

# The Effect of Composition on the Dynamic and Mechanical Properties of Natural Rubber–Poly(methylmethacrylate) Blends

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**ABSTRACT:** The miscibility of the components in natural rubber–poly(methylmethacrylate) blends for potential use as reinforced rubbers was evaluated using the glass transition temperatures, peak widths of the loss tangent peak at the glass transition and the complex heat capacity data obtained from dynamic mechanical thermal analysis (DMTA), and modulated differential scanning calorimetry (MDSC). In addition, the effect of the poly(methylmethacrylate) content on the dynamic mechanical and the physical properties such as tensile behavior and hysteresis loss was studied. DMTA and MDSC data clearly indicated that the blends were phase-separated. Nevertheless, the glass transition temperature of the natural rubber component in the 30–50 wt % NR/PMMA blends has shifted to higher

temperatures compared to the natural rubber treated under the same condition, indicating some limited extent of mixing of components in these blends. The physico-mechanical properties including moduli at 100, 300, and 500% and tensile strength of the NR/PMMA blends were determined. Incorporation of PMMA into NR matrix improved the strength properties of the NR/PMMA blends prepared reasonably akin to interpenetrating polymer networks (IPN) polymerization method. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3217–3224, 2009

**Key words:** compatibility; crosslinking; interpenetrating polymer networks; phase separation; synthesis; natural rubber; poly(methylmethacrylate)

## INTRODUCTION

Blends with improved properties are often technically important materials. They may be produced by combining two or more polymers<sup>1</sup> either in solution, in latex form or in the solid state. The vast majority of polymer blends are incompatible and only very few binary polymer blends are found to be totally miscible.<sup>1</sup> The mixing of a glassy polymer with natural rubber (NR) ultimately leads to a product either referred to as a thermoplastic elastomer or an impact-resistant plastic, depending on its composition.<sup>2</sup> In this article, we are concerned with the production of rubbery materials with enhanced physical properties.

The most widely studied glassy polymers in combination with NR are poly(styrene)<sup>3–5</sup> and poly(methylmethacrylate) (PMMA).<sup>3,6</sup> Recently, more attention had been paid to the preparation of NR/PMMA blends<sup>7,8</sup> since such combinations are expected to provide useful properties. NR possesses

excellent physical properties and PMMA exhibits weather resistance and excellent clarity. By combining these two particular polymers, physical properties may possibly be improved. However, the physical properties of the resultant blends have been found to be inferior due to the marked incompatibility of the components.<sup>7,8</sup> However, the physical properties had been improved greatly by the addition of PMMA-grafted NR as a compatibilizer for NR/PMMA blends.<sup>9</sup>

An interpenetrating polymer network (IPN) is defined as a combination of two or more polymers in network form and is synthesized by polymerizing at least one polymer in the presence of the other polymer.<sup>10</sup> Because of the unique structure of IPNs, in which interpenetration of polymer molecules/phases presumably take place resulting in limited phase separation, the IPN polymerization method would be a potential method for the modification of NR.<sup>2</sup> Such materials may be employed in applications such as impact-resistant articles and reinforced materials, where they can be used in automobile components and molded parts.<sup>9</sup>

To date, IPNs based on NR have not been widely studied, but will be discussed by the authors of this article in a number of subsequent publications. Latex

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IPNs based on NR and PMMA<sup>3,6</sup> or NR and PS<sup>3-5</sup> have been prepared. The initiator system and the elastomer/plastomer ratio were varied. The synthesis method of these composite latices was similar to the IPN synthesis method, and, therefore, these latex composites are latex IPNs (LIPNs). Certain physical properties, tensile behavior, tear strength, and hysteresis of these IPNs were investigated.<sup>3,6</sup> Furthermore, the morphologies were evaluated by TEM studies, SEM, and dynamic mechanical thermal analysis (DMTA). The oil-soluble initiator, *t*-butyl peroxy 2-ethyl hexanoate (Triganox 21S), has proved to impart improved miscibility and satisfactory mechanical properties for NR/PS LIPNs.<sup>3</sup> The effect of crosslinking and the composition on physical properties and morphology of sequential semi-1 and full IPNs based on NR and a glassy polymer; either PMMA<sup>11</sup> or PS have also been investigated.<sup>12,13</sup> NR, obtained from Manihot glaziovii, has been used in the preparation of full and pseudo IPNs with brominated poly(2,6-dimethyl-1,4-phenylene oxide) (Br-PPO) as the second polymer by the simultaneous preparation method.<sup>14</sup> Despite the solubility differences of the pure components, fully miscible compositions for full IPNs with higher percentage of NR (70–90%) and for higher percentages of Br-PPO (90%) could be obtained.

