

## CHAPTER VI

### FLOW AND STRUCTURE OF COMPATIBILIZED NYLON12/NATURAL RUBBER BLEND WITH FUNCTIONAL COPOLYMER

#### 6.1 Abstract

Polyamide12 (PA12, Nylon12)/natural rubber (NR) blend was prepared by melt mixing in a Brabender mixer using polystyrene/maleated natural rubber (PS/MNR) copolymer as a reactive compatibilizer. The influence of compatibilizer loading (1, 3, 5, 7, and 10 phr), shear rate ( $10\text{-}500\text{ s}^{-1}$ ), and temperature ( $200\text{-}220\text{ }^{\circ}\text{C}$ ) on the flow properties (i.e. shear viscosity, power law index, flow activation energy, and extrudate swell) of [Nylon12/NR]/[PS/MNR] blends were investigated. The blends showed pseudoplastic behavior from an evident increase of shear stress and a reduction of shear viscosity with increasing shear rate. Shear viscosity ( $\eta$ ) and flow activation energy ( $E_a$ ) of the blends were also found to increase with the compatibilizer loading. It suggests that PS/MNR copolymer functioned properly and enhanced the compatibility and interfacial interaction between Nylon12 matrix and NR domains via the formation of amide and succinimide linkages at the interfaces. This reactive compatibilization also caused in a reduction of extrudate swell apparently due to slower elastic recovery of polymer chains.

**Keywords:** Nylon12, Natural rubber, Reactive compatibilization, Rheological properties

#### 6.2 Introduction

Melt rheology describes the deformation and flow of material under stress. It is mainly concerned with the properties of material determining its behavior that it is a relationship between external action (forces applied to a material) and internal reaction (changes of a material structure).<sup>1</sup> Melt rheological study of material is of superior importance in processes such as extrusion, injection molding, and fiber

spinning where flow behavior through dies determines various product properties and leads to optimization of processing operation. In general, the materials undergo various changes in polymer processing operation. Therefore, rheological parameters (shear stress and shear rate) affecting melt viscosity, flow activation energy, and extrudate swell have become important determinant. Many of the problems that arise during processing can be solved with proper understanding of the flow behavior.<sup>2</sup>

Thermoplastic polymer/rubber blends mostly exhibit immiscibility due to low entropy of mixing. In these systems, the lack of specific molecular interactions leads to high interfacial tension during processing and results in poor interfacial adhesion, rough phase structure, and therefore poor mechanical properties in finished products.<sup>3</sup> The blend properties can be significantly improved by adding a third component called compatibilizer into these systems. Generally, a compatibilizer for immiscible polymer blends is a specially synthesized copolymer with one part miscible in either of the phases in this context. The commercially available copolymers are not versatile enough to accommodate an array of different blend systems. Reactive blending approach is the most commonly used technique to form in situ-compatibilizers for immiscible blends. The reactive blending approach entails drop in strategy of previously synthesized molecule. Accordingly, ease of processing and lower capital expenses are two attributes in scale-up and commercialization. Our previous work showed that a compatibilized blend of polystyrene (PS) and natural rubber (NR) could be easily obtained due to the presence of PS-NR graft copolymers formed via their reactive blending with dicumyl peroxide (DCP) as an initiator. This non-reactive PS-NR blend was further used as a compatibilizer for Nylon12/NR blend.<sup>4</sup> The non-reactive compatibilizer molecules locate themselves between the homopolymers e.g. PS part interfaces Nylon12 phase while NR part is miscible with the NR phase. The compatibilizer forms the interface layer and leads to a unique inclusion morphology in the blend. Consequently, the contact between Nylon12 and NR is minimized and the enthalpy of mixing between Nylon12 and NR is reduced, leading to better compatibility between the phases via the copolymer and the enhancement of blend performance, e.g., toughness. The reactive compatibilizers functions via chemical reactions between the functional groups of component polymers of the blend. In past several years, a number of reactive materials were

used as compatibilizers of polyamide/elastomer blends. For instance, polyamide 6 (Nylon6) blends with poly (acrylonitrile-butadiene-styrene) (ABS) can be compatibilized by maleated polybutadiene (PB-g-MA),<sup>5</sup> styrene-maleic anhydride copolymer (SMA),<sup>6,7</sup> imidized acrylic (IA),<sup>8</sup> and glycidyl methacrylate/methyl methacrylate (GMA/MMA) copolymers.<sup>9</sup> Chlorinated polyethylene (CPE)<sup>10</sup> has also been used as a compatibilizer for Nylon6/nitrile rubber (NBR). Styrene-ethylene-butadiene-styrene block copolymer (SEBS),<sup>11</sup> polyethylene (PE),<sup>12</sup> and polypropylene (PP)<sup>13</sup> are functionalized directly with maleic anhydride (MA) and used as compatibilizers when these polymers are blended with Nylon6. In general, MA-functionalized polymers are widely used as the reactive compatibilizers because MA can be readily grafted onto many polymers at normal melt processing temperature.<sup>14</sup> These reactive compatibilizers not only act as dispersants for the elastomers in the Nylon6 phase but also increase the interfacial adhesion between two phases via chemical linkage. As a result, the blend properties are enhanced.

Utracki *et al.*<sup>15</sup> stated that the presence of a compatibilizer, a block or graft copolymer, not only reduced the interfacial tension, but also changed the molecular arrangement at the interface. In view of this, the reactive compatibilization may also affect the processability, the blend properties, and the flow behavior. The rheological properties of Nylon6/PP blend using MA-g-PP and SEBS-g-MA as compatibilizers were reported by Marco *et al.*<sup>13</sup> and by Holsti-Miettinen *et al.*<sup>16</sup>, respectively. They demonstrated that chemical reactions occurring between the components of the blends due to compatibilization at the interfaces increased the viscosity of the system. Moreover, a positive deviation of the viscosity from a log additive rule was found in compatibilized immiscible blends due to the enhancement of compatibility. Some research works also studied the effects of MA on the blend viscosity. Minkova *et al.*<sup>17</sup> revealed that SEBS-g-MA had a higher compatibilizing efficiency than SEBS at 2 phr loading, as apparent from an increase of zero shear viscosity of LDPE/PA6 blend from 5200 to 5400 Pa.s. Kim and Pal<sup>18</sup> reported that the shear viscosity of PP/wood fiber (WF) composites was the highest (1585 Pa.s) in the presence of SEBS-g-MA at 10 phr, followed by SEBS (1260 Pa.s), and without compatibilizer (1000 Pa.s). The reactions between WF and the polar compatibilizer were found responsible.

In this article, it is interesting to further improve the performance of a Nylon12/NR blend by reactive compatibilization using the functionalized PS/NR molecules. Natural rubber (NR) was functionalized by using maleic anhydride (MA). The reactive blend of polystyrene and maleated natural rubber (PS/MNR) was then prepared and used as a reactive compatibilizer for the Nylon12/NR blend. The aim was to enhance the interfacial adhesion between NR domains and Nylon12 matrix via chemical reaction. It was expected that the compatibilization of the immiscible polymer blends would affect their flow behavior. Therefore, the work extends to study the rheological characteristics of [Nylon12/NR]/[PS/MNR] blends by using a capillary rheometer. The influence of the compatibilizer content, shear rate, and temperature on the melt viscosity, flow activation energy and extrudate swell was investigated. This study illustrated that the flow activation energy of [Nylon12/NR]/[PS/MNR] blends closely related to their structure. The higher flow activation energy, the more formation of amide and succinimide linkages (bulky structure) would be occurred at the Nylon/Rubber interfaces. This also led to an increase of shear viscosity and a decrease of extrudate swell of the compatibilized blends with increasing PS/MNR loading up to 7 phr.

## 6.3 Experimental

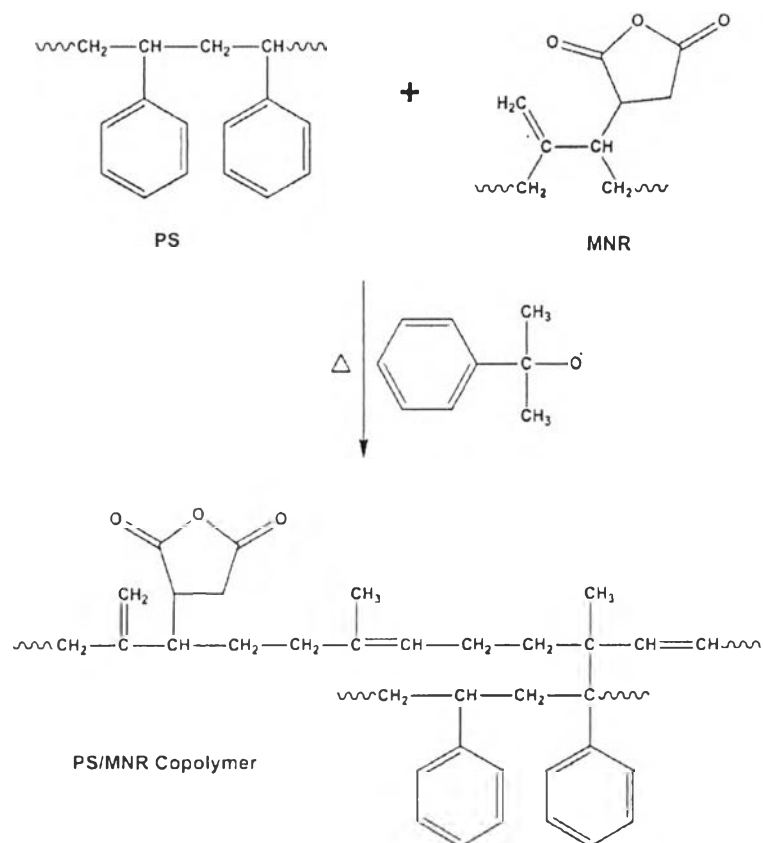
### 6.3.1 Materials

Polyamide12, product name Grilamid<sup>®</sup> L25 natural, was supplied by EMS-Chemie (Sumter, South Carolina). The polymer was available on a pellet form with crystalline melting temperature of 178 °C. Natural rubber (NR) grade STR 5L was purchased from Banpan Research Laboratory (Thailand) in yellow solid bulk form. Copolymer of polystyrene/maleated natural rubber (PS/MNR) used as a reactive compatibilizer was prepared in our laboratory. The composition of the reactive compatibilizer was 60 wt% of PS and 40 wt% of MNR.

