CHAPTER IV
NATURAL RUBBER-TOUGHENED NYLON12 COMPATIBILIZED BY POLYSTYRENE/NATURAL RUBBER BLEND

4.1 Abstract

Nylon12 (polyamide12)/natural rubber (NR-grade STR 5L)/compatibilizer blends were prepared by melt blending in a twin-screw extruder with various compatibilizer contents. The copolymer of polystyrene and natural rubber (PS/NR) was used as a compatibilizer. Then a scanning electron microscope was used to study the phase morphology and the mechanical and rheological properties. At the optimum compatibilizer content of 10 phr, the [Nylon12/NR]/[PS/NR] blends showed improved mechanical properties and fine phase morphology (good dispersion of NR in Nylon12 matrix). This is due to decreased domain size of the dispersed rubber phase, leading to decreased deformability of the rubber particle and increased compatibility of the blend. For the flow properties, increased interfacial interaction between NR domains and Nylon12 matrix can result in increased shear viscosity and decreased extrudate swell.

Keywords: Mechanical properties, Natural rubber, Nylon12 (Polyamide12), Reactive processing, Rheology

4.2 Introduction

In recent years, the development of rubber-toughened thermoplastic resins is an important contribution to the commercial polymer industry. A small amount of discrete rubber particles in the plastic can greatly improve the crack and impact resistance of normally brittle plastics (PS and PVC), including high-performance plastics (acetals, aromatic polyesters, and nylon) [1-3].

For Nylon12 (polyamide12), it is a thermoplastic material produced by opening up a monomer containing both amine and acid groups known as a laurolactam ring. Nylon12 is used in many applications such as nylon tubes, aircraft

interior parts, automotive exterior parts and cable jacketing due to its high flexible crack resistance, lowest moisture absorption, and high abrasion resistance. However, the drawbacks of most polyamides are low heat resistance, poor dimensional stability, and moderate impact strength [4]. The improvement of toughness behavior can be done by incorporating an elastomer in plastics.

Natural rubber (NR) is one of elastomeric materials that is used in toughness enhancement due to its good elastic properties, good resilience, and good damping behavior [5], including its sustainable as it is derived from trees. However, Nylon12 and NR are thermodynamically incompatible causing phase separation when they are blended. The phase compatibility is an important factor affecting the blend morphology and the blend properties.

Most immiscible polymers form coarse mixtures with comparatively large domain sizes and sharp interfaces, as a result of the high interfacial tension between the components, which further leads to poor interfacial adhesion [6-7]. The properties of a blend depend not only on the mechanical behavior of the interface, but also on the size of the respective polymer phases. Therefore, compatibilization of polymer blend will be carried out to reduce the scale of dispersion and to stabilize the morphology. This can be achieved by addition of compatibilizer into the system. This technique promotes dispersive mixing so that the interfacial tension becomes lower and leads to the reduction of particle size. At a particular compatibilizer loading, there is a balance of interfacial tension and particle deformation [8]. Compatibilizers are usually the copolymer that its components can be compatible with the blend components and thus it is rather difficult to find a suitable compatibilizer that matches well with the blend components. Our approach is to use the reactive blending of an incompatible polymer pair to form the graft copolymer to act as the compatibilizer suitable for that blend. This technique may need to use an additional initiator to allow a combination reaction, e.g. grafting between the blend components so that their copolymer could be formed and readily function as the compatibilizer. However, the reactive blends containing the graft copolymer can be employed as the compatibilizer for other blends as well. This approach is therefore very beneficial to the area of polymer blend as well as polymer waste recycle.

In this work, the Nylon12/NR blend was prepared by using PS and NR reactive blend (PS/NR) as the compatibilizer. Dicumyl peroxide (DCP) was used as a free radical initiator in the PS/NR blend to form the graft copolymer of PS and NR. Then the effect of the PS/NR compatibilizer content on the morphology and the mechanical and rheological properties of the Nylon12/NR blend was studied.

4.3 Experimental

4.3.1 Materials

Nylon12 (polyamide12), product name Grilamid® L25 natural 6112, was supplied by EMS-Chemie (Asia). The polymer is in a pellet-bead form. The melt volume flow rate is 20 cm^3/10 min (275 °C, 5 kg). The melting point of Nylon12 is 178 °C.

Natural rubber (NR) grade STR 5L was purchased from Banpan Research Laboratory (Thailand) in yellow solid bulk form.

Polystyrene (STYRON™ 656D) was supplied by Dow Chemical (Thailand). It is in an opaque-white pellet-bead from. The melt volume flow rate is 8 cm^3/10 min (ASTM D1238). Density is 1.05 g/cm^3.

4.3.2 Blend Preparation

4.3.2.1 Mastication of NR

The solid block natural rubber was masticated on a two-roll mill (Lab Tech, LMR 110) for 10 min at room temperature, and then cut into small pieces.

4.3.2.2 PS/NR [60/40 wt%] Reactive Blend

The PS/NR blend that was used as the compatibilizer in the Nylon12/NR blend was prepared in a twin-screw extruder (Labtech) with a screw diameter of 20 mm and a length/diameter ratio of 44. Prior to blending, PS was dried in a vacuum oven at 60 °C for 12 h in order to remove the absorbed water. Then PS (60 wt%), DCP (0.5 wt%), and NR (40 wt%) were fed into the extruder and mixed at different screw speeds (30-45 rpm). The operating temperatures of the extruder were

maintained at 100, 120, 135, 150, 160, 165, 165, 165, 165, and 165 °C that order from hopper to die. The extrudate was cooled in a water bath before being cut with a granulator into pellet form.

4.3.2.3 Determination of Graft Ratio

In PS/NR melt blending process using DCP as an initiator, many kinds of end products were produced in free radical reaction system, e.g., crosslinked NR, unreacted PS (PS short chain), a graft copolymer of PS and NR. To purify the blend, the crosslinked NR (gel) was extracted by using toluene for 24 h at 120 °C while the unreacted PS was extracted by methyl ethyl ketone for 24 h at 90 °C. The gel content, the unreacted PS content and the graft ratio (GR) were calculated by using Equations (4.1)-(4.3).

$$Gel\,(wt\%) = \left[\frac{weight\,of\,gel}{weight\,of\,crude\,blend} \right] \times 100 \qquad (4.1)$$

$$Unreacted\,PS\,(wt\%) = \left[\frac{weight\,of\,unreacted\,PS}{weight\,of\,crude\,blend} \right] \times 100 \qquad (4.2)$$

$$Graft\,ratio\,(GR) = \frac{weight\,of\,purified\,blend\,(PS-g-NR)}{weight\,of\,crude\,blend} \qquad (4.3)$$

4.3.2.4 Nylon12/NR [80/20 wt%]/[PS/NR] Compatibilizer Blends

Prior to blending, the crude blend of PS/NR and Nylon12 were dried in the vacuum oven at 60 °C for 12 h in order to remove the absorbed water. Then Nylon12, NR and PS/NR blend with various compatibilizer contents (5-25 phr) were fed into the twin-screw extruder and mixed at screw speed of 40 rpm. The operating temperatures of the extruder were maintained at 170, 175, 180, 185, 190, 200, 200, 205, 210, and 210 °C that order from hopper to die. The extrudate was cooled in a water bath before being cut with the granulator into pellet form, and then dried in the vacuum oven at 60 °C before further use.

4.3.3 Molding

The blends were dried at 60 °C for 12 h before being injected. Then the blends were molded in an injection molding machine (Asia Plastic – 90 Injection molding) into tensile (width 10.0 mm, thickness 3.2 mm) and impact testing specimens (width 12.7 mm, thickness 3.2 mm). The typical operating conditions used were a 250 °C nozzle temperature and a 90 °C mold temperature.

4.3.4 Mechanical Testing

Tensile properties of the blends were carried out by an Instron universal testing machine model 4206. All specimens were tested according to ASTM D638 at the gauge length of 50 mm, the load cell of 100 kN and the crosshead speed of 50 mm/min.