The aim of this study is to prepare a range of blends based on NR and PMMA by varying the PMMA content. These blends were prepared by swelling the NR component, in sheet form, in monomer/initiator solutions followed by polymerizing the second polymer in the molecular matrix of the first. This is similar to a route used for IPN synthesis, thus making these blend materials comparable with the semi-IPNs and full IPNs, whereas NR phase is in crosslinked state and the both components are in crosslinked state, respectively, which is to be reported later. The morphologies of the blends prepared in this study were evaluated, principally, by DMTA and modulated differential scanning calorimetry (MDSC) to compare the conclusions from the established DMTA technique with those from the much more recent MDSC technique. Transmission electron microscopy sections were difficult to prepare for these blends, but much easier for the IPN systems to be discussed in subsequent articles. Tensile properties of the blends have also been determined.

## EXPERIMENTAL

### Materials

The NR latex with 60 wt % dry rubber content (kindly donated by Ansell Lanka, Sri Lanka), the monomer (MMA) and the initiator Triganox 21S (kindly donated by Akzo Nobel) was used as

received with the exception of the monomer which needed purification. Purification of the monomer was carried out by passing them through a disposable column of quaternary ammonium anion exchange resin to remove inhibitors such as hydroquinone and hydroquinone monomethyl ether. Dilution of NR latex was carried out using deionized water to make the dry rubber content up to 40 wt % prior to use for preparation of films.

## METHODS

### Preparation of NR films

A known amount of diluted NR latex (40 wt % dry rubber content) was sieved using a mesh (60  $\mu\text{m}$ ) and poured onto open glass trays to obtain NR films with a thickness of  $\sim 1$  mm. Thereafter, these cast films were dried at room temperature until they were transparent. They were further dried by heating the sheet at 70°C for 1 h in an oven. Films thus obtained were then stored in sealed polythene bags and used in the preparation of the NR/PMMA blends.

### Synthesis of NR/PMMA blends

NR film was cut into the required shape and the initial weight of the NR sample was recorded. Then this sample was placed in a closed container, containing a mixture of monomer, methyl methacrylate, and the initiator at 1 mol % on monomer content. To prepare samples with different PMMA content, the samples were subjected to swelling process for different time periods until the swollen sample reach predetermined weight which comprise of 10% excess monomer. The swollen NR sheets were then placed in sealed polythene bags and stored at  $\sim 5$ –8°C for about 24 h allowing uniform distribution of MMA within the NR matrix. Thereafter, the swollen samples were placed in a mold, and polymerization of the MMA was allowed to take place by heating the mold at 80°C for 22 h. The samples were removed from the mold, weighed and further dried in a vacuum oven at  $25 \pm 2^\circ\text{C}$  for 1 week to remove any residual monomer. Details of the compositions of the NR/PMMA blends are given in Table I. Sample codes indicate the approximate composition by weight.

## PROPERTIES EVALUATION

### DMTA, MDSC, and stress–strain properties

Dynamic mechanical properties including loss tangent ( $\tan \delta$ ), mechanical storage modulus as a function of temperature were assessed by the DMTA using dynamic mechanical thermal analyzer (DMA 2980, TA Instruments). The DMTA scans were

**TABLE I**  
Composition Range of the NR/PMMA Blends

NR/PMMA blend	Target composition		Experimental composition	
	NR (wt %)	PMMA (wt %)	NR (wt %)	PMMA (wt %)
NR90:PMMA10	90	10	91	9
NR80:PMMA20	80	20	83	17
NR70:PMMA30	70	30	73	27
NR60:PMMA40	60	40	61	39
NR50:PMMA50	50	50	52	48

