

**CHAPTER V**  
**EFFECTS OF MIXING PROCEDURE AND MALEIC ANHYDRIDE**  
**CONTENT ON MECHANICAL PROPERTY AND MORPHOLOGY OF**  
**NATURAL RUBBER-TOUGHENED POLYSTYRENE**

**5.1 Abstract**

Toughness enhancement of polystyrene (PS) was done by incorporating a natural rubber (NR) into it. The compatibility of PS and NR was improved via reactive blending using dicumyl peroxide (DCP) as an initiator and maleic anhydride (MA) as a reactive functionalizer. Two different mixing procedures had been used: (a) one-step mixing in which the three components of PS (60 wt%), NR (40 wt%) and MA were simultaneously introduced in the mixer; (b) two-step mixing in which NR and MA were separately premixed before the final mixing with PS. Solvent extraction and acid-base titration were used to determine gel content and MA grafting efficiency, respectively. The influence of MA loading (3 and 5 wt%) on phase morphology, thermal and mechanical properties of PS-NR-MA blends were then investigated. The result showed a significant effect of different mixing procedures on the blend properties. The reduction of gel (crosslinked NR) content and the increasing of MA grafting efficiency were found in the blends obtained by using two-step mixing (PS/MNR). For thermal analysis, the glass transition temperature ( $T_g$ ) of PS shifted to higher values due to the formation of chemical linkage at PS/NR interfaces, making molecular chains stiff and difficult to move. The addition of 40 wt% NR into PS increased the impact energy by a factor of 2 due to high elasticity of NR promoting more energy absorption and energy dissipation. However, the impact energy of PS/NR/MA was slightly higher than that of PS/MNR. This is attributed to the decreased molecular weight of NR in the formerly prepared MNR of two-step mixing. Considering maleic anhydride loading, the increase of impact energy and the decrease of gel content were found in the blends having lower concentration of MA. This also related to the enhancement of interfacial adhesion at PS/NR interfaces and the reduction of rubber particle size.

**Keywords:** Polystyrene, Natural rubber, Impact property, Phase morphology

## 5.2 Introduction

Many thermoplastics such as polystyrene (PS), poly(vinyl chloride) (PVC) and polymethylmethacrylate (PMMA) are brittle when stressed, a property which limits applications. The improvement of toughness can be done by incorporating the elastomeric materials into such polymers, so called rubber toughening. The elastomeric chains form separate phases in the solid, typically 10-20 micrometers in diameter, so that when the material is strained, crazes form at their surfaces. This leads to the increasing of the energy needed to break the material. For instance, PVC can be toughened by using epoxy natural rubber (ENR) [1], nitrile rubber (NBR) [2, 3] and styrene-butadiene rubber (SBR) [4, 5]. Natural rubber (NR) [6-9], acrylic elastomer [10], copoly(ether-ester) [11] are used for toughening of PMMA. For PS, the toughness enhancement can be done by addition of NR [9] and SBR [12, 13].

The compatibility of two components (polymer and rubber) is the key factor to obtain good properties. Due to the lack of specific molecular interactions, it is difficult to get appropriate two-phase miscibility in polymer blends. To improve the blend performance, the immiscible polymer blends usually need compatibilization. Reactive blending is one of most effective methods used to produce the compatible polymer blend. The reactive blending relies on the in situ formation of copolymers or interacting polymers by chemical bonding reaction between the complementary groups of the blend components. The in situ reaction may be stimulated by addition of a free radical initiator during processing [14]. Besides, it is also known that maleic anhydride (MA) is widely used with vinyl monomers for the graft modification of polyolefins both thermoplastic polyolefin (PE, PP and PS) and elastomer (NR, EPR and EPDM). MA-modified polyolefins not only improve the adhesion of the polyolefins with polar polymers (polyamide, glass fibers, and metal), but they are also used as compatibilizer and impact modifiers in polymer blends [15-28]. Carone *et al.* [29] indicated that addition of MA to NR at room temperature prior to blending with PA6 led to an in situ graft copolymer formation. MA molecules reacted with

both NR and PA6 matrix during processing. This grafting reaction reduced the particle size of rubber domains dramatically. Bonner and Hope [14] studied the modification of nitrile rubber (NBR) with maleic anhydride to use as an impact modifier for Nylon6. The blend of Nylon6 and modified NBR (MA-g-NBR) showed the highest impact strength compared to Neat Nylon6 and Nylon6/unmodified NBR blend both at room temperature and at low temperature (-20 °C). It is attributed to the presence of a high level of grafted MA coupled with a relatively high degree of crosslinking in the MA-g-NBR.

On the basis of this approach, the toughness enhancement of polystyrene (PS) has been done by incorporating with natural rubber (NR) via reactive blending using dicumyl peroxide (DCP) as an initiator and maleic anhydride (MA) as a grafting modifier. However, crosslinking of natural rubber (gel) has often occurred during the free radical grafting reaction which it limits the high degree of grafting. Therefore, various parameters affecting gel content, maleic anhydride grafting efficiency, phase morphology, thermal and mechanical properties, i.e., an amount of maleic anhydride and a different mixing procedures were investigated.

### 5.3 Experimental

#### 5.3.1 Materials

Polystyrene (PS), product name STYRON™ 666D, was supplied by Americas Styrenics. The melt volume flow rate is 8 cm<sup>3</sup>/10 min (200 °C, 5 kg). The density is 1.04 g/cm<sup>3</sup>.

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

Maleic anhydride (MA) that used as a reactive functionalizer was purchased from Acros. This material was used in form of small white opaque flakes.

Dicumyl peroxide (DCP) that used as an initiator was purchased from Sigma-Aldrich. This material was used in form of small white opaque flakes with melting point of 56 °C.

### 5.3.2 Preparation of PS-NR-MA Blends

Prior to mixing, PS was dried in a vacuum oven at 60 °C for 12 h in order to remove the absorbed water. Then PS-NR-MA blends were prepared via reactive blending by using two different mixing procedures. The blend compositions are presented in Table 5.1.

