

The Effect of Composition and the Level of Crosslinking of the Poly(methylmethacrylate) Phase on the Properties of Natural Rubber-Poly(methylmethacrylate) Semi-2 Interpenetrating Polymer Networks

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ABSTRACT: The effects of the PMMA content and the cross-linker level in the poly(methylmethacrylate) component on the dynamic and physico-mechanical properties of semi-2 interpenetrating polymer networks based on natural rubber and poly(methylmethacrylate) were determined. The miscibility of the components in these semi-2 interpenetrating polymer networks was determined using the loss tangent data, obtained from dynamic mechanical thermal analysis and the interphase contents were calculated from modulated scanning calorimetric data. Some component mixing in these semi-2 interpenetrating polymer net-

works was evident from these modulated differential scanning calorimetric and dynamic mechanical thermal analysis data. The degree of component mixing increased with cross-linker level in the PMMA phase. The PMMA content in the semi-2 IPNs has a significant effect on the tensile and hysteresis behavior of these semi-2 interpenetrating polymer networks. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3558–3564, 2012

Key words: rubber; interpenetrating networks (IPN); glass transition; miscibility; phase separation

INTRODUCTION

Polymer blends have been widely studied^{1–3} since blending of polymers may lead to desirable properties which cannot be obtained by using a single polymer. Modification of natural rubber (NR), a bio synthesized polymer, has been extensively studied over recent decades. This research has been substantially limited to grafting, epoxidation, halogenation, and cyclization⁴ studies. The synthesis of interpenetrating polymer networks can also be considered as one of the methods that may be used to modify natural rubber.^{5–7} Among the modified forms of natural rubber, interpenetrating polymer networks (IPNs) have not been extensively studied.⁵ Interpenetrating polymer networks are a combination of different polymer networks in which one polymer is synthesized and/or crosslinked in the presence of another, leading ideally to permanent entanglements between the components without the formation of covalent bonds between individual polymer chain types.^{8–10} In a semi-IPN only one of the polymeric components is crosslinked.

This investigation is concerned with preparation of semi-2 IPNs based on NR and poly(methylmethacrylate) (PMMA) since incorporation of PMMA into the NR phase may lead to materials with improved strength, clarity and weather resistance and could have use in automobile and other applications. Past research has indicated that these desired physical properties were unobtainable⁵ because of the strong incompatibility of the individual components in conventional NR/PMMA blends.^{11,12} Hence, the IPN synthesis route may offer a potential method to prepare new materials based on natural rubber and PMMA since this method limits phase separation and thereby may lead to improved physical properties.^{5–7} Natural rubber/poly(methylmethacrylate) and natural rubber/polystyrene IPNs have been synthesized in the latex state and the dynamic mechanical and other mechanical properties determined by Romaine and Hourston.^{13,14} These studies have shown that the IPN synthesis method leads to improved compatibility and mechanical properties.^{13,14} NR/PMMA and NR/polystyrene (PS) semi-1 and full IPNs have been synthesized and results indicated that the mechanical properties had improved depending on the PMMA, or PS, content and the crosslinker level.^{15,16}

Studies on semi-2 IPNs based on the natural rubber/PMMA system have not been reported. In this investigation, semi-2 NR/PMMA IPNs, where only

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the second formed component (PMMA) is in network form, were synthesized varying the PMMA content and the level of PMMA crosslinking. The dynamic and static mechanical properties of the resultant semi-2 IPNs are discussed.

In the first paper of this series, the effect of composition of the PMMA component on the dynamic and physical properties and on the compatibility of components were described for conventional NR/PMMA blends.⁶ The added advantage of semi-2 IPNs over the NR/PMMA blends prepared according to the IPN⁶ synthesis route can be considered as improved miscibility due to the limitations of phase separation caused by the crosslinking of PMMA phases present in semi-2 IPNs.

EXPERIMENTAL

Materials

Most of the chemicals were used as received, except for the methyl methacrylate monomer and the crosslinker, ethylene glycol dimethacrylate, which were purified by passing them through a disposable column of quaternary ammonium anion exchange resin supplied by the Aldrich Company, to remove inhibitors such as hydroquinone and hydroquinone monomethyl ether. Tertiary-butyl peroxy-2-ethylhexanote (Triganox 21S) was used as the initiator for the preparation of the IPNs as it has been proven to improve miscibility of polystyrene in latex IPNs based on natural rubber.⁷

Centrifuged natural rubber latex with a 60 wt % dry rubber content (DRC) preserved with 0.7% (w/v) ammonia was used to prepare cast films after diluting it to 40% DRC. The films thus prepared were allowed to dry at room temperature until they were transparent. These films were further dried by heating the films at 70°C for 1 h in an oven.