obtained in the tension mode at 1 Hz frequency. The heating rate was set at  $3^{\circ}\text{C min}^{-1}$  and the scans were recorded from  $-100$  to  $200^{\circ}\text{C}$ . A TA Instruments (2920 Modulated DSC) was used to determine complex heat capacity as a function of temperatures. The MDSC scans were obtained by heating the sample from  $-130$  to  $180^{\circ}\text{C}$  at a heating rate of  $3^{\circ}\text{C min}^{-1}$ . Oscillation amplitude  $0.8^{\circ}\text{C}$  and oscillation period 60 s were used. Tensile testing was performed according to ISO 37 using a Hounsfield tensometer (Model No. H 5000M) to determine the tensile strength, moduli at 100, 300 and 500% and % elongation at break. Cycling test had also been carried out using a Hounsfield tensometer (Model No. H 5000M). Three consecutive cycles up to 300% strain were obtained for Dumbbell-shaped tensile test piece by subjecting to extension rate at  $20\text{ mm min}^{-1}$  (temperature  $25 \pm 2^{\circ}\text{C}$ ). Force against extension was plotted for each cycle and the area between the extension and the retraction curves was calculated as an energy value. In addition, hysteresis was determined by plotting stress versus strain curves for the extension and the retraction of the first cycle.

## RESULTS AND DISCUSSION

### Compatibility study

Throughout the present work, NR and PMMA have been chosen since such a combination of elastomeric and thermoplastic polymers might be expected to provide synergistic properties.<sup>2</sup> Compatibility study of these two components is vital as it affects the morphology, and, hence, the physical and dynamic mechanical properties of the blends.

The solubility parameters,  $\gamma$ , calculated according to the Small and Hoys<sup>15</sup> methods are given in Table II. According to the empirical criterion established by Pazonyi and Dimitrov,<sup>16</sup> compatibility is feasible when the difference of the cohesive energy densities,  $\gamma^2$ , is less than  $6.69 \times 10^4\text{ J m}^{-3}$ .<sup>16,17</sup> The difference between the cohesive energy densities ( $\gamma_{\text{PMMA}}^2 - \gamma_{\text{NR}}^2$ ) of the NR and the PMMA was found to be

**TABLE II**  
Solubility Parameter ( $\gamma$ ) Values for Natural Rubber and Poly(methylmethacrylate) Determined According to Small's and Hoy's Methods

Method	Solubility parameter ( $\text{MPa}^{1/2}$ )	
	Polymer	
	Natural rubber	PMMA
Small	16.73	18.6
Hoy	18.02	19.4
	$\gamma_p$	9.25
	$\gamma_h$	10.3
	$\gamma_d$	13.4

$\gamma_p$ , accounts for the permanent dipole-dipole interactions;  $\gamma_h$ , accounts for the hydrogen bonding forces;  $\gamma_d$ , accounts for the dispersive forces (Ref. 15).

$66.1 \times 10^6\text{ J m}^{-3}$ . Thus, NR is predicted to be strongly incompatible with PMMA.<sup>2</sup>

An alternative method for determining the compatibility of polymers, proposed by Krause,<sup>18,19</sup> utilizes the interaction parameter between the two polymers as well as the interaction parameter at the critical point on the phase diagram for that binary system. In this method, the two parameters were calculated as follows.

$$(\chi_{12}) = [V_r/RT](\gamma_1 - \gamma_2)^2 \quad (1)$$

$V_r$  is the molar volume of the smaller repeat unit,  $R$  is the gas constant and  $T$  is the temperature, which is 298 K.

$$(\chi_{12})_{\text{cr}} = 1/2(1/n_1^{1/2} + 1/n_2^{1/2})^2 \quad (2)$$

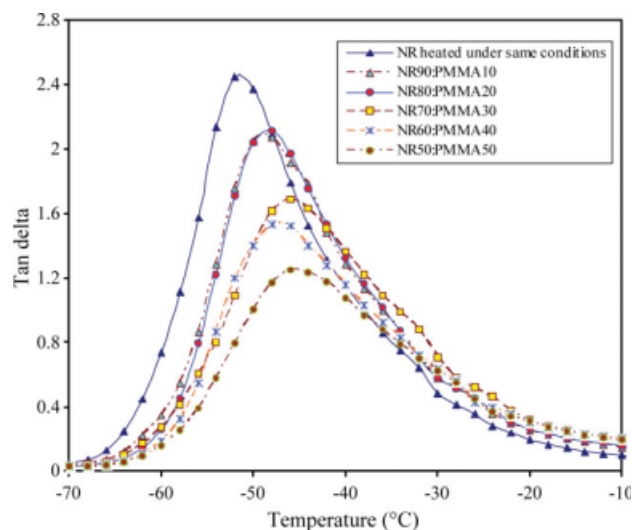
$n_1$  and  $n_2$  represent the degree of polymerization of each constituent polymer.