Impact energy of the blends was studied by an Izod pendulum impact tester (Zwick model 5113). All notched specimens were tested with the pendulum 21.6 J according to ASTM D256.

4.3.5 Blend Morphology

A JEOL JSM 5800LV scanning electron microscope (SEM) with magnification 2,500 times was used at 15 kV to investigate the morphology of the cross-sectional surface after coating by gold, a conductive material. For the preparation of the cross-sectional surface, the samples were cryogenically broken after dipping in liquid nitrogen for 1 h and then the rubber phase was removed by etching with toluene for at least 3 days at 100 °C.

4.3.6 Rheological and Extrudate Swell Measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer was used to investigate the melt rheology and the extrudate swell of the [Nylon12/NR]/[PS/NR] blends. The inner diameter and the length of the barrel used were 15 and 300 mm, respectively, while the length-to-inner diameter (L/D) was 0.5/1, 5/1 and 20/1 for the Bagley correction. All measurements were made at four test temperatures of 205, 210, 215 and 220 °C and the range of apparent shear rates varied from 100 to 4000 s^{-1}. The hold-on time and hold-on pressure for stages 1-3 were 200 s at 10, 20,

and 30 Pa, respectively. For the apparent shear stress (τ_{app}), it is defined as shown in Equation (4.4).

$$\tau_{app} = \frac{R\Delta P}{2L} \qquad (4.4)$$

where R is the radius of the die (mm), ΔP is the pressure drop across the die (Pa), and L is the length of the die (mm); and the apparent shear rate ($\dot{\gamma}_{app}$) is defined as shown in Equation (4.5).

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \qquad (4.5)$$

where Q is the volumetric flow rate. Then the procedures of Bagley [9,10] and Rabinowitsch [10] will be used to correct the actual shear stress and the actual shear rate, respectively. According to these corrections, the actual shear stress is defined as shown in Equation (4.6).

$$\tau_{actual} = \frac{R\Delta P}{2(L + eR)} = \frac{\Delta P}{2\left(\dfrac{L}{R} + e\right)} \qquad (4.6)$$

where e is a multiplication factor according to the Bagley correction; and the actual shear rate ($\dot{\gamma}_{actual}$) is defined as shown in Equation (4.7).

$$\dot{\gamma}_{actual} = \frac{3n'+1}{4n'}\dot{\gamma}_{app} \qquad (4.7)$$

where n' is the slope from a plot (in a double logarithmic scale) between the apparent shear rate and the apparent shear stress that was fitted to the Rabinowitsch correction. According to these values, the actual shear viscosity (η_{actual}) can be calculated by using Equation (4.8).

$$\eta_{actual} = \frac{\tau_{actual}}{\dot{\gamma}_{actual}} \tag{4.8}$$

For extrudate swell, it was measured by using an attached KEYENCE VG laser analytical device, which comprises a laser light source and a light sensor. The extrudate swell (B) is reported as the percentage of extrudate swell (%) as in the following Equation (4.9).

$$\%B = \frac{(D_e - D) \times 100}{D} \tag{4.9}$$

where D_e and D are the diameter of the extrudate and the die, respectively.

4.3.7 Thermogravimetric Analysis

The thermogravimetric analysis (TGA) was performed with a thermal analyzer (Perkin-Elmer Pyris). All blends were analyzed at temperature of 30-600 °C with the heating rate of 10 °C/min under the nitrogen gas atmosphere.

4.4 Results and Discussion

4.4.1 Determination of Gel Content

In the PS/NR reactive blend, gel may be the crosslinked NR. The effect of screw speeds on the gel content is shown in Figure 4.1. The result reveals that the gel content dramatically decreases as the screw speed increases. At low screw speed, grafting reaction need longer time to accomplish because of less chance for both NR and PS macroradicals to find each other. On the other hand, it reveals that the reaction of DCP to NR and PS prefers to cause crosslinking in NR phase rather than reaction in PS phase due to more reaction sites on NR molecules available for the radicals to react. However, it is possible that the reaction between PS and NR to form the graft copolymer of PS and NR shown in Figure 4.2 could occur at high screw speed. The gel formation is thus sensitive to screw speed.
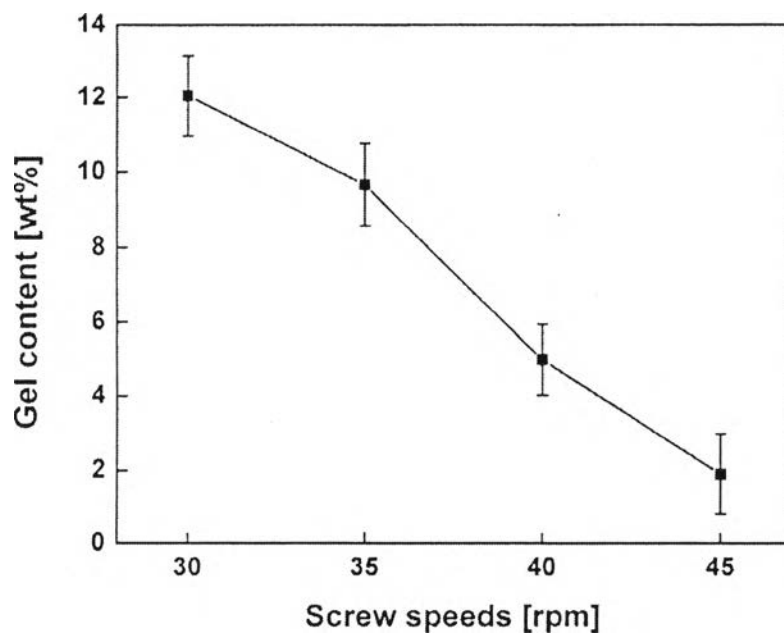
Figure 4.1 The effect of screw speeds on the gel content of PS/NR blend.
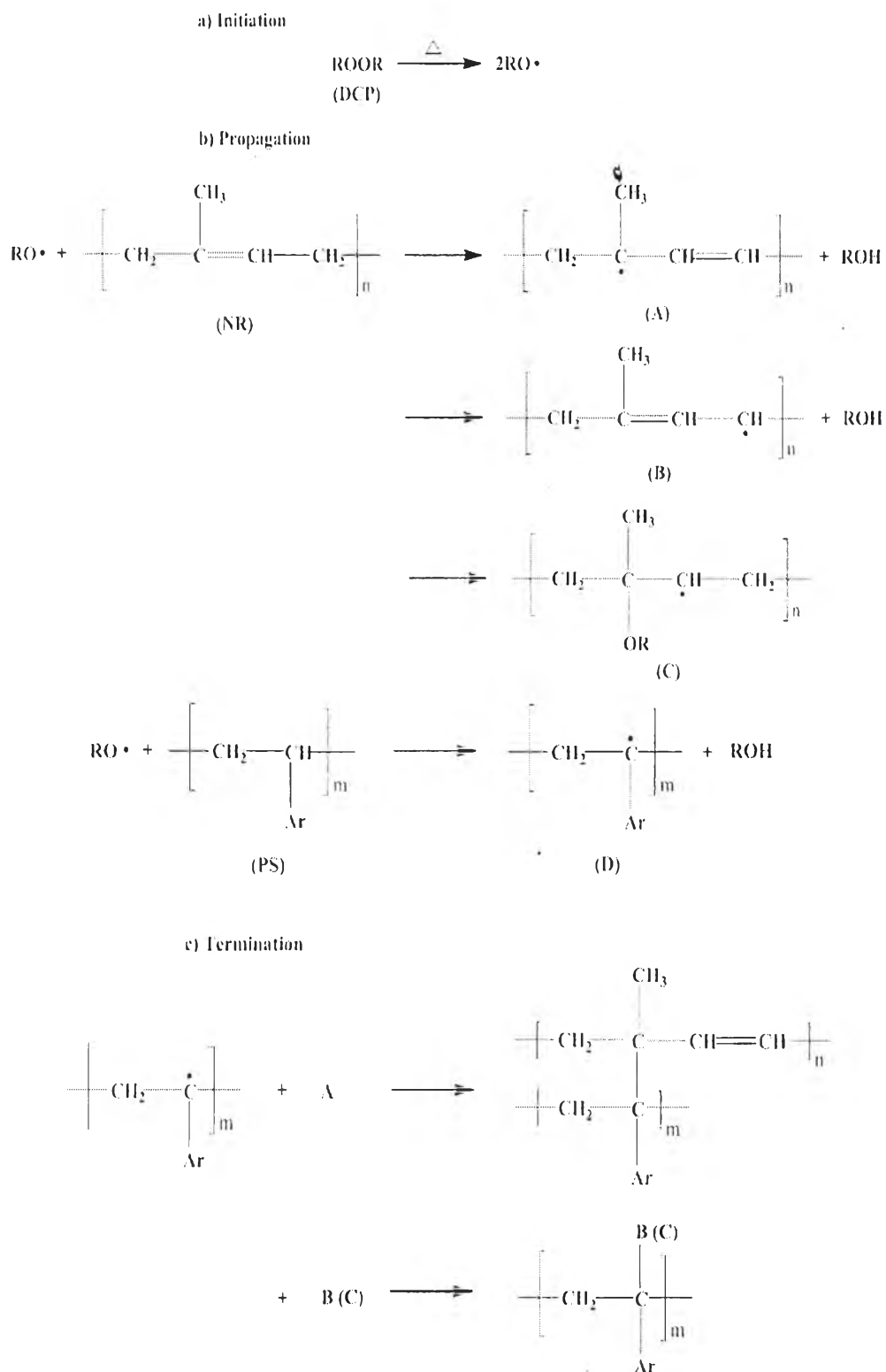
a) Initiation