#### - One-step Mixing

PS (60 wt%) was fed into the chamber of the Brabender mixer (Prep Center) to melt at the processing temperature of 170 °C and the rotor speed of 60 rpm for 3 min. Next, DCP (0.5 wt%) was added and mixed for 3 min. Finally, MA (3 and 5 wt%) and masticated NR (40 wt%) were fed into the chamber and mixed further for another 4 min. The obtained blend is termed PS/NR/MA in the rest of the paper.

#### - Two-step Mixing

The first step, masticated NR was induced in the Brabender mixer and mixed for 3 min at temperature of 135 °C and rotor speed of 60 rpm. MA was then incorporated, mixing it at the same temperature and rotor speed for 5min. Finally, the NR functionalized with MA, so called “maleated natural rubber (MNR)”, was removed from the chamber.

The second step, PS was added and melted for 3 min at the processing temperature of 170 °C and the rotor speed of 60 rpm. Next, DCP was added and mixed for 3 min. Finally, MNR was added to the molten PS and mixed for 4 min. The obtained blend is termed PS/MNR in the rest of the paper.

**Table 5.1** Blend compositions of PS-NR-MA blends

| <b>Materials</b> | <b>PS<br/>(wt%)</b> | <b>NR<br/>(wt%)</b> | <b>DCP<br/>(wt%)</b> | <b>MA<br/>(wt%)</b> | <b>Type of<br/>Mixing</b> |
|------------------|---------------------|---------------------|----------------------|---------------------|---------------------------|
| PS               | 100                 | -                   | -                    | -                   | One-Step                  |
| PS/NR            | 60                  | 40                  | 0.5                  | -                   | One-Step                  |
| PS/NR/MA-3       | 60                  | 40                  | 0.5                  | 3                   | One-Step                  |
| PS/NR/MA-5       | 60                  | 40                  | 0.5                  | 5                   | One-Step                  |
| PS/MNR-3         | 60                  | 40                  | 0.5                  | 3                   | Two-Step                  |
| PS/MNR-5         | 60                  | 40                  | 0.5                  | 5                   | Two-Step                  |

### 5.3.3 Determination of Gel Content, Graft Ratio and MA Grafting Efficiency

After mixing, gel (crosslinked NR) content was measured by using solvent extraction method. Gel was extracted by dissolving the crude blend of PS-NR-MA (2.0 g) in toluene (100 ml) for 24 h at 120 °C. After vacuum drying at 100 °C for 24 h, the gel (insoluble part) content was calculated by using Equation (5.1). For purification, the solution part (the blend without gel) was precipitated into 100 ml of acetone. The precipitate was then filtered and washed with acetone several times. At this step, the unreacted MA was also removed. After vacuum drying, the blend without gel was extracted by methyl ethyl ketone (good solvent for PS) for 24 h at 90 °C. The solution (unreacted PS) was then precipitated into 100 ml of ethanol, and its content was calculated by using Equation (5.2). The purified product was specified as the PS-g-MNR copolymer, and the graft ratio was calculated by using Equation (5.3).

$$\text{Gel (wt\%)} = \left[ \frac{\text{weight of gel}}{\text{weight of blend}} \right] \times 100 \quad (5.1)$$

$$\text{Unreacted PS (wt\%)} = \left[ \frac{\text{weight of unreacted PS}}{\text{weight of blend}} \right] \times 100 \quad (5.2)$$

$$\text{Graft ratio (GR)} = \frac{\text{weight of PS-g-MNR copolymer}}{\text{weight of blend}} \quad (5.3)$$

For maleic anhydride (MA) grafting efficiency, the purified product (1.0 g) was dissolved in 100 ml of toluene with the addition of 0.2 ml of distilled water at refluxing temperature for 2 h. By this procedure, the water plays a role in hydrolyzing anhydride functions into carboxylic acid functions. The carboxylic acid concentration was determined by titration with 0.1 N ethanolic KOH, after adding five drops of 1 % phenolphthalein in ethanol as an indicator. The carboxylic acid concentration was converted to the MA content using Equation (5.4), and the MA grafting efficiency was calculated by using Equation (5.5).

$$\text{MA (wt\%)} = \left[ \frac{98.06 \times N \times V}{2 \times W} \right] \times 100 \quad (5.4)$$

$$\text{MA grafting efficiency} = \left[ \frac{\text{weight percentage of MA grafted}}{\text{weight percentage of MA added}} \right] \times 100 \quad (5.5)$$

where N = concentrations (mol/l) of KOH  
 V = volume (l) of KOH  
 W = weight (g) of purified product

#### 5.3.4 Solid-state NMR

The presence of MA in the formerly prepared MNR and PS/MNR blend was determined by solid-state  $^{13}\text{C}$  NMR. The PS/MNR blend was packed into the  $\text{ZrO}_2$  rotor (4 mm in diameter). The experiments were performed at 50 MHz at room temperature with an Inova-200 solids NMR spectrometer using a cross

### 5.3.5 Thermal Property

Thermal property of the blends was studied by using a Differential Scanning Calorimeter (DSC Q200). The samples were heated, cooled and heated from -20 °C to 200 °C with the heating rate of 10 °C/min and the cooling rate of 5 °C/min under nitrogen purge in order to avoid any possible thermal degradation. The onset of the slope change of the heat capacity plot was determined as the glass transition temperature ( $T_g$ ) of polystyrene.

### 5.3.6 Mechanical Property

Impact energy of all blends was studied by Izod impact tester (TMI No. 43-1). All specimens were notched on the center of one longitudinal side, hence; the specimen size had a length of 60 mm, a thickness of 3 mm, and a width of 10.2 mm under notch. The test was done by using the pendulum of 13.6 J at room temperature. For each blend, ten replications were tested.

### 5.3.7 Phase Morphology

A JEOL JSM 7401 Scanning Electron Microscope (SEM) with magnification 500 times was used at 10 kV to investigate the phase morphology. For preparation of the cross-sectional surface, the impact bar specimen of each blend was cryogenically broken after dipping in liquid nitrogen for 5 min. Then all samples were coated by silver to be a conductive material.