### 6.3.2 Polystyrene/Maleated Natural Rubber (60/40 wt%) Blend

Polystyrene/maleated natural rubber (PS/MNR) blend was prepared by using two-step reactive mixing process. In the first step, masticated NR (275 g) was added into the Brabender mixer (Prep center) and mixed for 3 min at a processing temperature of 135 °C and a rotor speed of 60 r/min. 8.25 g of maleic anhydride (MA) was then incorporated into rubber and further mixed for 5 min. Finally, the NR functionalized with MA, so called “maleated natural rubber (MNR)”, was removed from the chamber. In the second step, PS (165 g) was added and melted for 3 min at a processing temperature of 170°C and a rotor speed of 60 r/min. Next, 1.38 g of dicumyl peroxide (DCP) was added and mixed for 3 min. Finally, MNR (110 g) was added to molten PS and mixed further for 4 min. The obtained blend is called PS/MNR in the rest of the paper. The reaction taking place in preparation of this compound is shown in Scheme 6.1. This reactive blending involved reactions by free radical mechanism. Thus, besides the formation of PS-g-MNR copolymer, it was possible to gain some other by products, e.g., crosslinked NR (gel) via radical recombination reaction as well as chain scission of PS occurring through the homolytic cleavage of weak bonds in the polymer chains.<sup>19,20</sup> In view of this, the solvent extraction method presented in our previous work<sup>4</sup> was used to determine the contents of gel and unreacted PS short chains. The results showed that gel and the unreacted PS found in PS/MNR blend were 10.95 wt% and 30.11 wt%, respectively.

For PS and NR blend, PS (165 g) was added into the Brabender mixer and melted for 3 min. Next, 1.38 g of DCP was added and mixed for 3 min. Finally, masticated NR (110 g) was added to the molten PS and mixed further for 4 min. The obtained blend is termed PS/NR in the rest of the paper.



**Scheme 6.1** Reaction between PS and MNR using DCP as an initiator.

### 6.3.3 [Nylon12/NR (80/20 wt%)]/[PS/MNR] Blends

The blends of 80/20 wt% of Nylon12/NR with PS/MNR used as the reactive compatibilizer at various contents (1, 3, 5, 7 and 10 phr) were prepared by melt-mixing process in the Brabender mixer. The condition was set at 210 °C for a processing temperature and 70 r/min for a rotor speed. First, Nylon12 was fed into the chamber and allowed to melt for 3 min. Then masticated NR and PS/MNR were added and mixed for another 4 min. Finally, the blends were taken out of the chamber, cooled down to room temperature, and ground into small pieces for study of rheological properties.

The solvent extraction method was used after blending process to determine the content of Nylon12-g-MNR in [Nylon12/NR]/[PS/MNR] blends by dissolving the crude blends in toluene at 120 °C for 3 days, and then by precipitating the solution in acetone. In the process, unreacted NR was removed from the blend.

After vacuum drying, the blends without unreacted NR were dissolved in formic acid at 70 °C for 4 days, and then precipitated in water. In this manner, the unreacted Nylon12 was removed from the materials. The purified product is specified in this paper as Nylon12-g-MNR, and its content (graft ratio) was calculated by using Equation (6.1). The chemical bonds formed by the reactions between maleic anhydride groups in compatibilizer and amine-end groups in Nylon12 of the purified products were investigated by using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). FTIR spectra of materials were recorded using a Nicolet 6700 infrared spectrometer in the range of 4000-600  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

$$\text{Graft ratio} = \frac{\text{weight of Nylon12 - g - MNR after solvent extraction}}{\text{weight of crude blend before solvent extraction}} \quad (6.1)$$

#### 6.3.4 Melt Rheological Measurements

Rosand RH7 capillary rheometer (twin bores with bore diameter of 15 mm and bore length of 290 mm) was used to investigate the melt rheology and the extrudate (die) swell of [Nylon12/NR]/[PS/MNR] blends. A capillary die with length-to-inner diameter (L/D) ratio of 32/1 was used. All measurements were made at three test temperatures of 200, 210 and 220 °C and the range of apparent shear rates varied from 10 to 500  $\text{s}^{-1}$ . For capillary flow, the values of apparent shear stress, apparent shear rate, and apparent shear viscosity were calculated using a derivative of the Poiseuille law.<sup>21</sup> The apparent shear stress ( $\tau_{\text{app}}$ ) is defined in Equation (6.2).

$$\tau_{\text{app}} = R\Delta P/2L \quad (6.2)$$

where R is the die radius (mm),  $\Delta P$  is the pressure drop across the die (Pa), and L is the die length (mm). Equation (6.3) presents an expression of apparent shear rate ( $\dot{\gamma}_{\text{app}}$ ).

$$\dot{\gamma}_{\text{app}} = 4Q/\pi R^3 \quad (6.3)$$

where  $Q$  is the volumetric flow rate ( $\text{m}^3/\text{s}$ ). According to these values, the apparent shear viscosity ( $\eta_{\text{app}}$ ) is defined as the ratio of apparent shear stress to apparent shear rate as shown in Equation (6.4).

$$\eta_{\text{app}} = \tau_{\text{app}} / \dot{\gamma}_{\text{app}} \quad (6.4)$$

The percentage of extrudate (die) swell (B) is reported by using Equation (6.5).

$$\%B = [(D_e - D)/D] \times 100 \quad (6.5)$$

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

## 6.4 Results and Discussion

### 6.4.1 Graft Ratio and Gel Content

As the reactive blend of PS/MNR was used as a reactive compatibilizer in preparation of 80/20 wt% Nylon12/NR blend, the formation of graft copolymer via an imidization reaction between MA groups of MNR and the amine-end groups of Nylon12 was possible. This reaction can produce the amide and succinimide linkages as shown in Scheme 6.2.<sup>22,23</sup> The reactive compatibilizer loading significantly affects the presence of Nylon12-g-MNR as shown in Table 6.1. The results demonstrate the increase of graft ratio from 0.23 for the purified blends containing 1 phr compatibilizer to approximately 0.46 when compatibilizer loading is increased up to 7 phr. In other words, the higher the reactive compatibilizer loading, the more the grafting reaction in the blends could occur. These suggest that PS/MNR blend acts as an effective compatibilizer, and leads to enhancement of compatibility between Nylon12 and NR via the formation of graft copolymers. In the presence of reactive compatibilizer, PS/MNR molecules ties Nylon12 phase and NR phase together via succinimide linkages. These bulky succinimide linkages could be located at the interfaces of Nylon12 and NR, leading to enhancement of interfacial

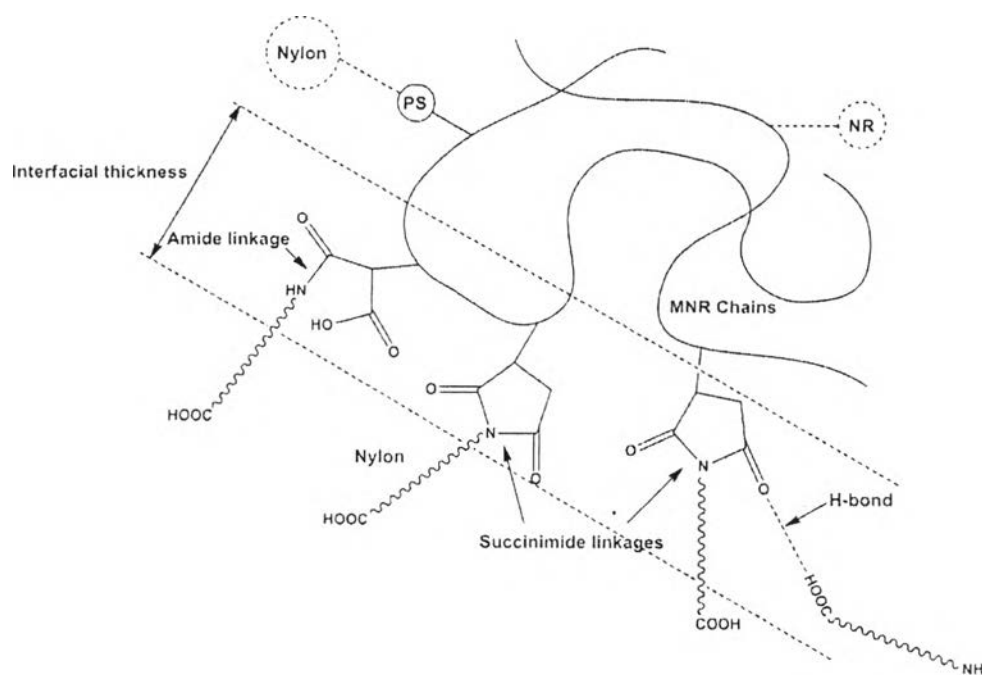


adhesion between the two phases as shown in Scheme 6.3. An increase of graft ratio also relates to a reduction of unreacted products both Nylon12 and NR in the blend. Beyond a particular compatibilizer content (7 phr); however, the graft ratio of the purified blends shows reduction. For example, at 10 phr of reactive compatibilizer, the graft ratio slightly decreased to around 0.42. This is probably due to the increase in crosslinked structure of NR (gel) as shown in Table 6.2 which obstructs the molecular chains of Nylon12 and MNR from reacting with each other; thus, resulting in the lowering of graft ratio at high PS/MNR compatibilizer content.