$$ROOR \xrightarrow{\triangle} 2RO\cdot$$
(DCP)

b) Propagation

(NR) → (A) + ROH

→ (B) + ROH

→ (C) OR

(PS) → (D) + ROH

c) Termination

Figure 4.2 The proposed reaction between PS and NR with DCP by melt blending.

4.4.2 Determination of Graft Ratio

In grafting reaction, the dispersion and the distribution of macroradicals are very important. At high screw speed, it gives an improvement of mixing in the extruder due to high shear rate [11]. In our case, the graft copolymer of PS and NR (graft ratio) increases with increasing screw speed as shown in Table 4.1. The result indicates that the dispersion and the distribution of PS and NR macroradicals become more efficient with using high screw speed, and this leads to the formation of the graft copolymer of PS and NR.

From these results, to avoid too high gel content, which may affect the long-term mechanical properties, the screw speed of 45 rpm is used to prepare the reactive blending of PS and NR for further use as the compatibilizer in the Nylon12/NR blend.

Table 4.1 Effect of screw speeds on unreacted PS content and graft ratio

Screw Speed [rpm]	Unreacted PS [wt%]	Graft Ratio
30	39.0	0.27
35	37.7	0.29
40	34.4	0.34
45	33.2	0.37

4.4.3 FT-IR Results of PS/NR Blend

Figure 4.3 shows the spectrum of PS, NR and the graft copolymer of PS and NR (PS/NR blend after purification) using screw speed of 45 rpm. For the graft copolymer of PS and NR, the characteristic absorption band at 839 cm^{-1} is assigned to $R_2C=CHR$ of isoprene. The signal at 1365 cm^{-1} is attributed to the aliphatic C-H stretching in natural rubber [12-13]. Also, the weak absorbance band at 1550 cm^{-1} is typical for a COO$^-$ group, caused by proteins and amino acids. While the absorbance bands at 699 cm^{-1} and 759 cm^{-1} are characteristic bands of out-of-plane bending vibrations and deformation vibration of the five –CH– groups in benzene ring, respectively [14-15]. These two bands are typical for the

monosubstituted benzene ring of polystyrene. Also, the absorbance at 1600 cm^{-1} is C=C stretching of the benzene ring of styrene. Thus it is suggestion that the graft copolymer of PS and NR is successfully obtained via reactive blending using DCP as the initiator.
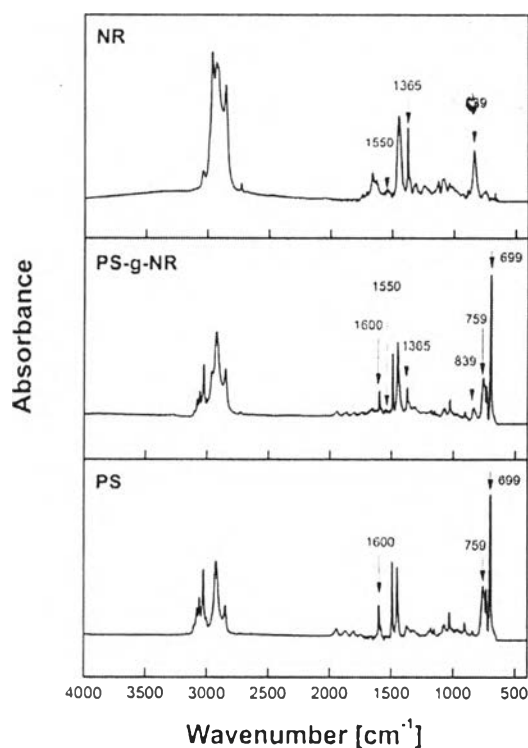

Figure 4.3 FT-IR spectra of PS, NR, and the graft copolymer of PS and NR using screw speed of 45 rpm.

4.4.4 Effect of PS/NR Compatibilizer Contents on Impact Energy of [Nylon12/NR]/[PS/NR] Blends

The impact energy of the blends was studied by Izod impact testing machine. The 21.6 J pendulum was used to test all specimens. They were not broken thoroughly. It is interesting that the crack region is clearly whitened as showed in Figure 4.4 revealing the energy dissipated greatly by craze formation.
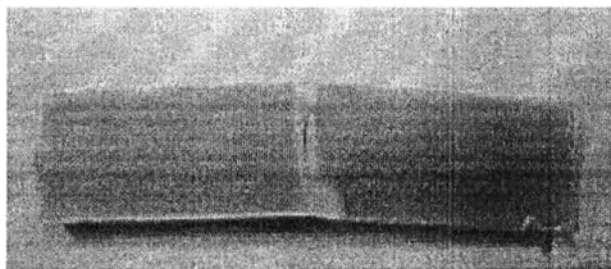
Figure 4.4 The tested specimen was not thoroughly broken into two pieces by Izod impact testing machine.

Neat Nylon12 and Nylon12/NR [80/20 wt%] binary blend have the impact energy of 112 and 230 J/m, respectively. The incorporation of 20 wt% NR into Nylon12 can increase the impact energy approximately twice. This is due to the void formation at the interface of the domain and matrix where encapsulation is not completed and this promote the energy dissipation [16]. In our case, the crack and whitening may occur by similar mechanism, and the rubber phase will help in toughening the Nylon12 matrix. For an addition of compatibilizer (Figure 4.5), with an increase of PS/NR contents, the impact energy of [Nylon12/NR]/[PS/NR] blends increases initially, and then it decreases continuously. At a small content of compatibilizer (10 phr), the increasing of impact energy closed to 400 J/m (about twice that of original binary blend) can result from the suitable dispersed phase size of 2.27 μm (the number averages of dispersed phase size measurements were estimated by averaging the diameter of about 100 domains randomly), the strength of Nylon12 matrix, the flexibility of NR, and proper morphology. Cigna *et al.* [17] stated that the particle size less than 3 μm increased the interfacial surface between rubber particles and polystyrene matrix. This can favor the formation of more crazed matter during fracture (as craze starts at the said interface) and then an increase of impact strength. From this result, it shows an effective use of the PS/NR reactive blend as the compatibilizer for the Nylon12/NR blend and toughening agent simultaneously.
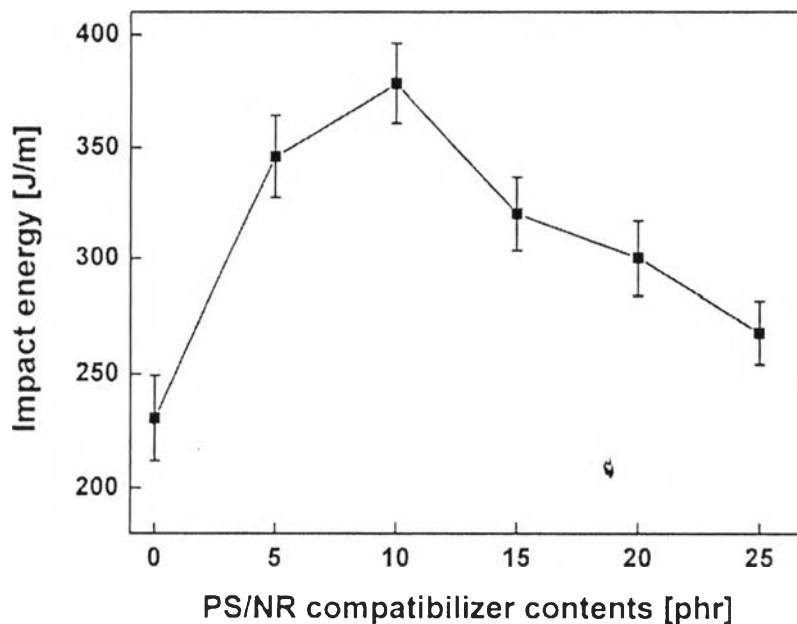
Figure 4.5 The impact energy from non-thoroughly broken samples of [Nylon12/NR]/[PS/NR] blends with various contents of PS/NR blend.