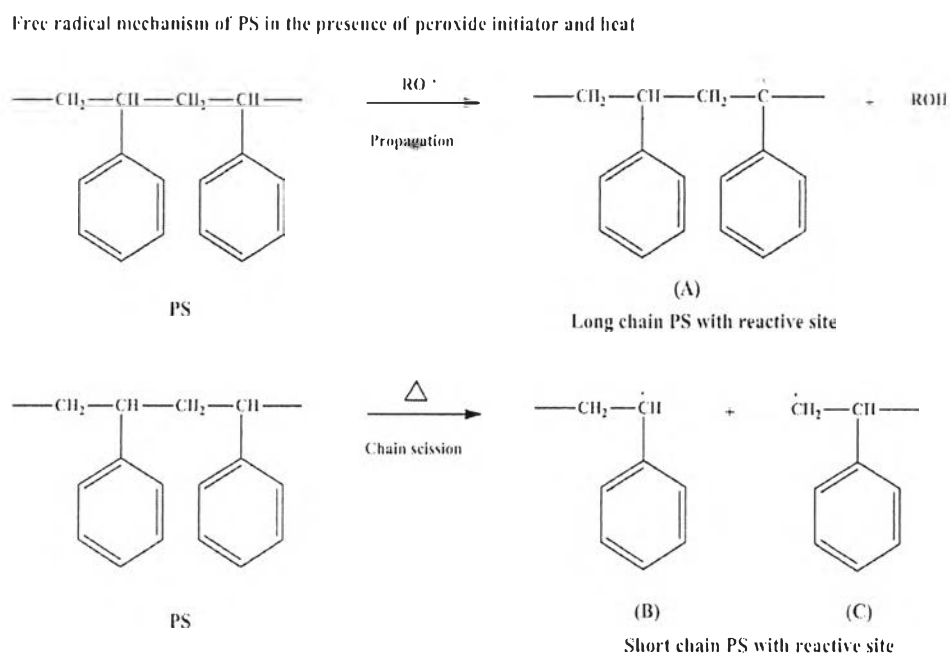
### 5.3.8 Rheological Property

The shear viscosity of all blends was measured using a Rosand RH7 twin-bore capillary rheometer fitted with 1.0 mm capillary die of 32 mm length. All measurements were made at test temperatures of 210 °C and the range of apparent shear rates varied from 10 to 2000 s<sup>-1</sup>.

## 5.4 Results and Discussion

### 5.4.1 Determination of Gel Content and MA Grafting Efficiency

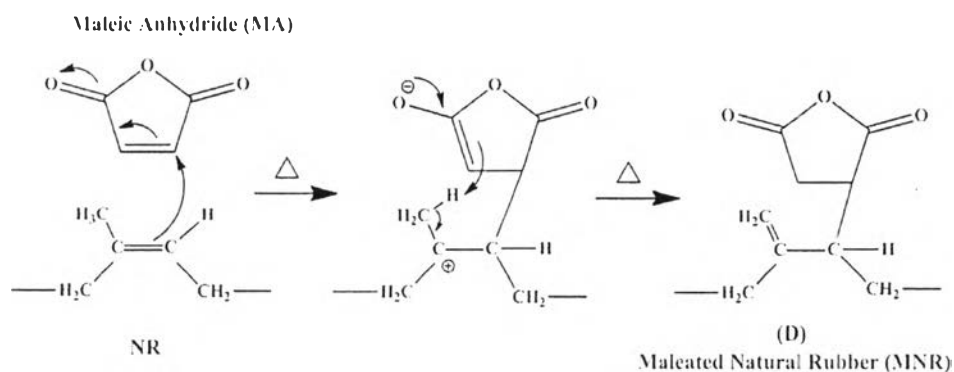
The possible reactions occurring via free radical mechanism are shown in Scheme 5.1-5.3. For free radical mechanism, besides the formation of PS-g-MNR copolymer, it is possible to gain a crosslinked structure of NR (gel) via radical recombination reaction [30]. Furthermore, with the generation of free radical by initiator and heat, chain scission of PS (PS short chain or unreacted PS) may be occurred through the homolytic cleavage of weak bonds in the molecular chains [31]. Consequently, the blends show the complex mixture of low molecular weight degradation products.



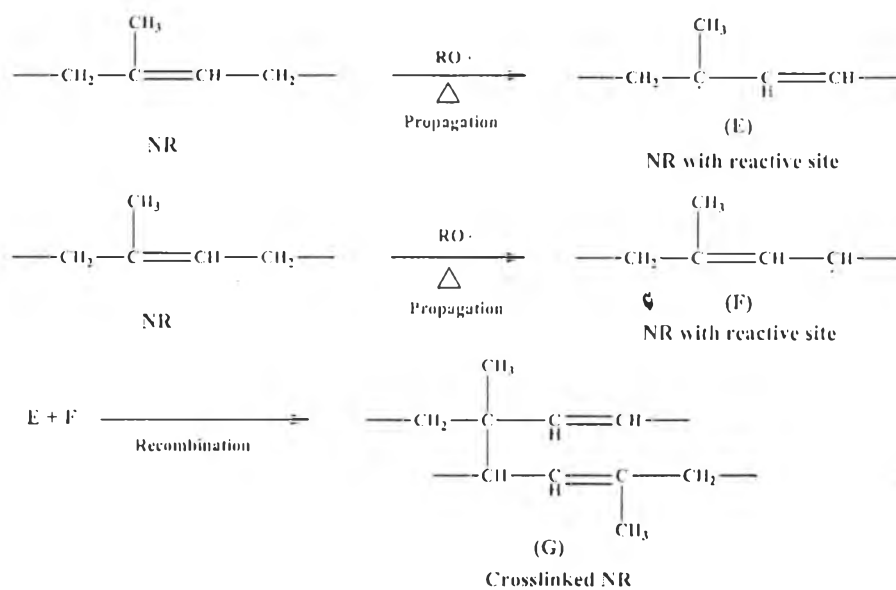
**Scheme 5.1** Possible reactions of polystyrene in the presence of initiator and heat.