**Table 6.1** Contents of unreacted products and graft ratio in the purified blends with various compatibilizer contents

Compatibilizer Content	Unreacted Products		Graft Ratio
	Nylon12 (wt%)	NR (wt%)	
1 phr	61.11	15.33	0.23
3 phr	55.32	14.98	0.31
5 phr	49.18	14.26	0.38
7 phr	42.98	12.57	0.46
10 phr	46.19	14.93	0.42



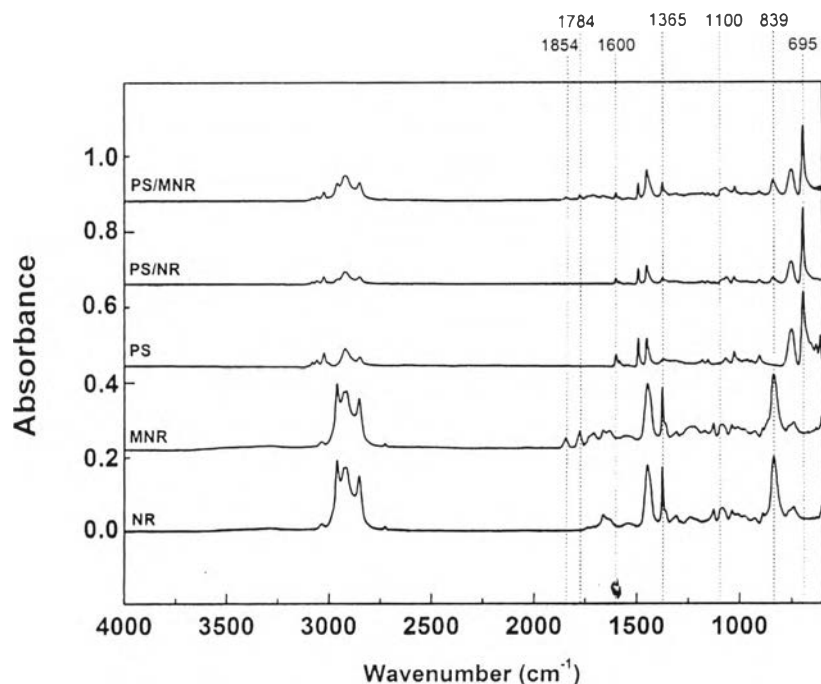
**Scheme 6.3** The presence of amide and succinimide linkages at Nylon12/NR interfaces.

**Table 6.2** Contents of gel (Crosslinked NR) and unreacted PS (PS short chain) in [Nylon12/NR]/[PS/MNR] blends with various compatibilizer contents

Compatibilizer Content	Gel (wt%)	PS Short Chain (wt%)
1 phr	0.11	0.30
3 phr	0.33	0.90
5 phr	0.55	1.51
7 phr	0.77	2.11
10 phr	1.10	3.01

#### 6.4.2 FTIR Results

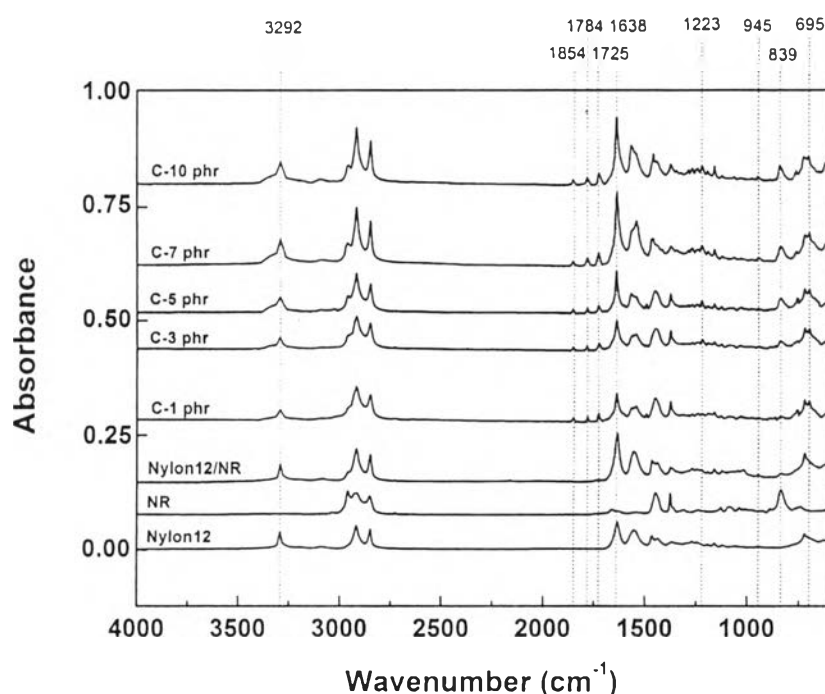
The reactive blending of PS and MNR (which contains both NR and NR-g-MA chains) can produce two compatibilizers: (1) polystyrene-g-natural rubber-g-maleic anhydride (SNR-g-MA) and (2) polystyrene-g-natural rubber (SNR). The former is a reactive compatibilizer as NR chains are functionalized with maleic anhydride and the latter is a non-reactive compatibilizer. The functional groups of reactive 60/40 wt% PS/MNR blend and 60/40 wt% PS/NR blend are shown in FTIR spectra in Figure 6.1. PS/NR and PS/MNR show their characteristic peaks of C-H bending and C=C stretching of benzene ring due to PS at  $695\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , respectively, while those of NR are at  $839$  and  $1365\text{ cm}^{-1}$  for C=C and aliphatic C-H stretching. The peak at around  $1100\text{ cm}^{-1}$  represents C-C-C bending suggesting the grafting position in in-situ graft copolymers SNR-g-MA and SNR formed in PS/MNR or PS/NR blends. The peaks at  $1784$  and  $1854\text{ cm}^{-1}$  of PS/MNR are respectively assigned to the symmetric and asymmetric C=O stretching vibration modes of five-membered cyclic anhydride.



**Figure 6.1** FTIR spectra of NR, MNR, PS, PS/NR and PS/MNR.

Figure 6.2 shows typical bands of Nylon12, NR, Nylon12/NR binary blend and the purified blends of [Nylon12/NR]/[PS/MNR] with various compatibilizer contents. For Nylon12 including Nylon12/NR binary blend and the purified blends, the signal at  $945\text{ cm}^{-1}$  is assigned to CONH in plane while the strong absorption of the amide carbonyl (C=O stretching) is positioned at  $1638\text{ cm}^{-1}$ . The characteristic peaks of NR ( $839\text{ cm}^{-1}$ ), PS ( $695\text{ cm}^{-1}$ ), and MA ( $1784$  and  $1854\text{ cm}^{-1}$ ) as discussed above are also seen in the purified blends. Furthermore, the C=O stretching of carboxylic acid produced from imidization is found at  $1725\text{ cm}^{-1}$ , while the succinimide linkages are notified from the obvious C-N stretching band at  $1223\text{ cm}^{-1}$  of the cyclic tertiary amide. It suggests that the reactive compatibilization of Nylon12 and NR using PS/MNR as the reactive compatibilizer was successfully obtained, leading to the formation of amide and succinimide linkages. In addition, the sharp peak at  $3292\text{ cm}^{-1}$  corresponds to N-H stretching of primary amine in Nylon12. For Nylon12/NR binary blend, the peak at this position is similar to that of neat Nylon12 due to the absence of reactions between Nylon12 and NR during processing. However, the FTIR spectra of the purified blends show the lowering of

peak intensity at  $3292\text{ cm}^{-1}$  and the presence of broader peak at  $3250\text{--}3400\text{ cm}^{-1}$ . It ensures that the imidization reaction occurred at Nylon12/NR interfaces, and the primary amines turned into secondary and tertiary amides providing amide and succinimide linkages, respectively. The absorbance of these characteristic peaks are seen to increase with an increase of compatibilizer content up to 7 phr as shown in Table 6.3. This reveals that the extent of a reaction between MA groups of MNR and the amine-end groups of Nylon12 increased with compatibilizer content. These observations are related in line with the arguments presented in relation to graft ratio as mentioned previously.



**Figure 6.2** FTIR spectra of Neat Nylon12, NR, Nylon12/NR binary blend, the purified blends of [Nylon12/NR]/[PS/MNR] with compatibilizer contents of 1 phr (C-1 phr), 3 phr (C-3 phr), 5 phr (C-5 phr), 7 phr (C-7 phr), and 10 phr (C-10 phr).

**Table 6.3** Absorbance of the purified blends with various compatibilizer contents

Compatibilizer Content	C=O	CONH	C-N	C=C
	A <sub>1784</sub>	A <sub>1638</sub>	A <sub>1223</sub>	A <sub>839</sub>
1 phr	0.015	0.057	0.018	0.012
3 phr	0.020	0.070	0.037	0.021
5 phr	0.024	0.104	0.046	0.033
7 phr	0.031	0.174	0.055	0.055
10 phr	0.026	0.146	0.049	0.046

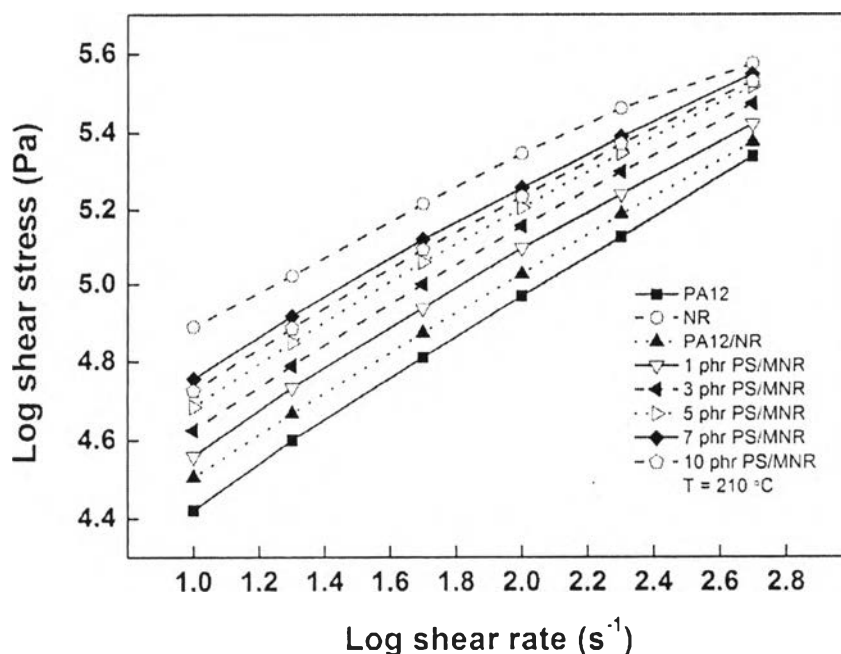
#### 6.4.3 Flow Properties

To study the flow properties of polymer melt for optimizing processing operations, the double logarithmic plot of relationship between shear stress and shear rate or “flow curve” was generated according to the Ostwald-de Waele equation<sup>2</sup> or “the power law equation” shown in Equation (6.6).