4.4.5 Effect of PS/NR Compatibilizer Contents on the Tensile Properties of [Nylon12/NR]/[PS/NR] Blends

Neat Nylon12 has the tensile modulus of 1,100 MPa and the tensile yield stress of 40 MPa. For the [Nylon12/NR]/[PS/NR] blends, the tensile modulus and the tensile yield stress are shown in Figure 4.6 and Figure 4.7, respectively. The results indicate that the incorporation of 20 wt% NR into Nylon12 decreases in the tensile modulus and the tensile yield stress approximately 1.3 and 1.8 times, respectively. This is due to the incompatibility of the phase in the blend [18].
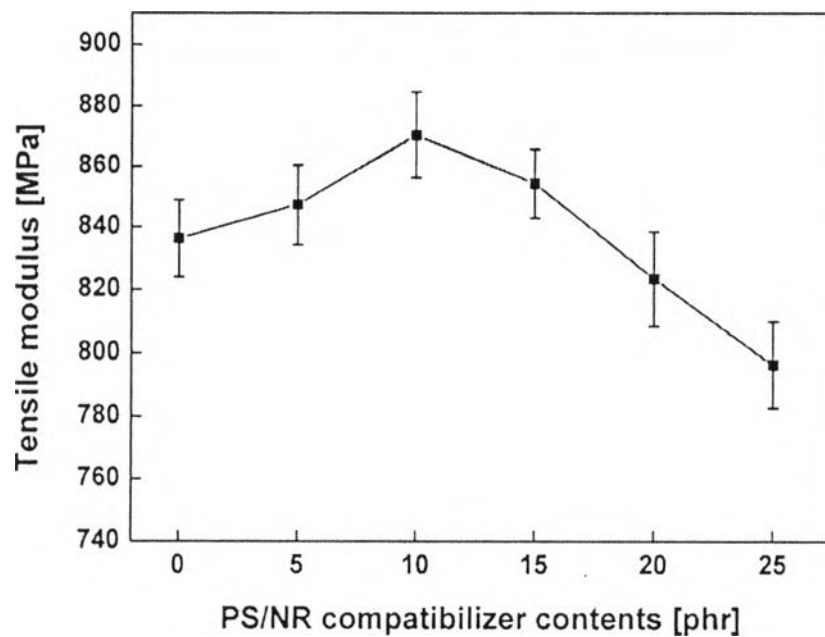
Figure 4.6 The tensile modulus of [Nylon12/NR]/[PS/NR] blends with various contents of PS/NR blend.
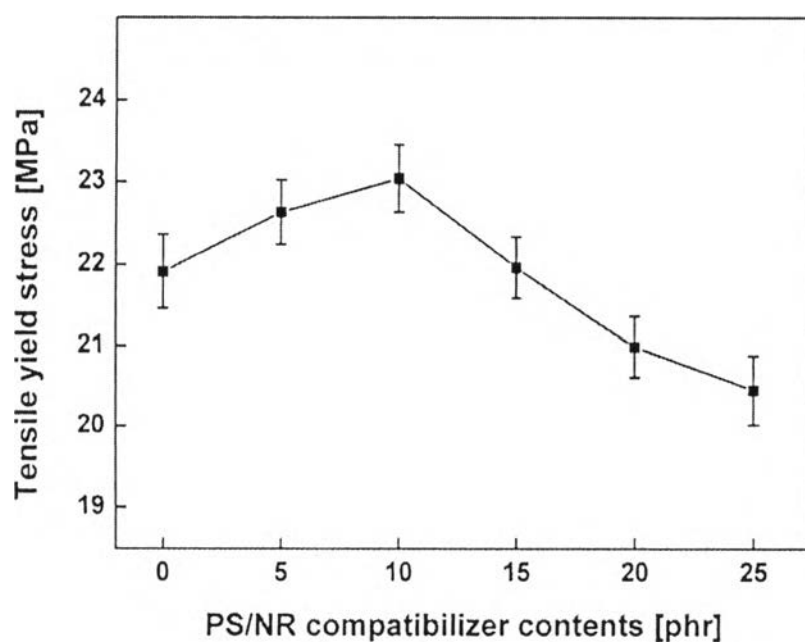

Figure 4.7 The tensile yield stress of [Nylon12/NR]/[PS/NR] blends with various contents of PS/NR blend.

The addition of compatibilizer into the polymer/rubber blend can improve compatibility between the two phases. The increased tensile modulus of [Nylon12/NR]/[PS/NR] blends is found as increasing content of PS/NR blend up to 10 phr. This could be attributed to the hard segment of PS (60 wt%) and the NR crosslinking to provide high modulus of the blends. However, at high PS/NR contents, the tensile modulus and the tensile yield stress decrease. This can result from the increasing gel content and more unreacted PS part in PS/NR crude blend. The blends also become relatively hard, and they do not show the elastomeric properties.