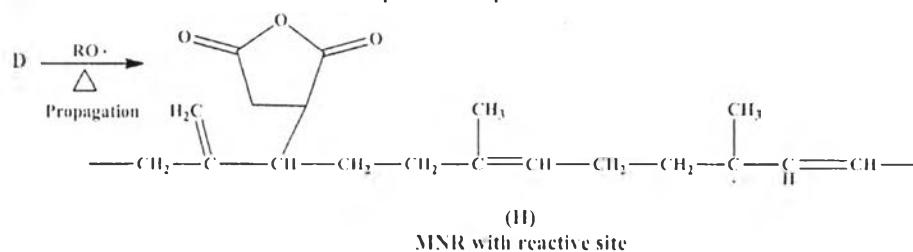
## 1. Reaction between NR and MA functionalizer in the presence of heat



## 2. Free radical mechanism of NR in the presence of peroxide initiator and heat

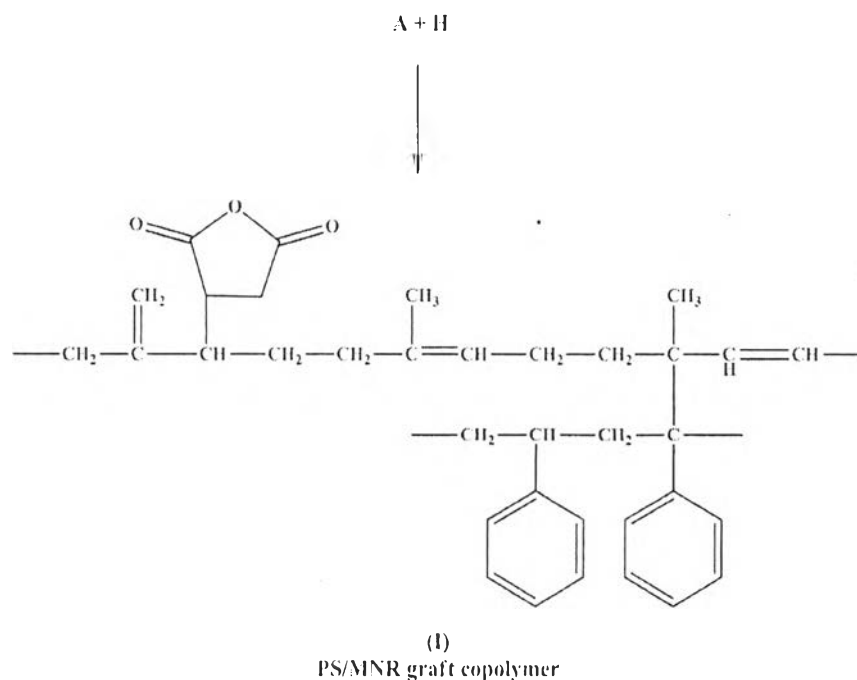


## 3. Free radical mechanism of MNR in the presence of peroxide initiator and heat



**Scheme 5.2** Possible reactions of natural rubber in the presence of maleic anhydride, initiator and heat.

## The formation of PS/MNR graft copolymer



**Scheme 5.3** Chemical structure of polystyrene/maleated natural rubber graft copolymer.

Table 5.2 shows the content of gel (wt%), unreacted PS (wt%) and graft ratio of the blends with various mixing procedures and MA loadings. Comparing with PS/NR blend, the functionalization of NR with MA decreases the crosslinking of rubber (gel) from 26.37 wt% to 18.26 wt% for PS/NR/MA-3 blend (one-step mixing) and 10.95 wt% for PS/MNR-3 blend (two-step mixing). Besides, the presence of MA helps in the distribution of NR domains in PS matrix leading to more grafting reaction between PS and NR. The results illustrate the increasing of graft ratio from 0.13 for the blend without MA to 0.21 and 0.29 for the blends with MA from one-step mixing and two-step mixing, respectively. Using two-step mixing, NR was functionalized with MA before blending with PS. This functionalization takes place without the presence of peroxide initiator; the shear action of the rotors is sufficient for generating the free radicals [32]. Therefore, more reaction of MA to NR results in the decreasing of crosslinked NR (gel) and the increasing of MA grafting efficiency as shown in Table 5.3. Considering MA loading, the blends

containing 3 wt% of MA show the lowering of gel content while their graft ratio and MA grafting efficiency demonstrate the higher values. It suggests that the polymer-MA radical sites exceed the NR macroradicals at low MA content. Therefore, the grafting is a dominant reaction. The increase of MA content up to 5 wt% leads to the decrease of graft ratio and MA grafting efficiency. This is probably because MA no longer interacts with PS and NR, but it reacts with itself via oligomerization of MA to poly(maleic anhydride).

**Table 5.2** The weight percentage (wt%) of gel and unreacted PS, and the graft ratio of PS/NR blend and PS-NR-MA blends with various mixing procedures and MA loadings