$$\tau = K (\dot{\gamma})^n \quad (6.6)$$

where  $\tau$  is the apparent shear stress (Pa),  $\dot{\gamma}$  is the apparent shear rate ( $s^{-1}$ ),  $K$  is the flow consistency index or the viscosity coefficient index, and  $n$  is the flow behavior index or the power law index. At the processing temperature of 210 °C, the flow curves obtained for neat Nylon12, NR, Nylon12/NR binary blend and [Nylon12/NR]/[PS/MNR] blends with various compatibilizer contents are shown in Figure 6.3. The results show an increase of shear stress of [Nylon12/NR]/[PS/MNR] blends with an increase of compatibilizer loading attributed to the enhancement of compatibility between Nylon12 and NR. The compatibilizer is compelled to locate at the interfaces between Nylon12 and NR phases during melt blending. The maleic anhydride groups in PS/MNR can undergo imidization reactions with the amine-end groups ( $-NH_2$ ) of Nylon12 providing the amide and the succinimide linkages. Many previous research studies elucidated that the reactions between the amine-end group

of nylon and the reactive groups of rubbers such as acrylate rubber and epoxidized natural rubber effectively increased the interfacial interactions.<sup>24-28</sup> These interactions lead to reduction of interfacial tension. In other words, the interfacial adhesion improves; thus, needing higher force (stress) for the materials to flow.



**Figure 6.3** Log shear stress of [Nylon12/NR]/[PS/MNR] blends as a function of log shear rate at varying compatibilizer contents.

From the flow curves, it is seen that the shear stress of all blends increased with increasing shear rate. However, the relation between shear stress and shear rate is not linear, indicating non-Newtonian fluid behavior. The flow behavior suggests more pseudoplastic nature for NR than Nylon12. The flow behavior of Nylon12/NR binary blend showed higher shear stress than Nylon12. For materials exhibiting pseudoplastic behavior, the asymmetric molecular chains are randomly oriented and/or extensively entangled at rest. At low shear rate, these chain entanglements impede severely the flow of the melt. As a consequence, the shear viscosity of the blends is high. The molecular chains undergo disentanglement at high shear rates, experience orientation in the flow direction resulting in a reduction



of shear viscosity.<sup>29</sup> Pseudoplasticity can be determined by power law index at values less than unity. Using power law relationship shown in Equation (6.6), the values of flow consistency index ( $K$ ) and the power law index ( $n$ ) are listed in Table 6.4. In general, the power law index depends on molecular structure and does not change much with temperature. In our case, the results demonstrated that the values of  $n$  slightly increased with increasing temperature. In the presence of reactive compatibilizer, the  $n$  values are seen to decrease from 0.5 for neat Nylon12 to 0.45 for [Nylon12/NR]/[PS/MNR] blends. In other words, the slopes of the flow curves or the power law indices reduce with increasing amount of PS/MNR and reach a minimum at 7 phr of PS/MNR. This suggests that less stress is required to initiate the flow at a given shear rate. One can attribute such lowering of shear stress to the bulky structure of the reactive compatibilization and the reaction products containing amide and succinimide linkages in the reactive blends. The bulky structure not only weakens the entanglement but also allows the existing entanglements to be unwound and oriented easily under high shear flow. The flow consistency index ( $K$ ) depends on temperature and chain mobility. The easier the chain mobility, the lower is the value of  $K$ . We see that the value of  $K$  for the compatibilized blends reduces with increasing temperature but increases with an increase of compatibilizer content.

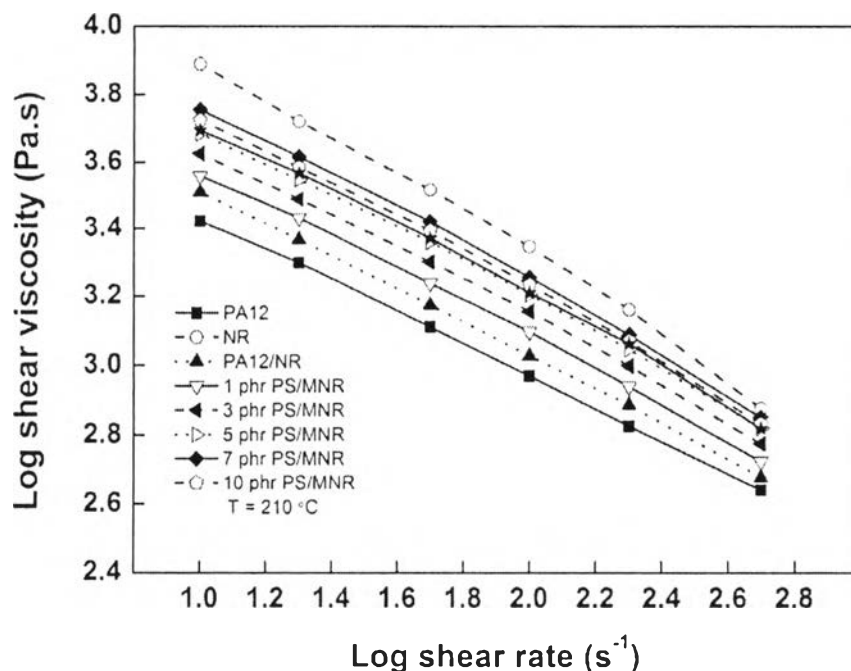
**Table 6.4** Flow consistency index ( $K$ ) and power law index ( $n$ ) of the compatibilized blends (C-Blends) at various temperatures and compatibilizer contents

Materials	$K$ (kPa)			$n$		
	200 °C	210 °C	220 °C	200 °C	210 °C	220 °C
Nylon12	9.85	8.30	7.00	0.5133	0.5216	0.5266
NR	45.25	38.38	33.28	0.3991	0.4131	0.4244
Nylon12/NR	13.33	10.31	9.01	0.4926	0.5019	0.5172
C-Blends						
1 phr	14.09	12.73	9.94	0.4717	0.4848	0.5118
3 phr	17.55	15.46	12.24	0.4618	0.4697	0.4874
5 phr	22.03	18.04	15.00	0.4571	0.4622	0.4771
7 phr	29.07	22.16	19.72	0.4280	0.4438	0.4451
10 phr	24.64	20.28	16.65	0.4471	0.4513	0.4666

The dependence of shear viscosity ( $\eta$ ) on shear rate ( $\dot{\gamma}$ ) is shown by Power-law Equation (6.7). The associated double logarithmic plot is shown in Figure 6.4.

$$\eta = K(\dot{\gamma})^{n-1} \quad (6.7)$$

At a given range of shear rate, NR exhibits higher viscosity than Nylon12, and the shear viscosities of [Nylon12/NR]/[PS/MNR] blends are in between those of the homopolymers.

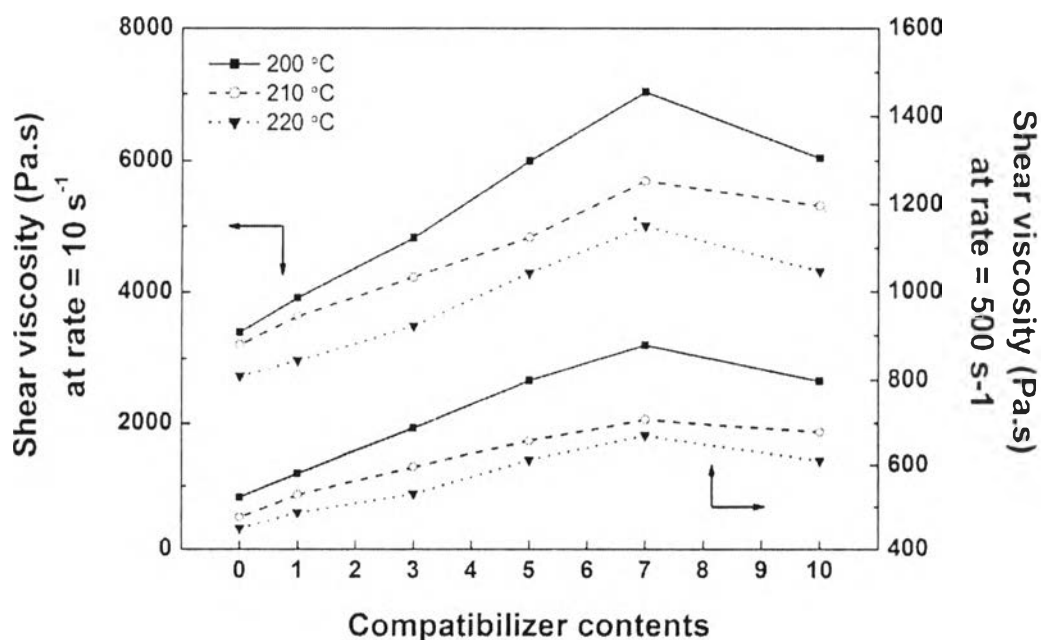


**Figure 6.4** Log shear viscosity of [Nylon12/NR]/[PS/MNR] blends as a function of log shear rate at varying compatibilizer contents.