Preparation of semi-2 IPNs

NR film was cut into the required shape and the initial weight of the NR sample was recorded. Then the sample was placed in a closed container, containing a mixture of monomer, crosslinker, and initiator, in which the initiator was at a level of 1 mol % on monomer content. The crosslinker level was at 0.5 mol % on monomer content for semi-2(0.5) IPNs and 1.5 mol % on monomer content for semi-2(1.5)IPNs, respectively. The immersed samples were allowed to swell in the monomer/initiator/crosslinker mixture until it reached a predetermined weight. Different elastomer to plastomer ratios were obtained by allowing the swelling for different periods of time. The swollen NR sheets were then placed in a sealed polythene bag and stored at ca.

TABLE I
Composition Details of the Semi-2 (0.5) IPNs

Target composition		Experimental composition	
NR (wt %)	PMMA (wt %)	NR (wt %)	PMMA (wt %)
90	10	91	9
80	20	83	17
70	30	71	29
60	40	63	37
50	50	52	48

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. Samples were removed from the mold, weighed, and further dried in a vacuum oven at room temperature for one week to remove any residual monomer. Details of the compositions of the NR/PMMA semi-2 IPNs are given in Table I. Sample codes indicate the approximate composition by weight.

Techniques

Dynamic mechanical thermal analysis

Dynamic mechanical properties of the semi-2 IPNs were determined using a dynamic mechanical thermal analyzer (DMA 2980, TA Instruments). Rectangular strips with a width of 3 mm and a thickness of ca. 1 mm were used in the tension mode. The samples were forced to oscillate sinusoidally up to a preset strain maximum amplitude (20 μm) at a frequency of 1 Hz. The temperature ramp was set at 3°C min⁻¹ and a static force, 0.01N, was used. Scans were recorded from –100 to 200°C.

Modulated differential scanning calorimetry

The Modulated differential scanning calorimetry (MDSC) technique was used to determine the interphase fractions to evaluate the extent of miscibility of the components. This type of determination of the interphase content in IPNs and semi-IPNs is a novel aspect of this paper. A TA Instruments 2920 Modulated DSC was used to determine the complex heat capacity at different temperatures. Samples were weighed (0.5 mg) and placed in aluminum pans and carefully sealed. The samples were heated from –130 to 180°C at a heating rate of 3°C min⁻¹. The reference was an empty pan. Experiments were performed using nitrogen as the purge gas at a flow rate of 60 mL min⁻¹.

MDSC data thus obtained were analyzed by using the Origin software program. Hence, the different

TABLE II
Half Peak Widths of the NR Transition and the T_g s of the NR and PMMA Transitions of the Semi-2 (0.5) IPNs

Sample	T_g -NR (°C)	Half peak width (°C)	T_g -PMMA ^b (°C)
Natural rubber ^a	-51	16	—
NR90:PMMA10	-48	21	—
NR80:PMMA20	-46	22	—
NR70:PMMA30	-46	24	160
NR60:PMMA40	-46	23	159
NR50:PMMA50	-48	27	154

^a Natural rubber with same thermal history as the semi-2 (0.5) IPNs.

^b T_g , the temperature at which the maximum $\tan \delta$ was obtained.

phases were identified and the quantitative analysis of each phase in the IPNs had been determined.^{17,18}

Stress-strain properties

Tensile testing was performed according to the ISO 37 standard using a Hounsfield tensometer (Model No. H 5000M). The dumb-bell test pieces were extended at a constant speed of 500 mm min⁻¹ with a 500N load cell. Tests were performed at room temperature (25°C) using five test pieces for each sample and the average values are reported.

Cycling test

The same Hounsfield tensometer, controlled by a computer program, was used for the cycling tests. The dumb-bell shaped test pieces were subjected to three consecutive cycles up to 300% strain at an extension rate of 20 mm min⁻¹ (temperature (25°C)). Force against extension curves were plotted for each cycle and the area between the extension and the retraction curves was calculated as an energy value (J). For each sample, four or five test pieces were assessed and the average values are reported.

RESULTS AND DISCUSSION

Effect of composition on the physical properties of the semi-2 IPNs (EGDM crosslinker at 0.5 mol %)

Effect of composition on miscibility

Dynamic mechanical thermal analysis (DMTA) is a widely used technique to predict the miscibility between the components in polymer blends.¹³⁻¹⁶ In most of the studies, DMTA data, including any shift of the glass transition temperature of one or both of the polymer components and the height of the loss tangent peak, are taken into consideration to determine the extent of miscibility or phase separation.^{13,16,19} In this study, it is noted that the semi-2