The molecular weight of the poly(isoprene) which is structurally similar to NR was considered as  $100,000\text{ g mol}^{-1}$  for this calculation. The molecular weight of the PMMA was varied from 5,000 to  $80,000\text{ g mol}^{-1}$ . The calculated values for the  $(\chi_{12})_{\text{cr}}$  coefficients are given in the Table III.

**TABLE III**  
The Calculated Values for  $(\chi_{12})_{\text{cr}}$  for the Binary System Consisting of Poly(isoprene) and PMMA

Polymer system	Molecular weight of PMMA (g/mol)	$(\chi_{12})_{\text{cr}}$
Poly(isoprene)/PMMA	80,000	0.0019
	60,000	0.0022
	40,000	0.0029
	20,000	0.0046
	10,000	0.0079
	5,000	0.014

$$(\chi_{12}) = 0.11.$$



**Figure 1** Effect of composition on the loss tangent of the NR component of the NR/PMMA blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

According to the Krause method, if  $\chi_{12}$  is greater than the  $(\chi_{12})_{cr}$ , then it implies the existence of incompatibility.<sup>17</sup> For this system,  $\chi_{12}$  was found to be 0.11. Hence, it can again be assumed that poly (isoprene) and PMMA are incompatible. However, synthesizing the PMMA in the NR matrix is expected to improve the extent of mixing. As at least one component is present in the monomer form, which massively favors the entropy factor, which contributes to the mixing unlike their polymeric counterparts where the entropy contribution is low.

### Effect of blend composition on miscibility

#### Dynamic mechanical properties

Dynamic mechanical thermal analysis is probably the most widely used technique to determine the miscibility between components in blends. It is accepted that a single glass transition would result due to the complete mixing of components at the molecular level. On the other hand, two glass transitions, corresponding to the homopolymers, indicate an immiscible blend.<sup>20</sup> However, with increasing miscibility, the two glass transitions shift to intermediate positions.<sup>21</sup> Therefore, the extent of miscibility of components in a blend can be determined depending on the positions of glass transitions and their characteristics.

The effect of composition on the loss tangent of the NR component for the NR/PMMA blends is shown in Figure 1. The  $T_g$  was taken as the  $\tan \delta$  maximum temperature. Compared with the NR, heated under the same conditions, the  $T_g$  of the NR component has shifted to higher temperatures by 3–6°C in the NR/PMMA blends containing 30–50 wt % PMMA (Fig. 1 and Table IV). This can be consid-

**TABLE IV**  
Half Peak Widths of the NR Transition and the  $T_g$ s of the NR and PMMA Transitions (From DMTA Data)

Sample	NR $T_g$ (°C)	Half peak width (°C)	PMMA $T_g$ (°C)
Natural rubber <sup>a</sup>	-51	16	
NR90:PMMA10	-49	17	-
NR80:PMMA20	-49	17	-
NR70:PMMA30	-46	22	156
NR60:PMMA40	-48	21	158
NR50:PMMA50	-45	23	154

<sup>a</sup> Natural rubber treated under the same conditions.

ered as evidence for some mixing of the components in these samples.<sup>6,22,23</sup> MDSC data also verified that some limited extent of mixing of components has occurred in the blend samples containing 30–50 wt % PMMA (see later Table V). Interpenetration and/or grafting of PMMA onto NR are believed to be the reasons for this behavior. Grafting of a polymer on to another polymer chain improves the extent of mixing and simultaneously restricts the segmental motions resulting in an increase in the glass transition temperature of the rubbery component. Similar trends have been observed in studies carried out on graft IPNs based on polyurethanes.<sup>24–26</sup> A shift of 4°C has also been observed in the NR  $T_g$  transition in PMMA radiation grafted NR,<sup>26</sup> suggesting that the grafting of PMMA to NR will result in an increase of the NR  $T_g$ .