#### 6.4.4 Effect of PS/MNR Content

Figure 6.5 shows the effect of PS/MNR content on shear viscosity. At two given shear rates, the increase of shear viscosity with compatibilizer content at low shear rate and at low temperature is more prominent than that at high shear rate and high temperature. This is due to greater chain entanglement at low shear rate and at low temperature. Also, the presence of compatibilizer increases the interfacial interaction between Nylon12 and NR phases via amide and succinimide linkages as well as via hydrogen bonds. These interactions tend to fix the molecular chains more strongly in position and resist deformation. As a consequence, the shear viscosity of the reactive compatibilized blends dramatically increases at low shear rate and at low temperature. With an increase in compatibilizer content up to 7 phr, the results show an increase of shear viscosity, corresponding to an increase of shear stress. This is attributed to an increase in the extent of imidization reaction, leading to more amide and succinimide linkages at Nylon12/NR interfaces. However, the shear viscosity of the blends containing 10 phr PS/MNR shows slight reduction. This is probably due

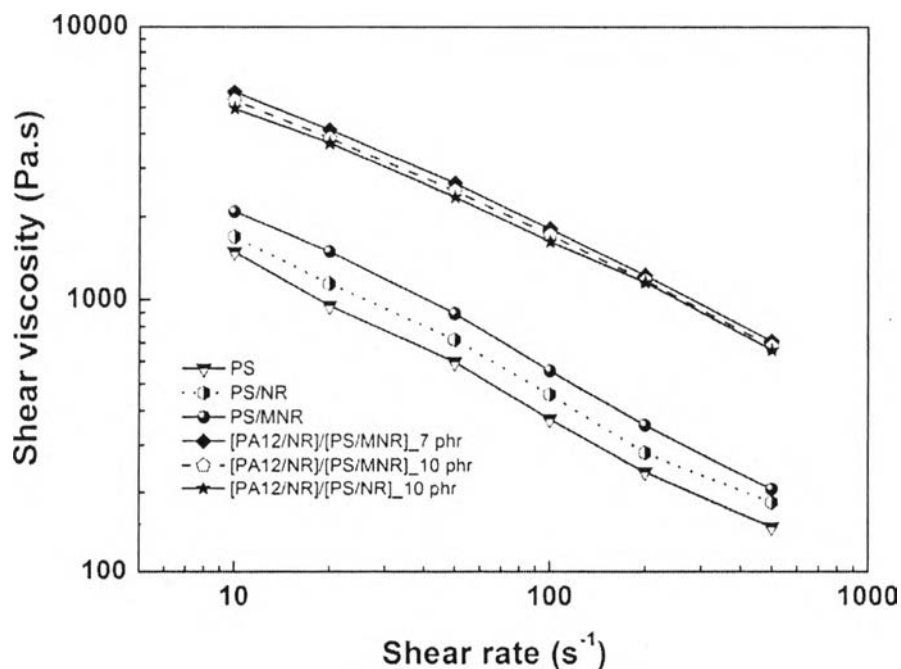
to the formation of low molecular weight product such as PS short chain that provides the plasticizing effect, leading to a reduction of cohesive strength between molecular chains.



**Figure 6.5** Shear viscosity as a function of compatibilizer contents at two constant shear rates ( $10$  and  $500 \text{ s}^{-1}$ ) and various temperatures.

We now discuss the effects of reactive compatibilizer (PS/MNR) and non-reactive compatibilizer (PS/NR) on viscosity of 80/20 wt% Nylon12/NR blends. It is seen in Figure 6.6 that each compatibilizer has much lower viscosity than those of Nylon12/NR/compatibilizer blends. At the same compatibilizer content of 10 phr, the shear viscosity of [Nylon12/NR]/[PS/MNR] blends is higher than that of [Nylon12/NR]/[PS/NR] blends approximately 1.07 times. Besides, it is found that in case of reactive compatibilizer PS/MNR, the maximum blend viscosity is at 7 phr, an optimum amount of reactive compatibilizer. At the 7 phr compatibilizer content, the reactive blend viscosity is found to be higher than that of non-reactive blend (data not shown) about 1.15 times. It is clear that the chemical interaction between Nylon12 and maleic anhydride (fraction in PS/MNR) provides additional adhesion or

compatibility between Nylon12 and NR phase over that of the physical interactions observed in the case of non-reactive compatibilizer PS/NR.



**Figure 6.6** The pseudoplastic behaviors of Neat PS, PS/NR, PS/MNR, the non-reactive compatibilized blends of [Nylon12/NR]/[PS/NR] at 10 phr PS/NR and the reactive compatibilized blends of [Nylon12/NR]/[PS/MNR] at 7 and 10 phr of PS/MNR.

In addition, the compatibility of polymer blend can be estimated by the log additive rule based on mass fraction and log viscosity of each component. This additive rule is a simple estimation of the properties based on combination of the nature of each component without any reaction between them. The log additive rule is shown in Equation (6.8).<sup>30,31</sup>

$$\log \eta_b = \sum W_i \log \eta_i \quad (6.8)$$

where  $\eta_i$  and  $\eta_b$  are the viscosity of the  $i$ th component and that of the blend and  $W_i$  is the weight fraction of the  $i$ th component. The measured value can be compared to the

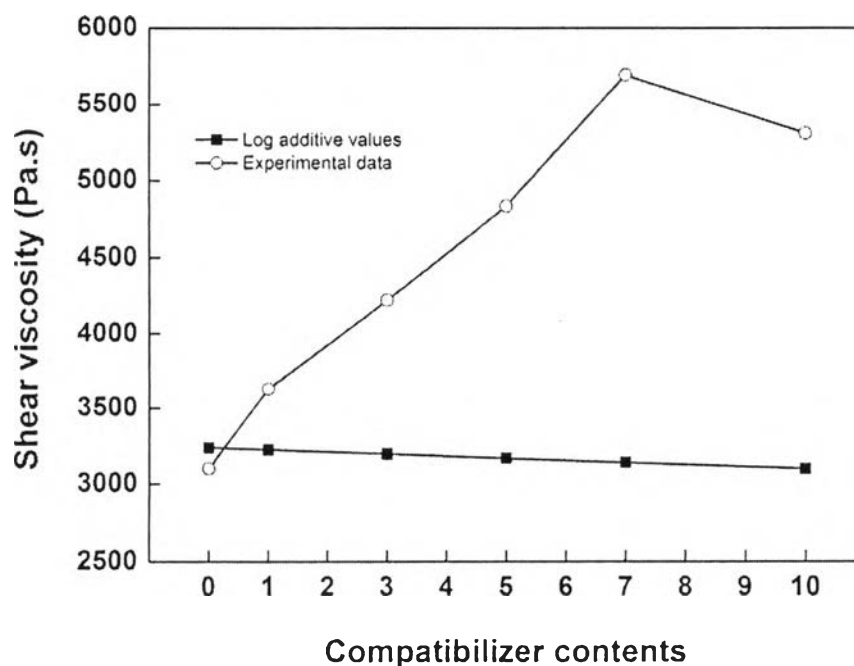
log additive value and is then used to study compatibility of the components in the mixtures or polymer blends. The polymer blends show a positive deviation in rheological properties e.g. viscosity and die swell for compatible or partially compatible polymer blends. These blends are also termed PDBs (positive deviation blends). On the other hand, a negative deviation is found for incompatible polymer blends. The log additive values of shear viscosity at shear rate of  $10 \text{ s}^{-1}$  are calculated by using Equations (6.9) and (6.10) and plotted in Figure 6.7.

$$\log \eta_b = (W_p \times \log \eta_{80/20\text{PA12/NR}}) + (W_c \times \log \eta_c) \quad (6.9)$$

$$\log \eta_b = (W_p \times 3.51) + (W_c \times 3.32) \quad (6.10)$$

where  $W_p$  and  $W_c$  are the weight fraction of polymer and compatibilizer, respectively. According to the log additive values, it is clear that the viscosity of the compatibilized blend linearly decreased with the content of the PS/MNR compatibilizer. Note that the viscosity of PS/MNR blend is lower than that of the binary blend. For the experimental data, the measured shear viscosity illustrates the negative deviation from a log additive value for Nylon12/NR binary blend. Nylon12/NR binary blend is not only immiscible, but also incompatible due to the polarity of amide groups in Nylon12 chains compared to the nonpolar structure of NR. Hence, there is no specific interaction between the two components of Nylon12 and NR, leading to the absence of adhesion and the incompatibility between the two phases in the blend. The compatibilized blends should have lower viscosity than the binary one as the compatibilizers are the low viscosity components. The shear viscosity of the compatibilized blend should lower at higher compatibilizer content. Conversely, the viscosity of the compatibilized blends is much higher than that of Nylon12/NR binary blend. It means that the compatibilizer PS/MNR makes the Nylon12/NR blend more compatible by providing strong interactions via amide and succinimide linkages as well as via hydrogen bonding between them. Van Puyvelde *et al.*<sup>32</sup> reported the same interaction of Nylon6 and EPR-g-MA as a reactive compatibilizer for ethylene-propylene rubber/polyamide6 (EPR/Nylon6) blends. In

this case, graft copolymer improved the interfacial adhesion and thus caused an increase of the blend viscosity. Compared to the log additive values, the viscosity of the compatibilized blends increased beyond the additive values (almost twice) as the content of compatibilizer was increased. It suggests that there is a positive deviation due to an additional mechanism to enhance viscosity e.g. phase interaction or good compatibility. The result also shows that the optimum content of the compatibilizer is at 7 phr, where the maximum viscosity of the 80/20 wt% Nylon12/NR/[PS/MNR] blend is achieved. At above 7 phr (e.g. 10 phr) of PS/MNR, the blend viscosity is reduced but still is much higher than the log additive value. This reversion of viscosity at high compatibilizer content can be explained by the excess amount of the PS/MNR compatibilizer added to minimize the interfacial tension, and the low viscosity nature of PS/MNR turns to play an important role. In addition, the log additive rule is useful to describe the reduction in viscosity as the low viscosity component is added and as more amount of the lower viscosity component is added. At the same amount of 10 phr, the compatibilized blend with non-reactive compatibilizer has lower viscosity than the reactively compatibilized blend (see Figure 6.6). Also, the viscosity of the reactively compatibilized blend with 10 phr compatibilizer is lower than that of 7 phr.



**Figure 6.7** Shear viscosity from log additive values and experimental data as a function of compatibilizer contents at shear rate of  $10 \text{ s}^{-1}$  and temperature of  $210 \text{ }^\circ\text{C}$ .