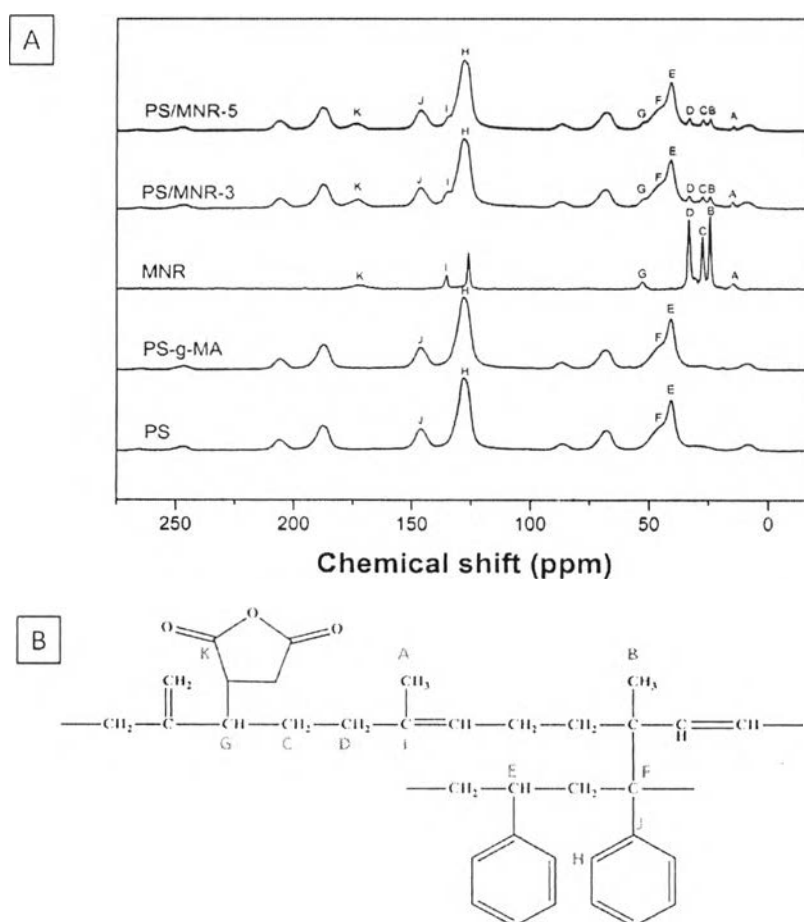
| Materials  | Gel Content (wt%) | Unreacted PS (wt%) | Graft Ratio |
|------------|-------------------|--------------------|-------------|
| PS/NR      | 26.37             | 46.28              | 0.13        |
| PS/NR/MA-3 | 18.26             | 38.41              | 0.21        |
| PS/NR/MA-5 | 20.13             | 40.24              | 0.16        |
| PS/MNR-3   | 10.95             | 30.11              | 0.29        |
| PS/MNR-5   | 13.58             | 33.07              | 0.19        |

**Table 5.3** The weight percentage (wt%) of MA grafted onto PS and NR, and the MA grafting efficiency of PS-NR-MA blends with various mixing procedures and MA loadings

| Materials  | MA Grafting (wt%) | MA Grafting Efficiency (%) |
|------------|-------------------|----------------------------|
| PS/NR/MA-3 | 1.26              | 42                         |
| PS/NR/MA-5 | 1.09              | 21                         |
| PS/MNR-3   | 1.76              | 58                         |
| PS/MNR-5   | 1.41              | 28                         |

### 5.4.2 Solid-state NMR

To investigate the grafting of MA onto NR and PS, the formerly prepared MNR and PS-g-MA were dissolved in toluene (good solvent for NR and PS) at 120 °C for at least 3 days. The solutions were then precipitated into acetone. The precipitates were filtered and washed with acetone several times. By this procedure, the unreacted MA was removed. Solid-state  $^{13}\text{C}$  NMR spectra of neat PS, PS-g-MA, MNR and PS/MNR blends (two-step mixing) with two different contents of MA were then observed as shown in Figure 5.1(a), relating to the chemical structure of PS/MNR blends shown in Figure 5.1(b).



**Figure 5.1** A) Solid-state  $^{13}\text{C}$  NMR spectra of neat PS, PS-g-MA, MNR and PS/MNR blends (two-step mixing) with various MA loadings, and B) the chemical structure of PS/MNR blends.

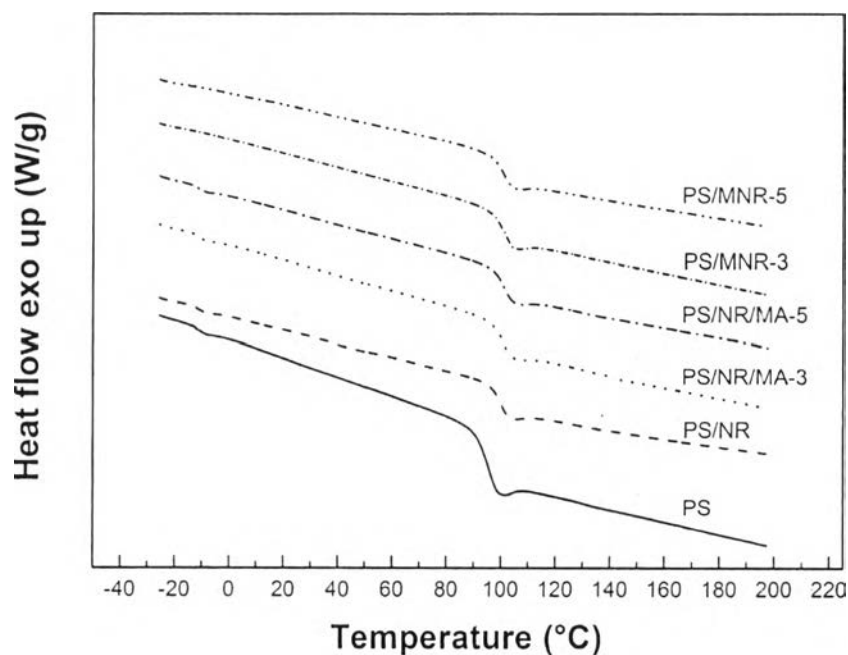
The typical chemical shifts in  $^{13}\text{C}$  NMR of the materials are shown in Table 5.4. For NMR spectra of PS/MNR blends, the results show the chemical shifts of  $\text{RCH}_3$  at 15 ppm (position A) and 24 ppm (position B),  $\text{R}_2\text{CH}_2$  at 27 ppm (position C) and 33 ppm (position D),  $\text{R}_3\text{CH}$  at 52 ppm (position G), and  $\text{C}=\text{C}$  at 135 ppm (position I) of NR backbone. The chemical shifts of  $\text{R}_3\text{CH}$ ,  $\text{R}_4\text{C}$ , and  $\text{C}$  in aromatic ring of PS are found at 42 ppm (position E), 47 ppm (position F), and 127 ppm (position H) and 146 ppm (position J), respectively. The carbon in ester group ( $-\text{COO}-$ ) of maleic anhydride (position K) shows the chemical shifts at 172 ppm. However, the peak intensity at this position of PS/MNR-3 blend is slightly higher than that of PS/MNR-5 blend. As discussed previously, the lower MA loading, the more polymer-MA grafting could be obtained. For MNR and PS-g-MA, these products were prepared by mixing PS for PS-g-MA and NR for MNR with MA in the absence of peroxide initiator. An NMR spectrum of PS-g-MA is quite similar to neat PS. Furthermore, the chemical shift at 172 ppm representing carbon in ester group of maleic anhydride (position K) is not found. It means that only shear action of rotors is not sufficient for generating the free radicals in the mixing of PS and MA. However, in the mixing of NR and MA, the shear action of rotors at speed of 60 rpm can generate NR macroradicals, leading to the formation of maleated natural rubber (MNR) and the presence of chemical shift at 172 ppm.