Figure 1 indicates, as expected,<sup>4,26,27</sup> increasing the percentage of PMMA caused a reduction in  $\tan \delta_{max}$  of the NR component. As the height of the  $\tan \delta$  peak reflects the relative quantities of each component present in such composites, this reduction can be primarily attributed to the reduction in rubber content.<sup>28,29</sup> An identical trend was found for the PMMA transition (Fig. 2). The transition due to the

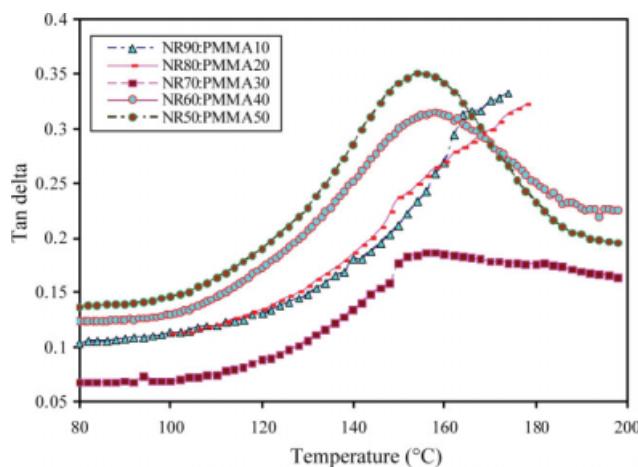
**TABLE V**  
Calculated Interphase Fractions ( $\mu$ ) and Multiple Peak Analysis Data for the NR/PMMA Blends

NR/PMMA ratio (wt %)	NR $T_g$ (°C)	Multiple peak analysis data		
		Interphase (%)	NR-rich phase	PMMA-rich phase
100/0 <sup>a</sup>	-68			
90/10	-67			
80/20	-66	25 <sup>b</sup>		
70/30	-65	16	12	11
60/40	-66	19	15	18
50/50	-66	23	16	14

Data obtained from the plot of  $dC_p/dT$  vs. temperature were used for the multiple-peak analysis.

<sup>a</sup> NR treated under the same conditions.

<sup>b</sup> Mixed phases include NR-rich phase, PMMA-rich phase and interphase.



**Figure 2** Effect of composition on the loss tangent of the PMMA Component of the NR/PMMA blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

PMMA component is not fully resolved in the dynamic spectra of the 90/10 and 80/20 NR/PMMA samples (Fig. 2). However, the absence of a prominent PMMA transition in the DMTA spectra is not an indication of complete mixing of PMMA component because of the resolution limitations of this technique. The PMMA transition of the NR70:PMMA30 blend is present as a broad minor peak, indicative of improved mixing of the components.

However, as shown in Table IV and Figure 2, as the PMMA content increased from 40 to 50 wt %, the PMMA  $T_g$  has shifted to lower temperature by 4°C. This inward shift could be the result of enhanced mixing with increasing PMMA content. This is further confirmed from the MDSC data shown in Table V.

Figure 3 depicts the effect of PMMA content on the storage modulus for three of the NR/PMMA blends. Both transitions corresponding to the NR and the PMMA components are clearly evident. The storage modulus value at 20°C had increased from 1.53 to 6.71 MPa with the increase of the PMMA content from 30 to 50 wt %. An identical trend had been observed for polyisobutene (PIB)-PMMA semi-1 IPNs, when the PMMA content was increased from 0 to 50 wt %.<sup>30</sup> This behavior is the result of the reinforcement effect imparted by the hard, glassy PMMA phases.

As the NR transition is prominent and the height between the glassy region and the rubbery region of NR transition is greater than that of the PMMA component (Fig. 3), it can be concluded that the NR phase is the continuous phase in all these samples. Therefore, the blends behave as reinforced elastomers.<sup>30</sup>