4.4.6 Phase Morphology of [Nylon12/NR]/[PS/NR] Blends

To study phase morphology of [Nylon12/NR]/[PS/NR] blends, the cryogenic fracture of the blends was observed by SEM after etching NR by toluene. The blends with variation of PS/NR contents show the decreasing of dispersed phase size at PS/NR content of 10 phr (Figure 4.8). This reveals that the PS/NR blend acts very efficiently as the compatibilizer for the Nylon12/NR blend. It can promote dispersive mixing, leading to reduce particle size and stabilize the morphology. In the Nylon12/NR blend using PS/NR as the compatibilizer, the interfacial tension between Nylon12 and PS is lower than the interfacial tension between Nylon12 and NR at the processing temperature as shown in Table 4.2. Therefore, PS part should faced to Nylon12 surface and NR part faced to NR phase. In other words, the PS/NR blend ties the two phases of Nylon12 and NR together, and allow energy to be transferred from one phase to the other. This helps the NR component to improve the mechanical properties of the Nylon12 component. However, the dispersed phase sizes increase continuously due to the coalescence of NR particles with increasing PS/NR contents, resulting in the reduction of the total blend performance.
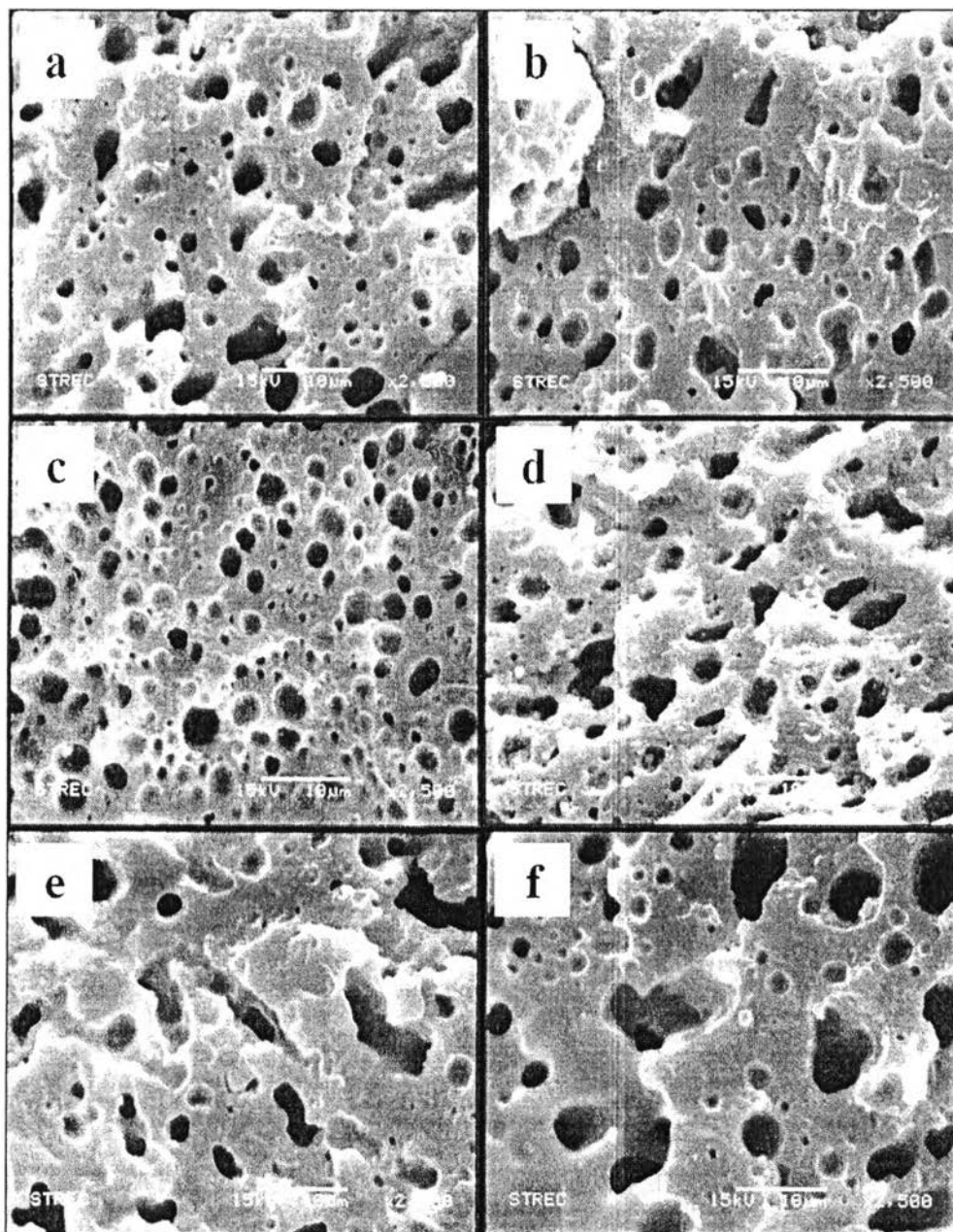
Figure 4.8 SEM micrographs of the cryofracture surfaces of the
[Nylon12/NR]/[PS/NR] blends with PS/NR compatibilizer contents of: (a) 0 phr, (b)
5 phr, (c) 10 phr, (d) 15 phr, (e) 20 phr and (f) 25 phr.

Table 4.2 The interfacial tension values of polymers at the processing temperatures of 190 °C [19] and 210 °C

Polymer Pairs	Interfacial Tension [mN/m]	
	190 °C	210 °C
Nylon12/NR	2.21	2.08
Nylon12/PS	0.28	0.23
NR/PS	3.14	2.97

4.4.7 Rheological Properties of [NYLON12/NR]/[PS/NR] Blends

4.4.7.1 Flow Properties

In order to characterize the processing properties of polymer melt, it is necessary to know the flow properties. Figure 4.9 shows the logarithmic plots of shear stress versus shear rate for neat Nylon12, Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blends with various PS/NR contents using the 20 mm die length at 210 °C. Flow curves of all materials illustrate that shear stress increases approximately linearly with increasing shear rate, whose intercept K and slope n correspond to the Ostwald-de Waele equation or "the power law equation" [9] as shown in Equation (4.10).

$$\tau = K(\dot{\gamma})^n \tag{4.10}$$

where K is the consistency of flow or viscosity coefficient index, and n is the power law index or the flow behavior index. The results show the increasing of shear stress of the [Nylon12/NR]/[PS/NR] blends at low compatibilizer contents. Then the shear stress decreases continuously at high PS/NR contents. The effect of PS/NR compatibilizer contents on the flow properties of the Nylon12/NR blend will be discussed in next section.
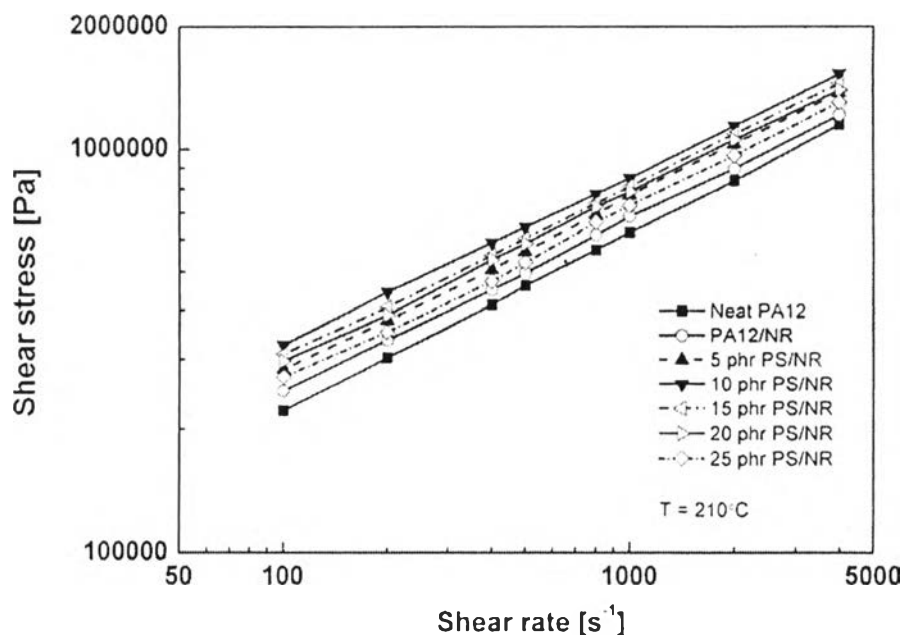
Figure 4.9 Shear stress as a function of shear rate of neat Nylon12. Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blends with various PS/NR compatibilizer contents (temp = 210 °C).