#### 6.4.5 Effect of Temperature

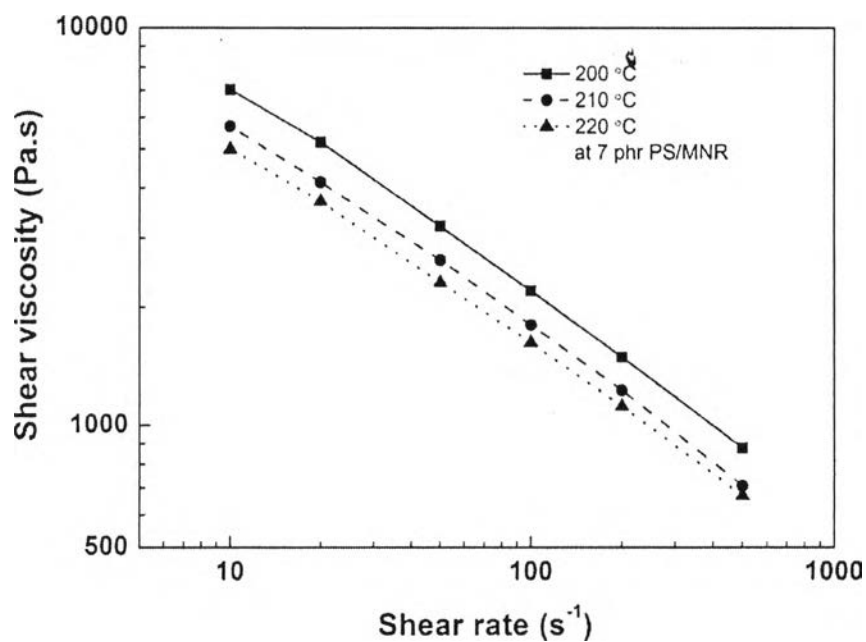
The effect of temperature on shear viscosity is given in Figure 6.8. The results demonstrate that the increase in temperature decreases the shear viscosity of [Nylon12/NR]/[PS/MNR] blends with compatibilizer content of 7 phr. Similar observations were made for any blends. In general, the viscosity of polymer melt decreases with increasing temperature due to greater free space available for molecular chain motion at higher temperature.<sup>33</sup> The temperature dependence of shear viscosity can yield information on flow activation energy of the blends, expressed in the form of Arrhenius-Frenkel Eyring Equation (6.11).

$$\eta = A_0 \exp\left(\frac{E_a}{RT}\right) \quad (6.11)$$

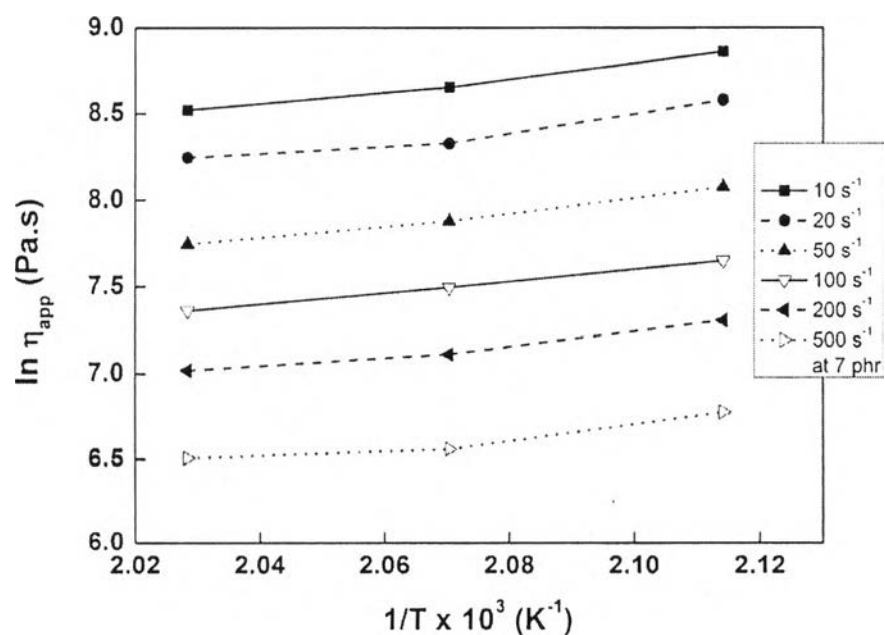
where  $\eta$  is the shear viscosity at a given shear rate,  $A_0$  is approximately a constant,  $E_a$  is the flow activation energy,  $R$  is the molar gas constant, and  $T$  is the absolute



temperature. The flow activation energy is determined by the slope of plots between  $\ln \eta$  versus the reciprocal of temperature ( $1/T$ ) as shown in Figure 6.9, and the  $E_a$  values are given in Table 6.5. The results show that the  $E_a$  reduces with increasing shear rate. This can be explained as follows. The number of entanglement coupling points reduces at higher shear rate, leading to reduction of interaction between chain segments.<sup>34</sup> With the addition of PS/MNR blend, the  $E_a$  of [Nylon12/NR]/[PS/MNR] blends increases with an increase of compatibilizer content up to 7 phr. This is due to the presence of amide and succinimide linkages causing the limitation of molecular chain motion and configuration. The increase in activation energy upon compatibilization had already been reported by George *et al.*<sup>35</sup> They found that compatibilization of the polypropylene/acrylonitrile-butadiene rubber (PP/NBR) blends with phenolic-modified polypropylene (Ph-PP) increased the melt viscosity and the activation energy at low concentrations of Ph-PP. In addition, the flow activation energy also provides valuable information on the sensitivity of the material towards the changes in temperature. The higher the flow activation energy, the stronger is the temperature sensitivity of the material. As mentioned above, the addition of compatibilizer results in higher flow activation energy. Thus, upon compatibilization, the blends become more temperature sensitive. In other words, the shear viscosity of the blends dramatically decreases when temperature increases and vice versa. The reason is described by molecular chain configuration and alignment to the flow field. The addition of reactive compatibilizer also increases chain interaction via the chemical linkages. The formation of the graft copolymers via the permanent bulky amide and succinimide linkages and non-permanent intermolecular bonding e.g. hydrogen bond (see Scheme 6.3) make the chains and the interfaces stiff such that the chains have limited configurations and are easily disentangled and aligned to the flow field. This mechanism suggests the loss of chain flexibility and also induces shorter relaxation time of the modified molecules than that of the unreacted molecules. This phenomenon will be verified later by the study of the extrudate swell which determines chain elasticity. On the other hand, at low temperature, the molecular chains lie close together leading to an increase in chain interactions e.g. by additional hydrogen bonding. Consequently, these interactions tend to decrease the chain mobility and the blend viscosity is thus increased.



**Figure 6.8** Shear viscosity of [Nylon12/NR]/[PS/MNR] blends at 7 phr as a function of shear rate at varying temperatures.

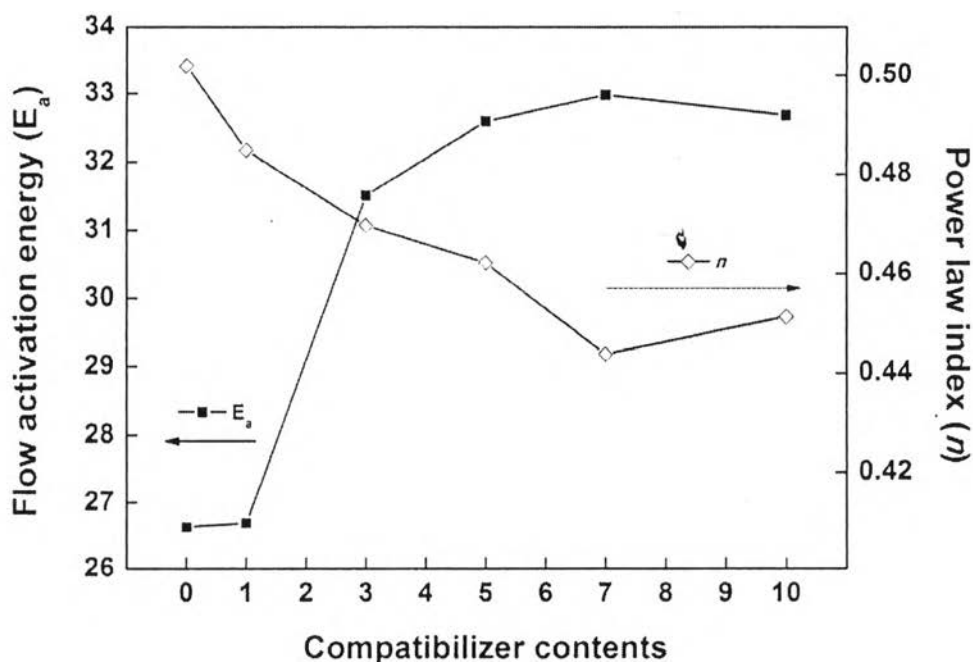


**Figure 6.9** Shear viscosity of [Nylon12/NR]/[PS/MNR] blends at 7 phr as a function of reciprocal temperatures ( $1/T$ ) at various shear rates.

**Table 6.5** Flow activation energy ( $E_a$ ) of the compatibilized blends (C-Blends) with various shear rates and compatibilizer contents at processing temperature of 210 °C

Materials	Activation Energy (kJ/mol)					
	10 s <sup>-1</sup>	20 s <sup>-1</sup>	50 s <sup>-1</sup>	100 s <sup>-1</sup>	200 s <sup>-1</sup>	500 s <sup>-1</sup>
Nylon12	29.92	28.57	28.13	27.97	27.20	24.09
NR	25.27	23.84	21.50	19.69	19.00	16.91
Nylon12/NR	26.64	25.73	21.81	20.37	19.19	17.05
C-Blends						
1 phr	26.70	25.99	23.95	23.52	19.28	17.15
3 phr	31.51	29.93	29.04	27.97	26.98	25.41
5 phr	32.59	31.25	29.38	28.18	27.96	25.92
7 phr	32.98	32.20	31.85	28.30	28.14	26.37
10 phr	32.68	31.27	29.66	28.26	28.10	26.07

Thus the flow behavior determined from the chain mobility (which can be limited by reactive compatibilizers) can be demonstrated by the enhancement in activation energy. This also reveals the flow sensitivity to temperature and the flow sensitivity to shear rate or time. Tables 6.4-6.5 and Figure 6.10 show variations of the power law index and the flow activation energy with various compatibilizer contents. The reactive compatibilizer changes the activation energy dramatically at low content but beyond 5 phr the activation energy changes gradually with the optimum (maximum) value at 7 phr. The power-law index decreases with compatibilizer content to a minimum value at 7 phr. These optimum values correspond to the optimum content of the compatibilizer for the maximum value of viscosity. Hence, these three flow parameters indicate well the effect of compatibilizer content and are useful in determining the optimum content of the compatibilizer.