It has been reported<sup>31</sup> that the activation energy of the chain backbone motion is related to the area under the tan delta curve. Therefore, the activation energy for a particular transition can be calculated by using the following equation.<sup>31</sup>

$$T_A = (\ln E_G - \ln E_R)(R/E_A)(\pi/2)(T_g)^2 \quad (3)$$

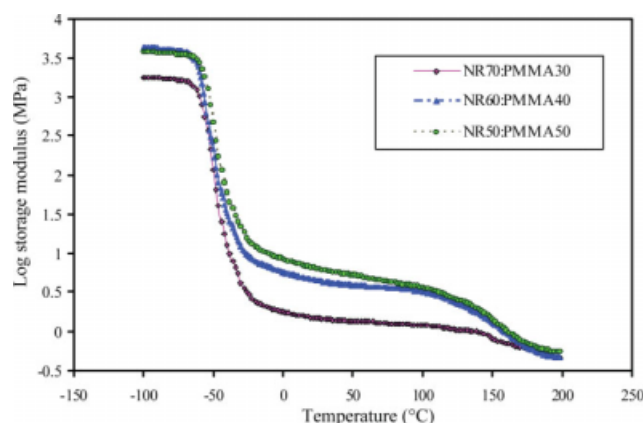
$T_A$  is the area under the tan delta curve and  $E_G$  and  $E_R$  are the storage modulus values in the glassy ( $-100^\circ\text{C}$ ) and rubbery regions ( $20^\circ\text{C}$ ), respectively.  $E_A$  is the activation energy.  $R$  and  $T_g$  are the gas constant and the glass transition, respectively.

This equation had been used for the calculation of the normalized activation energy by comparing the data for each blend with the data for NR treated under the same conditions.

The results obtained for the normalized activation energies of the blends of NR and PMMA are listed in Table VI. Increasing the percentage of PMMA from 30 to 50 wt % caused an increase in the normalized activation energy. A similar trend had been found for the normalized activation energy of PMMA grafted NR samples in which grafting was performed by radiation.<sup>26</sup> This behavior had been attributed to the restriction of backbone motion with increasing PMMA content resulting in an increase in the activation energy.<sup>2,26</sup>

### Analysis of MDSC data

MDSC data have been used for the analysis of multiphase systems by Hourston et al.<sup>32</sup> According to their study, the area under the peak corresponding to glass transition region is related to the heat capacity of the phase represented by the peak. Multiphase analysis for the  $dC_p/dT$  curves is done using a computer program. For this purpose, a baseline correction was made. In this work, the curve has



**Figure 3** Effect of composition on the storage modulus of the NR transition of the blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

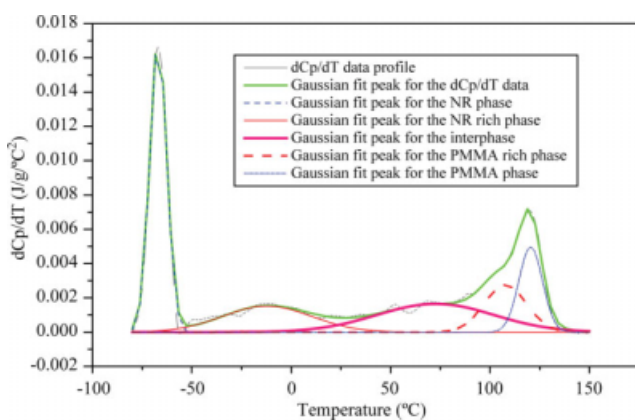
**TABLE VI**  
Calculated Normalized Activation Energies of the NR Transition for the NR/PMMA Blends

Sample	Normalized activation energy
Natural rubber <sup>a</sup>	1.0
NR90:PMMA10	1.04
NR80:PMMA20	1.06
NR70:PMMA30	1.05
NR60:PMMA40	1.11
NR50:PMMA50	1.21

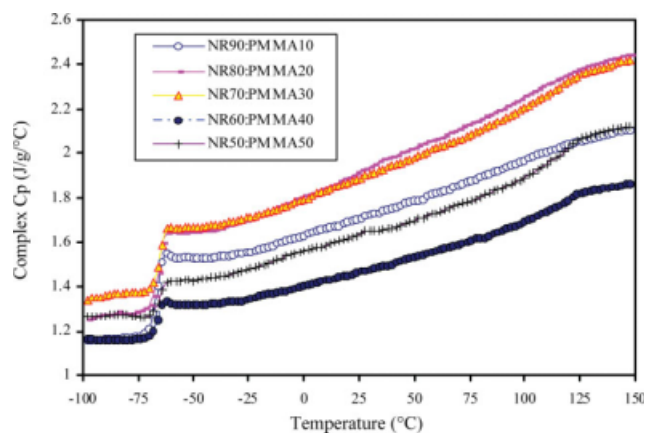
<sup>a</sup> Natural rubber treated under the same conditions.