At 210 °C with using the 20 mm die length after the corrections have been applied, plots of shear viscosity versus shear rate are shown in Figure 4.10. The shear viscosity of all blends decreases with increasing shear rate, indicating shear-thinning or pseudoplastic behavior of the polymer melts. For pseudoplastic behavior, asymmetric molecular chains are randomly oriented and/or extensively entangled at rest. Under shear, molecular chains become oriented in the flow direction, and the chain entanglements are reduced, resulting in the decrease of viscosity. At very high shear rate, the orientation may be complete, and near Newtonian behavior may be observed [20]. Over the entire range of shear rate studied, the results also show that viscosity of Nylon12 is lower than that of NR. Therefore, the shear viscosity of all blends lie in between that of the homopolymer.
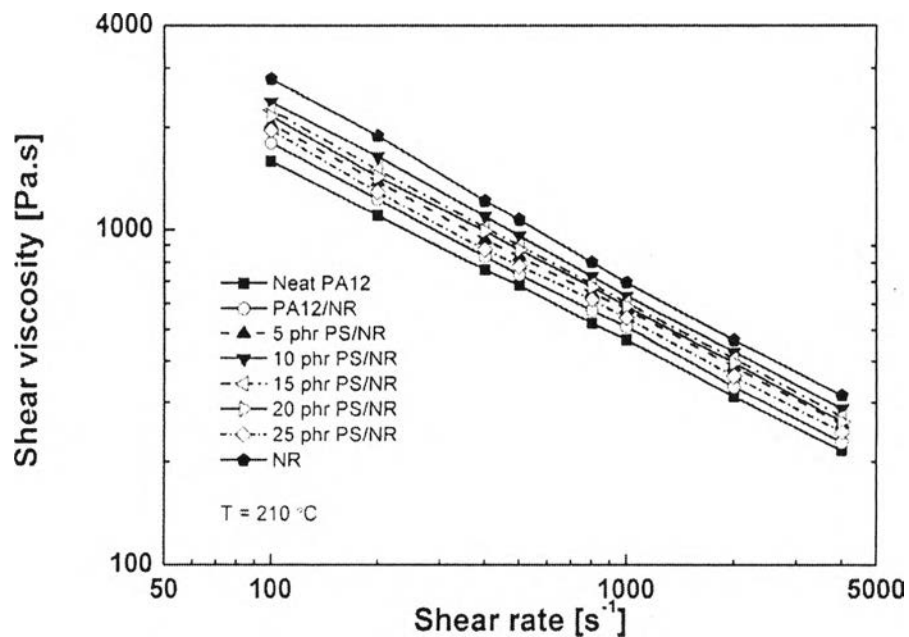
Figure 4.10 Shear viscosity *versus* shear rate of neat Nylon12, Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blends with various PS/NR compatibilizer contents (temp = 210 °C).

For the power law index (n), the n values are less than one as shown in Table 4.3, confirming pseudoplastic behavior at processing temperature. With an increase in temperature, the n values increase, i.e. the materials become less pseudoplastic or more Newtonian or indicating more stable flowability with increasing temperature. On the other hand, the incorporation of 20 wt% NR into Nylon12 and the addition of PS/NR blend enhance the pseudoplasticity of Nylon12, leading to the decrease of power law index.

Table 4.3 Power law index (*n*) of the [Nylon12/NR]/[PS/NR] blends at various temperatures

Materials	Power Law Index [*n*]			
	205 °C	210 °C	215 °C	220 °C
Neat Nylon12	0.4378	0.4447	0.4503	0.4626
Nylon12/NR	0.4267	0.4301	0.4398	0.4453
[Nylon12/NR]/[PS/NR]				
5 phr	0.4203	0.4221	0.4307	0.4391
10 phr	0.4095	0.4153	0.4256	0.4301
15 phr	0.4013	0.4124	0.4175	0.4268
20 phr	0.3967	0.4085	0.4092	0.4149
25 phr	0.3911	0.4029	0.4074	0.4101

4.4.7.2 Effect of PS/NR Compatibilizer Contents

For the addition of compatibilizer, when small contents of PS/NR blend (5-10 phr) are added into the Nylon12/NR blend, it is clear that the PS/NR blend makes the Nylon12/NR blend more compatible. This is because the PS/NR blend can reduce the interfacial tension of the melt and leads to the fine dispersion of NR domains in the Nylon12 matrix providing an increased interfacial interaction. As a result, the shear viscosity of [Nylon12/NR]/[PS/NR] blends increases as shown in Figure 4.11. However, at higher PS/NR contents (15-25 phr), the shear viscosity of the blends decreases continuously. It can result from the possibility of NR chain degradation and coalescence of NR particles (more NR content by the addition of PS/NR blend) which then act like a plasticizer. Although the higher PS/NR content added to the blend of Nylon 12/NR suggests the higher amount of gel, the viscosity that should be increased is suppressed by more NR chain degradation with increasing NR content.
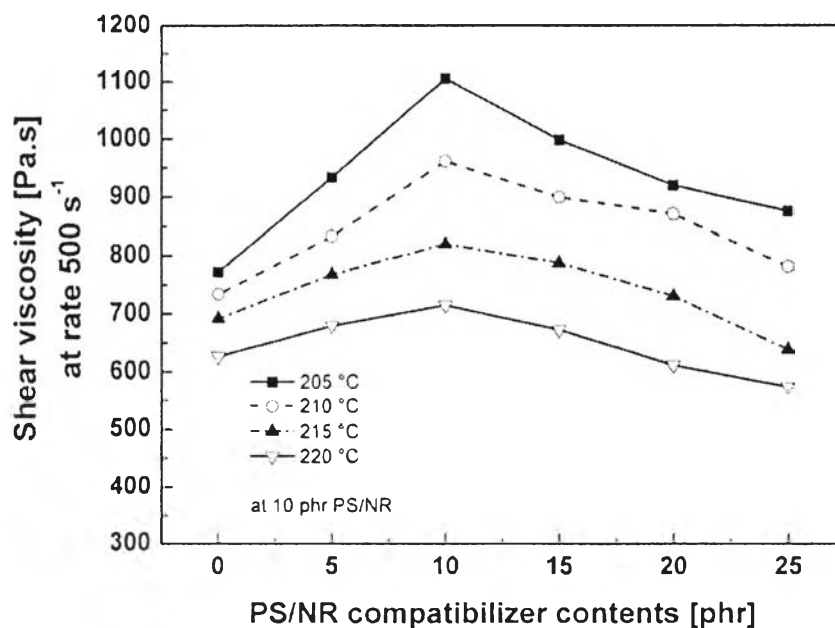
Figure 4.11 Shear viscosity as a function of PS/NR compatibilizer contents at shear rate of 500 s^{-1} and various temperatures.

4.4.7.3 Effect of Temperatures

In the polymer melt, increasing temperature results in the decrease of viscosity as shown in Figure 4.12. This is due to greater free space available for molecular chain motion at higher temperature [20,21]. For the flow activation energy, the temperature dependence of shear viscosity was fitted using the following Arrhenius–Frenkel Eyring Equation (4.11).

$$\eta = A_0 \exp\left(\frac{E_a}{RT}\right) \tag{4.11}$$

where η is the shear viscosity at a particular shear rate, A_0 is approximately a constant, and R, T, and E_a are taken to be the molar gas constant, the absolute temperature, and the flow activation energy, respectively. The E_a values, which can be calculated from the slope of plot between ln η versus 1/T at various shear rates (Figure 4.13), are tabulated in Table 4.4. The activation energy for viscous flow

decreases with increasing shear rate. The shearing reduces number of entanglement coupling points and, hence, results in the decrease of interaction between chain segments [22]. The activation energy for flow of Nylon 12/NR binary blend is less than that of Nylon 12 indicating the degradation of NR at high temperature. For the addition of compatibilizer, at each shear rate, the flow activation energy becomes greater than that of Nylon12/NR blend and also increases with increasing PS/NR content up to 10 phr, and then it decreases continuously. This is due to the limitation of molecular chain motion [23] by the increased interfacial interaction between Nylon12 and NR phases at the optimum compatibilizer content, and more energy is required to break the interactions and allow the material to flow. Beyond the optimum amount of compatibilizer, the degradation of NR becomes dominant bringing down or facilitating the flow.
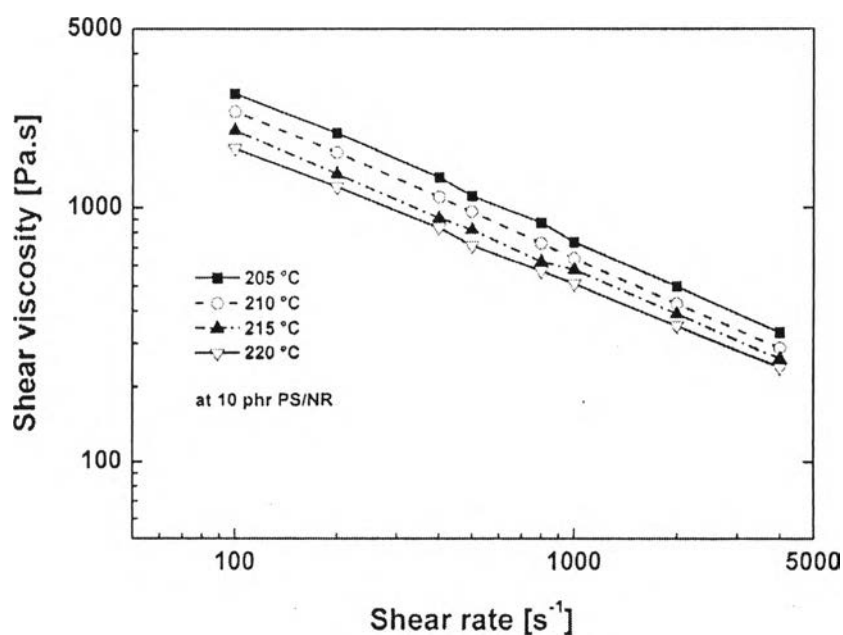