**Table 5.4** The typical chemical shifts in  $^{13}\text{C}$  NMR

| Carbon Environment               | Chemical Shift (ppm) |
|----------------------------------|----------------------|
| $\text{C}=\text{O}$ (in esters)  | 165 - 175            |
| $\text{C}$ in aromatic rings     | 125 - 150            |
| $\text{C}=\text{C}$ (in alkenes) | 115 - 140            |
| $\text{RCH}_3$                   | 8 - 35               |
| $\text{R}_2\text{CH}_2$          | 15 - 50              |
| $\text{R}_3\text{CH}$            | 20 - 60              |
| $\text{R}_4\text{C}$             | 30 - 45              |

### 5.4.3 Thermal Property

Glass transition temperature ( $T_g$ ) at onset that occurs at the lowest temperature and relates to mechanical failure was measured [33]. Figure 5.2 and Table 5.5 show DSC thermograms and  $T_g$  of the blends with various mixing procedures and MA loadings. The incorporations of NR and MA into PS matrix result in an increase of  $T_g$  at onset from 90 °C for Neat PS to around 98 °C for PS/NR, PS/NR/MA and PS/MNR blends. This is attributed to the formation of PS/NR graft copolymer via free radical reaction between PS and NR in the presence of peroxide initiator (see Scheme 5.3). Chain-chain interactions presented at PS/NR interfaces lead to the enhancement of chain stiffness and the limitation of molecular chain motion. Furthermore, the rigidity of gel part also causes the glass transition temperature to shift to higher values.



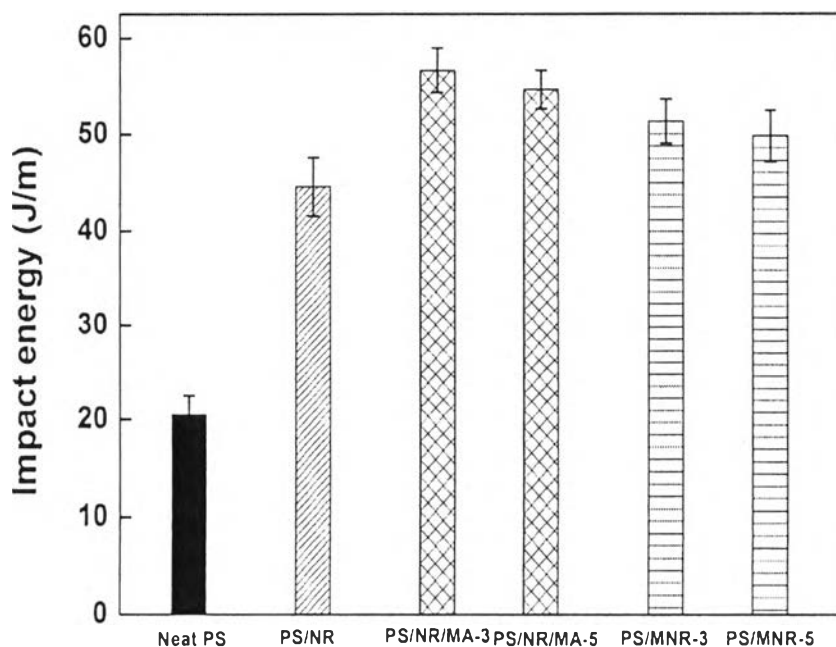
**Figure 5.2** DSC thermograms of Neat PS, PS/NR, PS/NR/MA and PS/MNR blends with various MA loadings.

**Table 5.5** Glass transition temperature ( $T_g$ ) at onset of Neat PS, PS/NR, PS/NR/MA and PS/MNR blends with various MA loadings

| Materials  | $T_g$ at Onset ( $^{\circ}\text{C}$ ) |
|------------|---------------------------------------|
| Neat PS    | 90.0                                  |
| PS/NR      | 97.5                                  |
| PS/NR/MA-3 | 98.0                                  |
| PS/NR/MA-5 | 98.8                                  |
| PS/MNR-3   | 98.0                                  |
| PS/MNR-5   | 98.3                                  |

#### 5.4.4 Impact Property

Impact energy of various blends is shown in Figure 5.3. It indicates that the incorporation of NR into PS increases the impact energy up to 45 J/m (about twice that of neat PS) due to more energy absorption and energy dissipation of rubber [34]. For addition of maleic anhydride, it helps natural rubber distribute well in PS matrix. Besides, more formation of graft copolymer increases the interfacial adhesion at PS/NR interfaces, resulting in the enhancement of impact energy. The chemical linkages presented at their interfaces tie two phases of PS and NR together, and allow more stress or energy to be transferred from one phase to another phase. Consequently, the impact energy of PS-NR-MA blends was found to increase up to 50 J/m approximately. However, the impact energy of PS/MNR blends using two-step mixing is slightly lower than that of PS/NR/MA blends using one-step mixing. This suggests that more shear force applied to NR during two-step mixing causes the heat generation, leading to the increase in temperature of material being mixed. Hence, the thermal degradation of NR molecular chains could occur, leading to the reduction in the average molecular weight of NR [35]. Considering MA loading, the decreasing of impact energy is found in the blends containing MA 5 wt%. This is attributed to the non-homogeneous blends, resulting from the increasing of gel content.