been resolved into five Gaussian curves<sup>33</sup> corresponding to the NR phase, a NR-rich phase, an interphase, a PMMA-rich phase and the PMMA phase as shown in Figure 4. The percentage interphase ( $\mu$ ) was calculated as the ratio of the area of the middle peak, corresponding to interphase, to the total area of all the peaks and by multiplying by 100. Similarly, the percentages of NR-rich phase and the PMMA-rich phase were also calculated. The calculated percentage of each phase is given in Table V. When the whole set of results (Table V) are considered, a substantial amount of the NR, or PMMA, component was found in the interface region. Nonetheless, the total mixed phase contents of samples containing 30–50 wt % of PMMA were significantly higher than for the sample with 20 wt % of PMMA and were in agreement with the DMTA data. This is an expected trend since the higher the PMMA content, the greater are the chances for mixing of the NR with the PMMA component. In addition, grafting of PMMA onto NR can be considered as one of the probable causes for the demonstrated improved mixing.

Effect of composition on the complex heat capacity  $C_p$  for the blends is shown in Figure 5. Two distinct glass transitions were observed for the blends con-



**Figure 4** Temperature dependence of  $dC_p/dT$  for the NR50:PMMA50 blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

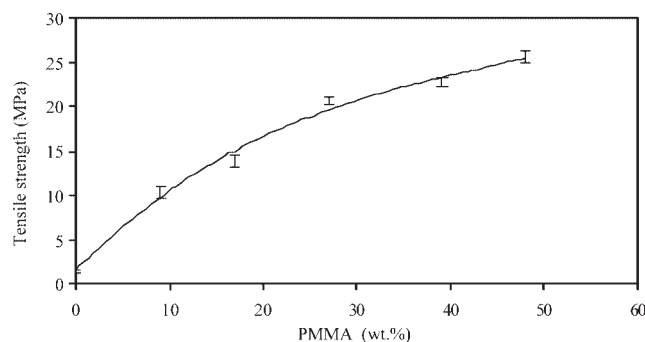


**Figure 5** Effect of composition on the complex heat capacity  $C_p$  for the NR/PMMA blends (\*Complex  $C_p$  refers to the ratio of amplitude of the heat flow to the heating rate). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

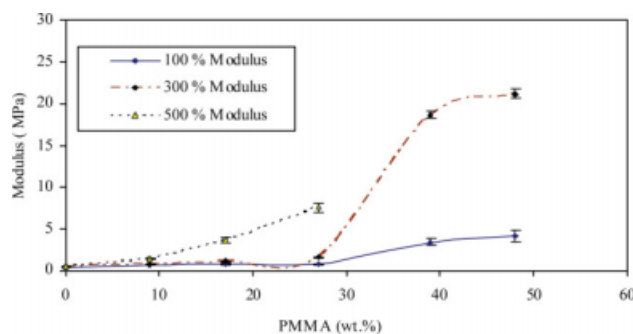
taining 10 wt % and more PMMA, indicating phase separation. When comparison of the  $T_g$ s of the PMMA transitions in the NR/PMMA blends with the  $T_g$  of the homopolymer (91°C, determined by MDSC) was made, it was found that the  $T_g$ s of the PMMA transitions in the blends were higher. Therefore, this shift of  $T_g$  of the PMMA component to higher temperature is primarily attributed to a reduction of mobility of PMMA chain segments in the final material. A similar trend was also reported<sup>30</sup> for the PMMA component in the poly(isobutylene) (PIB)/PMMA semi-1 IPNs which was attributed to the confined environment experienced by the PMMA chains present inside the PIB network.

#### Effect of composition on stress–strain behavior

Figures 6–8 show the effects of composition on the tensile properties of the blends. Incorporation of PMMA leads to a significant increase in tensile strength of the NR90:PMMA10 blend compared with

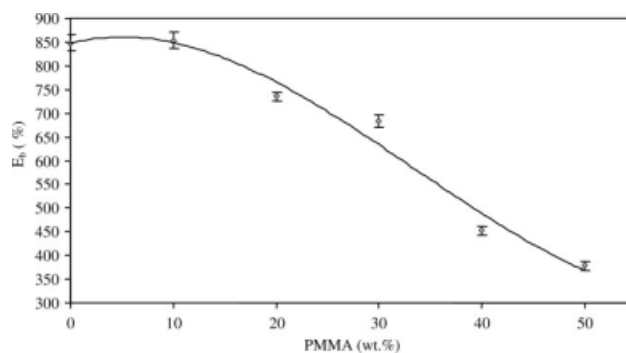


**Figure 6** Effect of composition on the tensile strength of the NR/PMMA blend.



**Figure 7** Effect of composition on the 100, 300, and 500% moduli of the NR/PMMA blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