Figure 4.12 Shear viscosity of [Nylon12/NR]/[PS/NR] blends at PS/NR compatibilizer content of 10 phr as a function of shear rates at various temperatures.
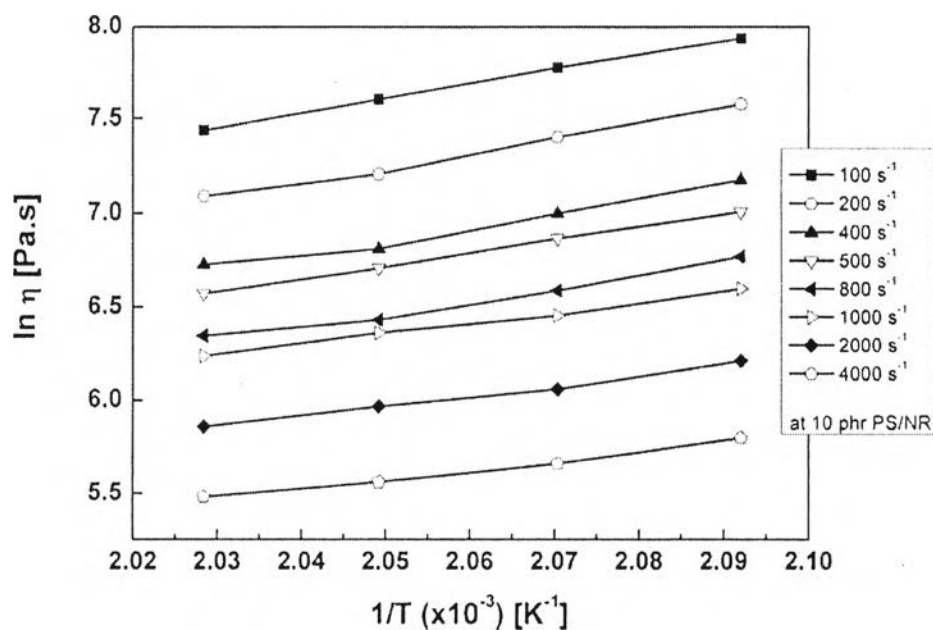
Figure 4.13 Shear viscosity of [Nylon12/NR]/[PS/NR] blends at PS/NR compatibilizer content of 10 phr as a function of reciprocal temperatures (1/T) at various shear rates.

Table 4.4 The activation energy (E_a) for viscous flow of Neat Nylon12, Nylon12/NR, and [Nylon12/NR]/[PS/NR] blends at shear rates of 100-4000 s^{-1}

Materials	Activation Energy (Ea) [kJ/mol]							
	100	200	400	500	800	1000	2000	4000
Neat Nylon12	65.70	65.11	61.63	59.99	58.41	49.00	46.84	44.21
Nylon12/NR	62.04	60.42	58.37	55.74	54.12	44.39	42.70	38.98
[Nylon12/NR]/[PS/NR]								
5 phr	63.68	62.01	59.57	56.73	55.12	45.46	43.76	39.83
10 phr	65.17	64.95	60.22	57.42	56.41	46.64	44.82	41.39
15 phr	64.02	63.95	59.89	56.96	55.73	46.00	44.15	39.62
20 phr	63.61	63.45	58.39	56.13	54.32	44.98	43.24	37.47
25 phr	61.94	59.80	57.54	55.30	53.38	43.65	41.87	37.12

To study a thermal stability of the blends, TGA thermograms of Neat Nylon12, NR, PS/NR blend, Nylon12/NR blend and [Nylon12/NR]/[PS/NR] blends at compatibilizer loading of 10 phr are represented in Figure 4.14. It is obvious that NR and Neat Nylon12 exhibit one step of decomposition while two steps of decomposition are found in PS/NR compatibilizer and Nylon12/NR binary blend. For [Nylon12/NR]/[PS/NR] blend, the decomposition temperature of PS is close to that of Nylon12 as shown in Table 4.5. Therefore, the separated step of these two polymers cannot be observed in the TGA thermograms. The results reveal that all main components decompose at temperature above 300 °C. For the thermal stability of NR, the decomposition temperature of NR shifts to higher values for polymer/rubber blend, compared to that of neat NR. However, NR consists of a small amount (less than 2 %) of proteins and amino acids. Furthermore, the presence of the proteins in NR increases its moisture absorption [24]. These components may degrade on prolonged heating at rheological test temperatures, leading to the decreasing of shear viscosity and the change in color of extrudates.
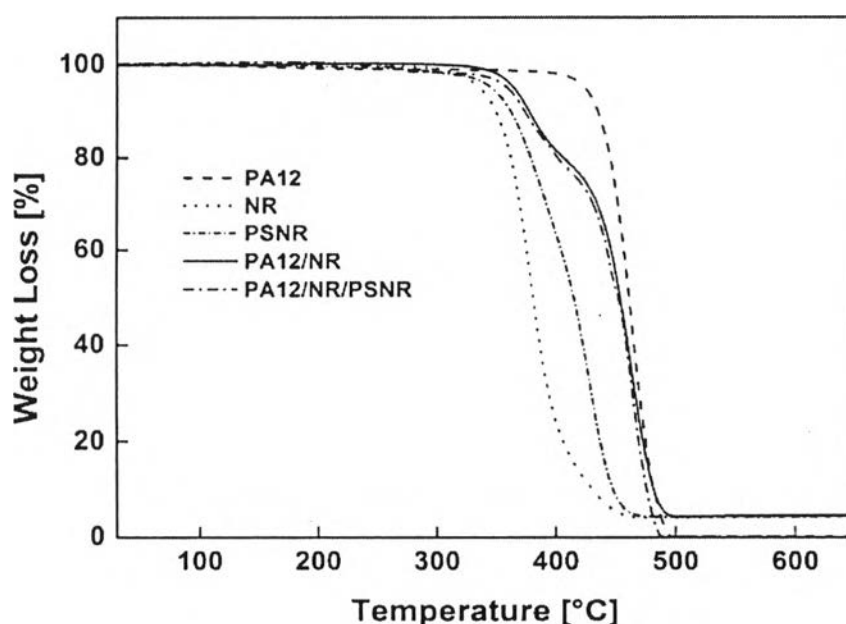

Figure 4.14 TGA thermograms of Neat Nylon12, NR, PS/NR compatibilizer, Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blend.

Table 4.5 Decomposition temperatures of Neat Nylon12, NR, PS/NR compatibilizer, Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blends

Materials	Decomposition Temperature (onset) [°C]		
	NR	PS	Nylon12
Neat Nylon12	-	-	441.3
NR	354.7	-	-
PS/NR	356.3	400.0	-
Nylon12/NR	357.1	-	441.7
[Nylon12/NR]/[PS/NR]	356.0	Merged with Nylon12	441.5

4.4.7.4   Extrudate Swell

The extrudate swell or die swell highly depends on the polymer properties, like molecular weight and its distribution, as well as the flow conditions such as shear rate, die length, temperature, etc. Generally, the extrudate swell is closely related to elastic properties and occurs as a result of the recovery of the elastic deformations imposed in the capillary [25]. When the molten polymer flows through the capillary under shear, it will maintain orientation of molecular chains. As the melt leaves the die, recoiling of molecular chains occurs, leading to the phenomenon of extrudate swelling [26]. Therefore, understanding the factors which control extrudate swell is important for extrusion processes.