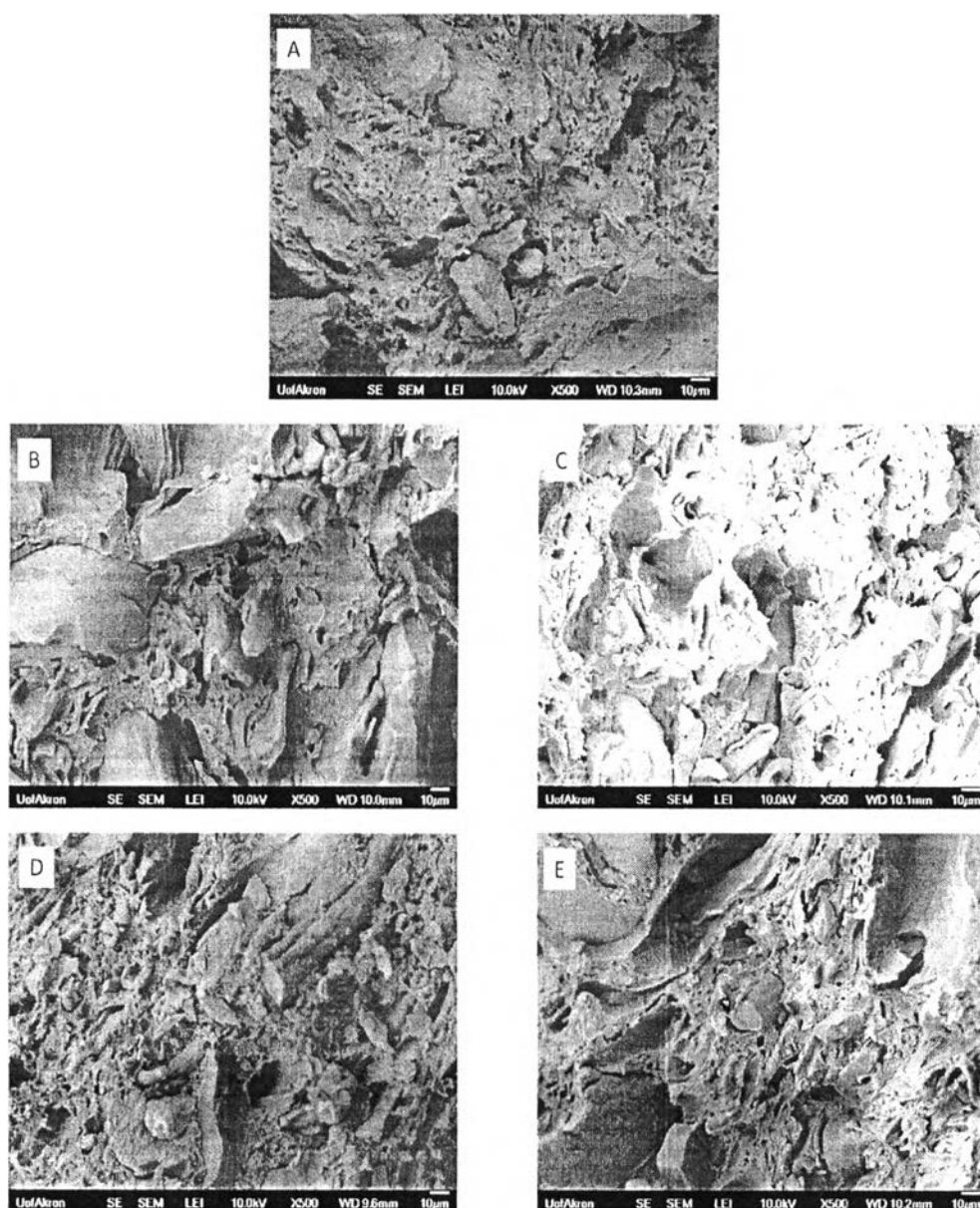
**Figure 5.3** Impact energy (J/m) of Neat PS, PS/NR, PS/NR/MA and PS/MNR blends with various MA loadings.

#### 5.4.5 Phase Morphology

For an incompatible blend, the Gibbs free energy of mixing depending on the interfacial tension was reported by Krause [36]. They stated that the higher the interfacial tension of the blend, the higher the free energy of mixing is. The Gibbs free energy of mixing is positive; hence, phase separation could occur when two components are blended together. For PS/NR blend in the absence of initiator, it is not only immiscible but also incompatible blend. This is due to a lack of interfacial interaction providing high interfacial tension at their interfaces. The addition of peroxide initiator can generate PS and NR macroradicals, and then these two active sites react with each other resulting in the formation of PS-g-NR copolymer. Although this interaction increases the interfacial adhesion, it is not sufficient. Consequently, voids at PS/NR interfaces are found as shown in Figure 5.4(A) and a good distribution of NR domains in PS matrix cannot be obtained. The presence of MA in PS/NR/MA and PS/MNR blends increases the compatibility of PS and NR as shown in Figure 5.4(B-E). SEM micrographs show a good distribution of NR