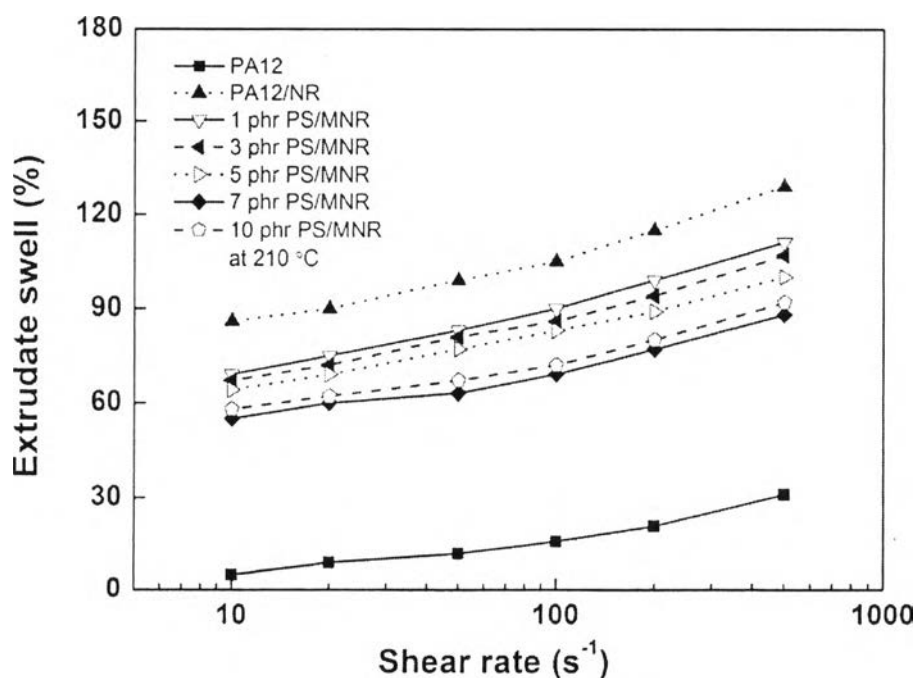
**Figure 6.10** Flow activation energy ( $E_a$ ) at shear rate of  $10 \text{ s}^{-1}$  and power law index ( $n$ ) at  $210 \text{ }^\circ\text{C}$  of [Nylon12/NR]/[PS/MNR] blends with various PS/MNR contents.

#### 6.4.6 Extrudate Swell

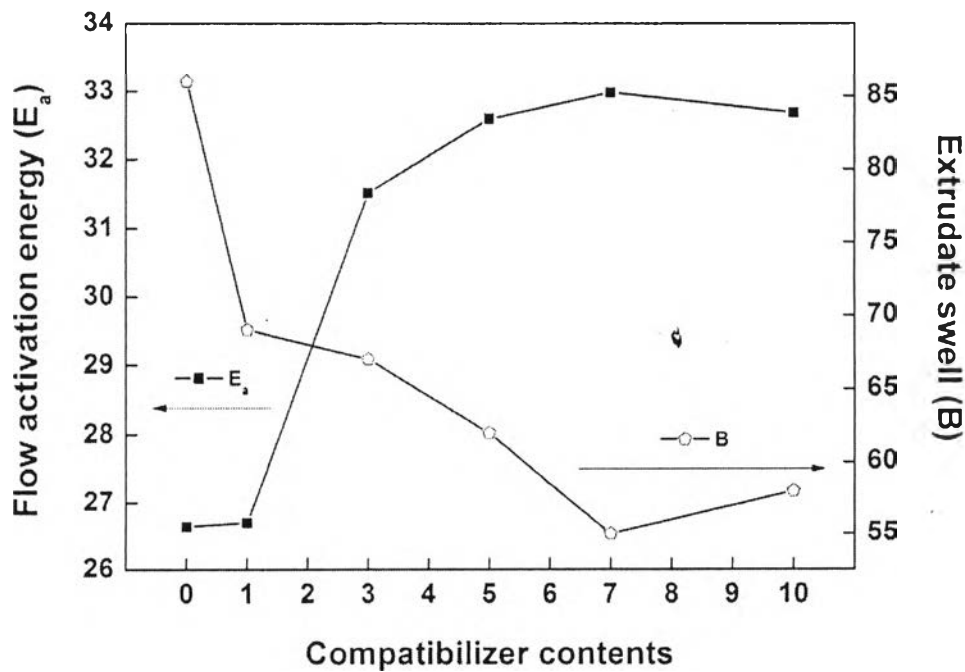
##### 6.4.6.1 Effect of Compatibilizer Content on the Extrudate Swell

For studying rheological characteristic, the molten polymer is forced to flow through the capillary die under shear. Note that chains undergo substantial orientation in the process. The recoiling of molecular chains occurs as the melt emerges from the die, leading to the phenomenon of extrudate swelling. Generally, the extrudate swell is closely related to the elastic properties of the polymer that it also depends on the flow conditions such as shear rate, die length, temperature, etc.<sup>36</sup> In this part, the effect of shear rate on the extrudate swell is investigated. Some representative data are shown in Figure 6.11. The extrudate swell of all blends increased with increasing shear rate in a non-linear relationship. This is due to shorter residence times in the capillary at high shear rate. As a consequence, more recoverable elastic energy stored in the polymer melt provides higher extrudate swell. Owing to a highly elastic structure of rubber, the addition of NR into Nylon12 dramatically increased the extrudate swell from 5 % to 85 % at shear rate of  $10 \text{ s}^{-1}$ .

However, the improved compatibility of Nylon12/NR blend with PS/MNR decreases the extrudate swell marginally as shown in Figure 12. This suggests the decrease in the chain relaxation time and also chain elasticity. It is attributed to the reduction in the elastic recoil of NR molecular chains and the increase of rigidity due to the formation of amide and succinimide linkages at the interfaces between Nylon12 and NR. Based on above discussions, it can be concluded that the maximum flow activation energy corresponds to the minimum die swell, implying the best interaction between Nylon12 and NR at compatibilizer content of 7 phr.



**Figure 6.11** Extrudate swell (%) as a function of shear rates of [Nylon12/NR]/[PS/MNR] blends with various PS/MNR contents at 210 °C.



**Figure 6.12** Flow activation energy ( $E_a$ ) and extrudate swell (B) at shear rate of  $10 \text{ s}^{-1}$  of [Nylon12/NR]/[PS/MNR] blends with various PS/MNR contents.

#### 6.4.6.2 Effect of Temperature on the Extrudate Swell

The correlation between extrudate swell (B) and temperature (T) can be represented by Equation (6.12).<sup>37</sup>

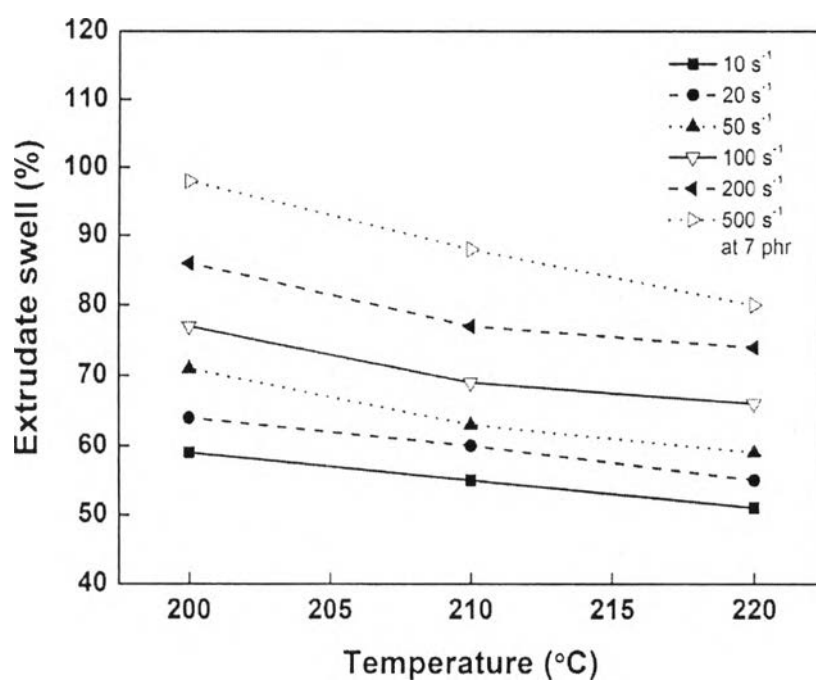
$$B = \alpha_1 + \beta_1 T \quad (6.12)$$

where  $\alpha_1$  and  $\beta_1$  are the coefficients related to the polymer properties. The results of a linear fit to this expression are listed in Table 6.6. The sensitivity of extrudate swell (B) of [Nylon12/NR]/[PS/MNR] blends at 7 phr on temperature is more significant at high shear rate. The slope of plot between B and T or  $\beta_1$  decreases sharply as given in Figure 6.13. It means that the extrudate swell decreases with the increase in temperature. For viscoelastic materials, the molecular chain motion exactly depends on the temperature. This shows that the viscous response is much greater than the elastic response at higher temperature, resulting in lesser ability of the polymer melt to recover to its original structure. Furthermore, at higher temperature, the shear

viscosity is lower. Consequently, the motion of molecular chains is easy and the relaxation time of the polymer melt is shorter.