The extrudate swell of the Nylon12/NR blend as a function of PS/NR compatibilizer contents and shear rates at 210 °C from the 20 mm die length is shown in Figure 4.15. The result reveals that the extrudate swell increases with increasing shear rates. This is because a high shear rate means shorter residence times in the capillary and less time for relaxation. As a consequence, more recoverable elastic energy stored in the polymer melt provides a high extrudate swell. Addition of NR into Nylon12 causes more swelling due to its highly elastic structure. For the addition of compatibilizer, the percentages of extrudate swell decrease gradually with increasing PS/NR contents. At small contents of compatibilizer, PS/NR blend enhances the interfacial adhesion between Nylon 12 matrix and NR

domains. This results in limiting the movement of the molecules during elastic recovery upon leaving the die, resulting in the decreasing of swelling. However, at high PS/NR contents, it is suggestion that the degradation of NR chains cause the decreasing of swelling.
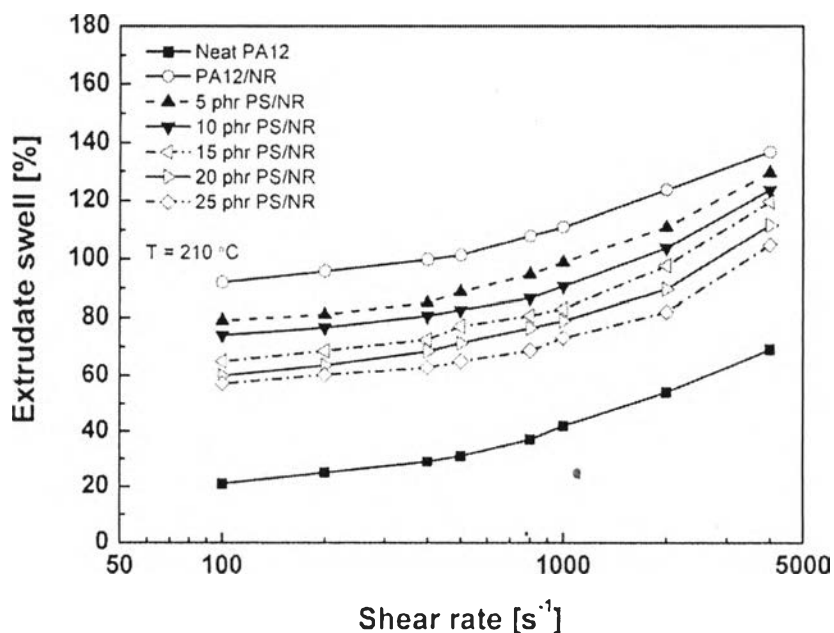

Figure 4.15 The extrudate swell (%) of neat Nylon12, Nylon12/NR binary blend and [Nylon12/NR]/[PS/NR] blends as a function of shear rates (temp = 210 °C).

4.5 Conclusions

The influence of the screw speed on the reactive blending of PS and NR reveals the possibility of NR cross-linking (gel) at low screw speed. The reaction of PS to NR to form the graft copolymer of PS and NR was better achieved at a high screw speed. Therefore, the PS/NR (60/40 wt%) blend at the screw speed of 45 rpm was used as the compatibilizer. The [Nylon12/NR]/[PS/NR] blends show improved mechanical, morphological, and flow properties at the optimum compatibilizer content of 10 phr. This could be attributed to the improved interfacial adhesion as seen by the size reduction of rubber domains, i.e., reducing the scale of dispersion and stabilizing the morphology. An excess of PS/NR content leads to the coalescence

of NR domains, more gel, poorer interfacial interaction, and more NR chain degradation.

Melt rheological properties and extrudate swell of the [Nylon12/NR]/[PS/NR] blends were investigated using a capillary rheometer. The blends show shear thinning or pseudoplastic behavior at the processing temperature. The incorporation of 20 wt% NR into Nylon12 and the addition of PS/NR blend enhance the pseudoplasticity of Nylon12. At the optimum compatibilizer content, the blends show a maximum in shear viscosity and flow activation energy. This is due to increased interfacial interaction between NR domains and Nylon12 matrix. The extrudate swell of the [Nylon12/NR]/[PS/NR] blends also decreased with increasing PS/NR content, suggesting improved interfacial adhesion between Nylon12 and NR. Therefore, the success of using the PS/NR blend as a compatibilizer for a Nylon12/NR immiscible blend is ensured by the higher viscosity, higher flow activation energy, and lower extrudate swelling.

4.6 Acknowledgements

4.7 References

1. Phinyocheep, P.; Saelao, J.; Buzare, J.Y. Polymer 2007, 48, 5702-5712.
2. Tanrattanakul, V.; Sungthong, N.; Raksa, P. Polym Test 2008, 27, 794-800.
3. Borggreve, R.J.M.; Gaymans, R.J.; Schuijer, J.; Ingen Housz, J.F. Polymer 1987, 28, 1489-1496.

4. Huang, J.W.; Chang, C.C.; Kang, C.C.; Yeh, M.Y. Thermochim Acta 2008, 468, 66-74.

5. Asaletha, R.; Groeninckx, G.; Kumaran, M.G.; Thomas, S. J Appl Polym Sci 1998, 69, 2673–2690.

6. Helfand, E.; Tagami, Y. J Polym Sci Pol Lett 1971, 9, 741-746.

7. Helfand, E.; Sapse, A.M. J Chem Phys 1975, 62, 1327-1331.

8. Asaletha, R.; Kumaran, M.G.; Thomas, S. Rubber Chem Technol 1995, 68, 671-687.

9. Brydson, J.A. Flow properties of polymer melts, Van Nostrand Reinhold: New York, 1970.

10. Cogswell, F.N. Polymer melt rheology: A guide for industrial practice, Woodhead Publishing: Cambridge, 1996.

11. Premphet, K.; Chalearmthitipa, S. Polym Eng Sci 2001, 41, 1978-1986.

12. Charmondusit, K.; Kiatkamjornwong, S; Prasassarakich, P. J Sci Chula Univ 1998, 23.

13. Lenka, S.; Nayak, P.L.; Das, A.P. J App Polym Sci 1985, 30, 2753-2759.

14. Munteanua, S.B.; Vasile, C. J Optoelectron Adv M 2005, 7, 3135-3148.

15. Jin, C.Y.; Michael, J.J.; Jimmy, W.M. Polymer 2002, 43, 5125-5132.

16. Horiuchi, S.; Matchariyakul, N.; Yase, K.; Kitano, T. Macromolecules 1997, 30, 3664-3670.

17. Cigna, G.; Matarrese, S.; Biglione, G.F. J Appl Polym Sci 1976, 20, 2285-2295.

18. Laosee, T.; Phinyocheep, P.; Axtell, F.H. J Sci Soc Thailand 1998, 24, 251-264.

19. Magaraphan, R.; Totanapoka, C.; Alexander, J.M. Des Monomers Polym 2004, 7, 165-180.

20. Muksing, N.; Nithitanakul, M.; Grady, B.P.; Magaraphan, R. Polym Test 2008, 27, 470-479.

21. Saini, D.R.; Shenoy, A.V.; Nadkarni, V.M. Polym Composite 1986, 7, 193-199.

22. Li, S.; Järvelä, P.K.; Järvelä, P.A. J Appl Polym Sci 1999, 71, 1641-1648.

23. Li, D.; Jia, D.; Zhou, P. J Appl Polym Sci 2004, 93, 420-427.

24. Bhowmick, A.K.; Stephens, H.L. Handbook of Elastomers: Second edition, revised and expanded, Marcel Dekker: New York, 2001.

25. Bajaj, P.; Jha, N.K.; Jha, R.K. Brit Polym J 1989, 21, 345-355.

26. Kumar, C.R.; Nair, S.V.; George, K.E.; Oommen, Z.; Thomas, S. Polym Eng Sci 2003, 43, 1555-1565.