the die swell of the blend.

Menon (2003) studied the melt rheology of ethylene propylene diene rubber (EPDM) before and after modification with phosphorylated cashew nut shell liquid prepolymer (PCNSL) over a wide range of temperature and shear rates. He concluded that the presence of PCNSL in EPDM effected to decrease in melt viscosity, consistency index, shear modulus and activation energy of melt flow.

In 2002, Nakason *et al.* investigated the rheological properties of maleated natural rubber (MNR) and natural rubber (ADS and STR 5L) blends. They found that the Mooney viscosities of MNR-ADS/ADS blends were higher than those of MNR-STR/STR 5L blends. The power law index in all cases of blends exhibited very high pseudoplasticity or shear thinning ($n < 0.25$). The rheological properties could be confirmed that the MNR/NR blends were compatible.

Nakason *et al.* (2006) studied the rheological properties of maleated natural rubber (MNR)/polypropylene (PP) blends using the compatibilizers of phenolic modified polypropylene and polypropylene-*g*-maleic anhydride. They found that the apparent shear stress and shear viscosity increased with an increase in apparent shear rate over a range of loading levels of compatibilizers of 0-5%. However, increasing levels of compatibilizers beyond their critical micelle concentration caused formation of micelles dispersed in the MNR matrix, which acted as a lubricant in the polymer melt flow, resulted in lowering the apparent shear stress and shear viscosity.

In 1997, Wood *et al.* investigated the effect of mastication and temperature on the flow visualization of natural rubber in the barrel of capillary rheometer. It was found that the flow patterns in the barrel of the capillary rheometer used were very complex and were a function of piston displacement only. Moreover, the reduction in molecular entanglements resulting from mastication led to decrease the apparent shear stress and shear viscosity.

Asaletha *et al.* (1998) studied the melt rheology and morphology of physically compatibilized natural rubber-polystyrene blends by the addition of natural rubber-*g*-polystyrene. The blends were prepared by both melt mixing and solution casting techniques. In both cases, the shear viscosity decreased with the increase of shear stress, indicating pseudoplastic nature. The viscosity of the system was found to increase with the increase of the rubber content and a few percent of the compatibilizers (NR-*g*-PS), but decrease in viscosity at higher graft loading caused by micelle formation. Morphology analysis revealed that the dispersed domain size of PS had been reduced significantly at high shear rate.

In 2004, the rheological properties of styrene-butadiene rubber (SBR) loaded with dual phase filler were investigated by Bhowmick *et al.*. The effect of electron beam modification of dual phase filler in the absence and presence of

trimethylol propane triacrylate (TMPTA) or triethoxysilylpropyltetrasulphide (Si-69) on melt flow properties of SBR was also studied. The viscosity of all the systems decreased with shear rate indicating their pseudoplastic or shear thinning nature. Die swell of the modified filler loaded SBR is slightly higher than that of the unmodified filler loaded rubber, which is explained by calculating normal stress difference for the systems. Activation energy of the modified filler loaded SBR systems was also slightly higher than that of the control filler loaded SBR system.