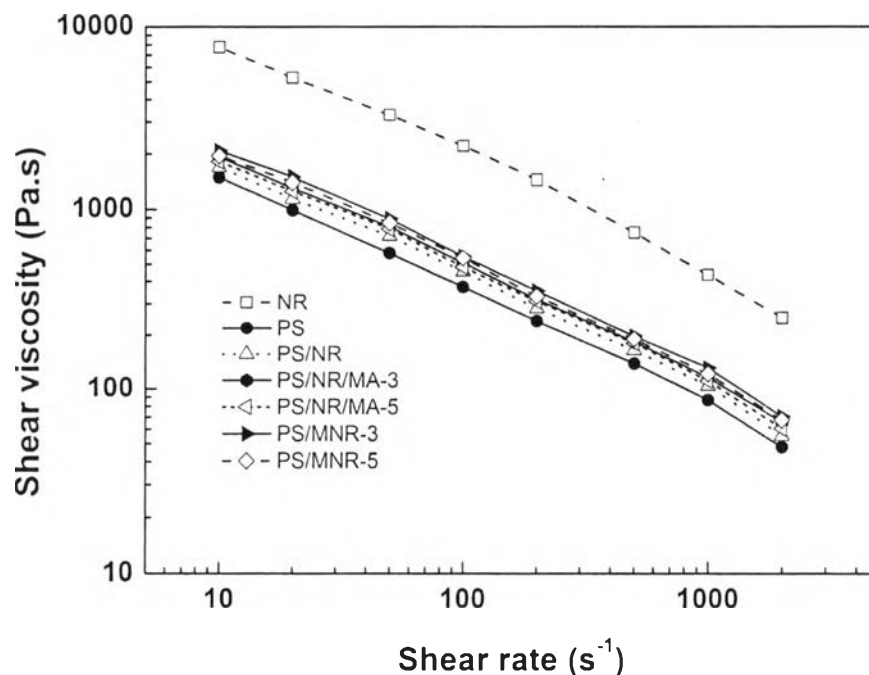
domains in PS matrix for PS/MNR blends (two-step mixing). Furthermore, the interfacial adhesion between PS phase and NR phase is increased in PS/MNR blend containing MA 3 wt%, PS/MNR-3, leading to the lowering of voids at their interfaces as shown in Figure 5.4(D). This is attributed to more polymer-MA grafting (less unreacted PS and gel content) of PS/MNR-3 blend.



**Figure 5.4** SEM micrographs of the cryofracture surfaces of injection molded impact specimens of A) PS/NR, B) PS/NR/MA-3, C) PS/NR/MA-5, D) PS/MNR-3, and E) PS/MNR-5 blends.

#### 5.4.6 Viscosity

The rheological characteristic of PS/NR and PS-NR-MA blends were studied by capillary rheometry, with reference to the effect of mixing procedure and MA loading. The results demonstrate that shear viscosity of all blends decreases monotonically with increasing shear rate as shown in Figure 5.5, indicating their shear-thinning or Pseudoplastic behavior. For Pseudoplastic behavior, asymmetric molecular chains are randomly oriented and/or extensively entangled at rest. Under low shear rate, these chain entanglements impede severely the flow of the melt. Consequently, the shear viscosity of the blends is still high. The molecular chains are then disentangled by high shear rates, and they become oriented in the flow direction, resulting in the decrease of shear viscosity [37]. At a given range of shear rate, NR exhibits higher viscosity than does PS, and the shear viscosities of PS/NR, PS/NR/MA (one-step mixing) and PS/MNR (two-step mixing) with two different MA loadings are placed in between those of the homopolymers. Basically, the crosslinked structure of NR (gel) makes the molecular chains stiff and difficult to move; hence, the shear viscosity of PS/NR blend should be higher than that of PS/NR/MA and PS/MNR blends. However, the results show that the presence of maleic anhydride increases the shear viscosities of both PS/NR/MA and PS/MNR blends although these blends have less gel content as compared with PS/NR blend. Furthermore, the use of two-step mixing provides the blends (PS/MNR) having higher shear viscosities. This reversed effect (shear viscosity increases at low gel content) can be explained by more grafting reaction that turns to play an important role to increase the blend viscosity. As discussed previously, in PS/MNR blends, the grafting reaction between PS and NR macroradicals in the presence of MA providing the graft copolymer is more predominant than the recombination of NR macroradicals providing crosslinked NR (gel). Hence, the increase of interfacial interaction and interfacial adhesion between PS phase and NR phase also causes the limitation of molecular chain motion and the increasing of shear viscosity. With increasing MA loading up to 5 wt%, the shear viscosities of the blends (both PS/NR/MA-5 and PS/MNR-5) are found to decrease slightly. It suggests that the increasing of gel obstructs the formation of graft copolymer between PS and NR at their interfaces, leading to the lowering of graft ratio as well as the blend viscosity.



**Figure 5.5** Shear viscosity (Pa.s) of Neat PS, PS/NR, PS/NR/MA and PS/MNR blends with various MA loadings.

## 5.5 Conclusions

The difference of mixing procedures and MA contents affected obviously on gel (crosslinked NR) content, MA grafting efficiency, and graft ratio. Comparing with PS/NR blend, the addition of MA resulted in the decrease in gel content and the increase in graft ratio of PS/NR/MA and PS/MNR blends. The reduction of gel content and the increasing of MA grafting efficiency and graft ratio were also found in the blends using two-step mixing and low MA content (3 wt%), PS/MNR-3. This is due to more reaction of MA to NR in PS/MNR-3 blend as compared with the blends using one-step mixing (PS/NR/MA-3 and PS/NR/MA-5) and the blend containing higher MA content (PS/MNR-5). Thermal analysis showed the increase in glass transition temperature of PS from 90 °C for neat PS to around 98 °C for PS/NR, PS/NR/MA and PS/MNR blends with various MA contents. For rheological study, the shear viscosity of PS/MNR-3 showed the highest values. It suggested that more formation of graft copolymer between two components of PS and NR via free

radical reaction increased the chain-chain interactions and the chain stiffness, and caused the limitation of molecular chain motion. Consequently, the glass transition temperature and the blend viscosity were increased. Furthermore, the morphology observation demonstrated that the distribution of NR domains in PS matrix of PS/MNR-3 blends was better than that of PS/MNR-5 and PS/NR/MA blends. The increase of interfacial interaction by grafting increased the interfacial adhesion between PS phase and NR phase, leading to the decreasing of voids at their interfaces. Hence, more stress or energy could be transferred from one phase to another phase, resulting in the increasing of impact energy of PS/MNR blends as compared with PS/NR blend. The usefulness of these reactive blends containing the graft copolymer is not only to provide the compatible blend, but to be employed as the compatibilizer for other blends. This approach is very therefore beneficial to the area of polymer blend as well as polymer waste recycle.

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