**Table 6.6** The values of  $\alpha_1$  and  $\beta_1$  for [Nylon12/NR]/[PS/MNR] blends at 7 phr with various shear rates

Shear Rate ( $s^{-1}$ )	Effect of T on B (at 7 phr PS/MNR)		
	$\alpha_1$	$\beta_1$	R
10	63.00	-4.0	1.0000
20	68.67	-4.5	0.9959
50	76.33	-6.0	0.9643
100	81.67	-5.5	0.9356
200	91.00	-6.0	0.9231
500	106.67	-9.0	0.9959



**Figure 6.13** Extrudate swell (%) as a function of temperatures of [Nylon12/NR]/[PS/MNR] blends with various shear rates.

## 6.5 Conclusions

For thermoplastic polymers, rheological studies give initial information on how these polymers behave during actual polymer processing. In this research work, melt rheological properties of Nylon12/NR compatibilized by PS/MNR blend were investigated using a capillary rheometer. The [Nylon12/NR]/[PS/MNR] blends exhibited shear-thinning or pseudoplastic behavior. This is attributed to the decreasing of shear viscosity with increasing shear rate. With increasing compatibilizer content up to 7 phr, the shear viscosity of the blends was found to increase. The results also showed the positive deviation of shear viscosity from the log additive values, indicating compatible or partially compatible blends. This work discloses that when the compatibilization induces strong interaction between the components in the blend such that the chemical structure can be altered as well as the flexibility of the molecular chains, the flow behavior is thus affected by the change in the molecular mobility. It suggests that PS/MNR blend acts as the reactive compatibilizer for Nylon12/NR blend by providing the amide and succinimide linkages at the interface through the chemical reaction between polar functional groups of PS/MNR and those of Nylon12. Consequently, the rigidity of molecular chains was increased while the elastic recovery was reduced, leading to the increasing of flow activation energy and the decreasing of power law index and extrudate swell. The understanding of these rheological properties of the material is highly useful in selecting the optimum conditions for product processing in the future.

## 6.6 Acknowledgements

This work was financially supported by Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program, Thailand (PHD/0101/2551). The authors thank the faculty members and staffs both from at Department of Polymer Engineering, The University of Akron and from at The Petroleum and Petrochemical College, Chulalongkorn University for their knowledge and assistance, including providing the equipment used in this research.



## 6.7 References

1. Malkin AY and Isayev AI. *Rheology: Concepts, Methods, and Applications*. Toronto: ChemTec Publishing, 2006.
2. Brydson JA. *Flow Properties of Polymer Melts*. New York: Van Nostrand Reinhold, 1970.
3. Ibrahim BA and Kadum KM. Influence of Polymer Blending on Mechanical and Thermal Properties. *Modern Applied Science* 2010; 4: 157-161.
4. Saengthaveep S and Magaraphan R. Natural rubber-toughened Nylon12 compatibilized by polystyrene/natural rubber blend. *Advances in Polymer Technology*. 2013; 32: 1-11.
5. Lai SM, Liao YC and Chen TW. The preparation and properties of compatibilized nylon 6/ABS blends using functionalized polybutadiene. Part I: Impact properties. *Polymer Engineering & Science*. 2005; 45: 1461-1470.
6. Mohammadian-Gezaz S, Ghasemi I and Oromiehie A. Study of the properties of compatibilized ABS/PA6 blends using response surface methodology. *Journal of Vinyl and Additive Technology*. 2009; 15: 191-198.
7. Bose S, Bhattacharyya AR, Kodgire PV and Misra A. Fractionated crystallization in PA6/ABS blends: Influence of a reactive compatibilizer and multiwall carbon nanotubes. *Polymer*. 2007; 48: 356-362.
8. Kudva RA, Keskkula H and Paul DR. Fracture behavior of nylon 6/ABS blends compatibilized with an imidized acrylic polymer. *Polymer*. 2000; 41: 335-349.
9. Araújo EM, Hage E and Carvalho AJF. Acrylonitrile-butadiene-styrene toughened nylon 6: The influences of compatibilizer on morphology and impact properties. *Journal of Applied Polymer Science*. 2003; 87: 842-847.
10. Kumar CR, Nair SV, George KE, Oommen Z and Thomas S. Blends of nylon/acrylonitrile butadiene rubber: Effects of blend ratio, dynamic vulcanization and reactive compatibilization on rheology and extrudate morphology. *Polymer Engineering & Science*. 2003; 43: 1555-1565.
11. Kusmono, Mohd Ishak ZA, Chow WS, Takeichi T and Rochmadi. Influence of SEBS-g-MA on morphology, mechanical, and thermal properties of

- PA6/PP/organoclay nanocomposites. *European Polymer Journal*. 2008; 44: 1023-1039.
12. Agrawal P, Rodrigues AWB, Araújo E and Mélo TA. Influence of reactive compatibilizers on the rheometrical and mechanical properties of PA6/LDPE and PA6/HDPE blends. *J Mater Sci*. 2010; 45: 496-502.
  13. Marco C, Ellis G, Gómez MA, Fatou JG, Arribas JM, Campoy I and Fontecha A. Rheological properties, crystallization, and morphology of compatibilized blends of isotactic polypropylene and polyamide. *Journal of Applied Polymer Science*. 1997; 65: 2665-2677.
  14. Olabisi O. *Handbook of Thermoplastics*. New York: Marcel Dekker, 1997.
  15. Utracki LA. Compatibilization of Polymer Blends. *The Canadian Journal of Chemical Engineering*. 2002; 80: 1008-1016.
  16. Holsti-Miettinen RM, Seppälä JV, Ikkala OT and Reima IT. Functionalized elastomeric compatibilizer in PA 6/PP blends and binary interactions between compatibilizer and polymer. *Polymer Engineering & Science*. 1994; 34: 395-404.
  17. Minkova L, Yordanov H, Filippi S and Grizzuti N. Interfacial tension of compatibilized blends of LDPE and PA6: the breaking thread method. *Polymer*. 2003; 44: 7925-7932.
  18. Kim JK and Pal K. Effect of Compatibilizers in WPC Composites. *Recent Advances in the Processing of Wood-Plastic Composites*. Berlin Springer, 2010, p. 103-127.
  19. Mascia L. *Polymers in Industry from A-Z*. Wiley-VCH, 2011.
  20. Ebewele RO. *Polymer Science and Technology*. Florida: CRC Press, 2000.
  21. Cogswell FN. *Polymer Melt Rheology – A Guide for Industrial Practice*. Cambridge: Woodhead Publishing, 1996.
  22. Bonner JG and Hope PS. Compatibilisation and reactive blending. In: Folkes MJ and Hope PS, (eds.). *Polymer Blends and Alloys*. London: Blackie Academic, 1993, p. 46-74.
  23. Kim BC. Modification of Nylon. In: Meister JJ, (ed.). *Polymer Modification: Principles, Techniques, and Applications*. New York: Marcel Dekker, 2000, p. 433-480.

24. Xie BH, Yang MB, Li SD, Li ZM and Feng JM. Studies on polyamide-6/polyolefin blend system compatibilized with epoxidized natural rubber. *Journal of Applied Polymer Science*. 2003; 88: 398-403.
25. Lievana E and Karger-Kocsis J. Impact modification of PA-6 and PBT by epoxy-functionalized rubbers. *Macromolecular Symposia*. 2003; 202: 59-66.
26. Jha A, Dutta B and Bhowmick AK. Effect of fillers and plasticizers on the performance of novel heat and oil-resistant thermoplastic elastomers from nylon-6 and acrylate rubber blends. *Journal of Applied Polymer Science*. 1999; 74: 1490-1501.
27. Jha A and Bhowmick AK. Influence of dynamic vulcanization and phase interaction on the swelling behavior of the thermoplastic elastomeric blends of nylon-6 and acrylate rubber in various solvents and oil. *Journal of Applied Polymer Science*. 1998; 69: 2331-2340.
28. Jha A and Bhowmick AK. Thermoplastic Elastomeric Blends of Nylon-6/Acrylate Rubber: Influence of Interaction on Mechanical and Dynamic Mechanical Thermal Properties. *Rubber Chemistry and Technology*. 1997; 70: 798-814.
29. Muksing N, Nithitanakul M, Grady BP and Magaraphan R. Melt rheology and extrudate swell of organobentonite-filled polypropylene nanocomposites. *Polymer Testing*. 2008; 27: 470-479.
30. Nakason C, Kaesaman A, Samoh Z, Homsin S and Kiatkamjornwong S. Rheological properties of maleated natural rubber and natural rubber blends. *Polymer Testing*. 2002; 21: 449-455.
31. Saedan M, Navarat T and Sombat A. Grafting of maleic anhydride on natural rubber molecules in a molten state. *The National Research Council of Thailand*. 1997: 49-60.
32. Van Puyvelde P, Oommen Z, Koets P, Groeninckx G, Moldenaers P, Leuven KU, Eindhoven TU and Leuven KU. Effect of reactive compatibilization on the interfacial slip in nylon-6/EPR blends. *Polymer Engineering & Science*. 2003; 43: 71-77.
33. Saini DR, Shenoy AV and Nadkarni VM. Melt rheology of highly loaded ferrite-filled polymer composites. *Polymer Composites*. 1986; 7: 193-200.

34. Li S, Järvelä PK and Järvelä PA. Melt rheological properties of polypropylene-maleated polypropylene blends. I. Steady flow by capillary. *Journal of Applied Polymer Science*. 1999; 71: 1641-1648.
35. George S, Ramamurthy K, Anand JS, Groeninckx G, Varughese KT and Thomas S. Rheological behaviour of thermoplastic elastomers from polypropylene/acrylonitrile-butadiene rubber blends: effect of blend ratio, reactive compatibilization and dynamic vulcanization. *Polymer*. 1999; 40: 4325-4344.
36. Bajaj P, Jha NK and Jha RK. Rheological behaviour of titanate coated mica-filled polypropylene. *British Polymer Journal*. 1989; 21: 345-355.
37. Liang JZ and Ness JN. The melt die-swell behaviour during capillary extrusion of LDPE/PP blends. *Polymer Testing*. 1998; 17: 179-189.