NR treated under the same conditions. The results clearly show that the tensile strength has increased significantly with increased PMMA content. A significant increase of the 100 and 300% moduli has been noted with the addition of 30–50 wt % of the PMMA content (Fig. 7) and is in agreement with the storage modulus and MDSC data. The 500% modulus increased with increase of the PMMA content up to 30 wt %. However, 500% modulus values could not be obtained for the blends having 40–50 wt % PMMA content due to the breaking down of samples resulted by the less extensibility. This behavior could be due to the reduction of elastomeric phase with increase of the PMMA content. This was accompanied by a decrease in the elongation at break with increase in the PMMA content. These results are in agreement with other studies.<sup>11</sup> The improved tensile properties of these blends are probably the results of a reinforcement effect and the improved miscibility resulting from some interpenetration and/or grafting of PMMA onto the NR chains. Comparison of the tensile strength for the blends prepared according to this method and the blends prepared by solution state mixing<sup>8</sup> indicate that the tensile strengths of these blends are significantly higher than the tensile strength values reported for the solution state mixing of NR and



**Figure 8** Effect of composition on the elongation at break for the NR/PMMA blends.

PMMA.<sup>8</sup> In this case, NR was mixed with the monomer, which will have an appreciable entropy of mixing. Hence, it would be expected that the extent of mixing of the polymeric component with a monomer would be higher than in a solution blend of polymeric components. This, higher level of mixing would render better physical properties than the blends prepared by mixing two polymers. In addition, the NR component was obtained via drying of the NR latex as a cast sheet without subjecting it to the mastication process. This also results in improved physical properties.

### Hysteresis

Cycling tests have been carried out to determine the effect of the PMMA content on the hysteresis behavior (HL) and hysteresis (energy loss) of the blend. Energy loss is defined as the area between the loading and unloading force versus extension curves. Moreover, the hysteresis behavior, which is referred to as the ratio of the energy lost to the energy recovered (stored) was also determined and the data presented in Table VII. The amount of energy dissipated as heat also increased with increasing PMMA content. The increase in the amount of energy dissipated during cycling testing with increase of PMMA could be attributed to the occurrence of friction between the

**TABLE VII**  
Energy Loss and Hysteresis Behavior for the NR/ PMMA Blends

Composition	Cycle 1		Cycle 2		Cycle 3	
	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
NR <sup>a</sup>	0.57	0.45				
90/10	0.11	0.28	0.04	0.11	0.03	0.07
80/20	0.15	0.47	0.07	0.23	0.07	0.21
70/30	0.64	1.26	0.38	0.84	0.33	0.75
50/50	4.01	2.5	x	x	x	x

HL, Hysteresis behavior calculated as the ratio of the amount of energy lost to the amount of recovered in each cycle; x, Permanent set exhibited by the stretched sample.

<sup>a</sup> NR, treated under the same conditions.

hard glassy PMMA phases and the rubber phases during the deformation. This observation is in agreement with the findings of earlier studies conducted on IPNs based on NR and PMMA.<sup>3,6</sup> On the other hand, it may be assumed that in these blends, the PMMA phases might have undergone a plastic deformation resulting in the breakdown of structure causing softening of the material. It could be anticipated that most of the phase structures break down in that cycle, resulting in maximum strain softening in the first cycle. The strain softening and hysteresis are indeed lower in the subsequent cycles as revealed from Table VII. After several cycles, the stress-strain behavior is stabilized.<sup>34</sup>

### CONCLUSIONS

From this study, it can be concluded that the IPN polymerization method is a viable method to prepare NR/PMMA blends. Synthesis of PMMA by polymerizing MMA with in the NR matrix results uniform film/sheets with improved phases adhesion and it will improve the compatibility as was evident from DMTA and MDSC data. Incorporation of the PMMA component increased the tensile strength, moduli 100%, 300%, and hysteresis.

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