IPNs with 30 wt % to 50 wt % PMMA content exhibit two glass transitions (Table II and Fig. 1) corresponding to their individual components indicating extensive phase separation.^{13,14} Nevertheless, the glass transition of the NR component in the semi-2 IPNs was shifted significantly to higher temperatures by 3–5°C, which is indicative of a certain extent of component mixing. Interpenetration of PMMA into the NR matrix and/or grafting of PMMA onto NR molecules can be considered as the prime causes of this limited extent of mixing. A unique feature imparted by interpenetration is the formation of entanglements between the two components. This will impart some forced component mixing, in a similar way to the enforced mixing resulting from a crosslinking process.¹ Crosslinking of the PMMA component might also affect the miscibility^{5,7} by preventing extensive phase separation of the PMMA component, unlike in NR/PMMA blends prepared in conventional methods.^{11,12}

When the loss tangent peak (NR transition) corresponding to natural rubber is considered, the activation energy also provides information on the mobility of polymer chains. The activation energy for NR transition can be calculated by using the following equation.²⁰

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

T_A is the area under the $\tan \delta$ curve and E_G and E_R are the storage modulus values in the glassy and rubbery regions, respectively. E_A is the activation energy. R and T_g refer to the gas constant and the glass transition temperature, respectively.

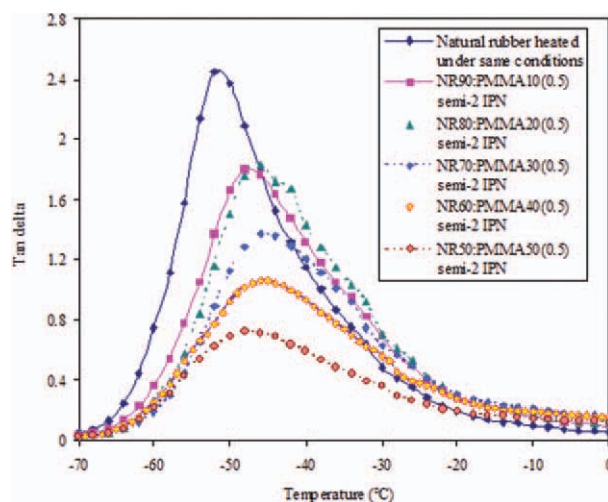


Figure 1 Effect of composition on the loss tangent of the NR component of the semi-2 IPNs prepared using 0.5 mol % EGDM crosslinker. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Calculated Relative Activation Energies of the NR Transition for the Semi-2 (0.5) IPNs

Sample	Normalized activation energies
NR90:PMMA10	1.08
NR80:PMMA20	1.08
NR70:PMMA30	1.17
NR60:PMMA40	1.13
NR50:PMMA50	1.38

The calculated normalized activation energies for the semi-2 IPNs are given in Table III. The normalized activation energy significantly increased with increase of PMMA content at 30 wt % and 50 wt % and could be ascribed to the restrictions in mobility of the NR polymer chain segments caused by the interpenetrated PMMA chain segments and/or grafted material.

Miscibility of the PMMA component has also been determined using the DMTA data. To highlight the shifts of the PMMA transition in the DMTA spectra, the PMMA transition region is plotted versus temperature and is shown in Figure 2. The transition due to the PMMA component appeared as a broad peak in the NR70:PMMA30 sample, indicating some mixing. In this series, compared with the NR60:PMMA40(0.5) semi-2 IPN, the T_g of the PMMA transition shifted towards lower temperature by 5°C (Table II) with increase of PMMA content, indicating some mixing of the PMMA and NR components. A similar trend had been observed for a poly(isobutene)—PMMA IPN, where the T_g of the PMMA decreased with increasing the PMMA content.¹⁵ This trend is probably attributed to the increase of contact area between phases with increase of PMMA content, thus enhancing the possible extent of mixing between the components. In this case, the PMMA is mixed with a more mobile compo-

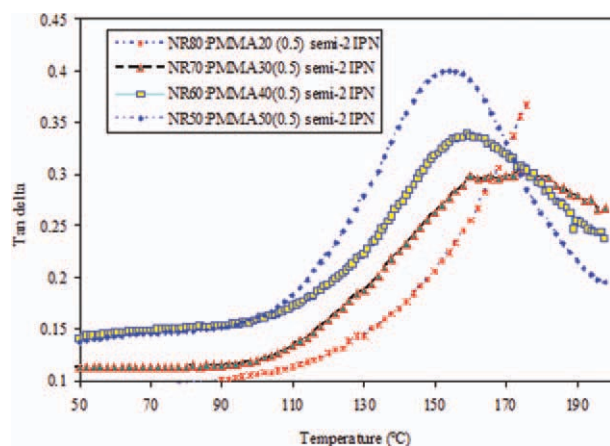


Figure 2 Effect of composition on the loss tangent of the PMMA component of the semi-2 IPNs prepared using 0.5 mol % EGDM crosslinker. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE IV
Multiple Peak Analysis Data For the Semi-2 (0.5) IPNs

Sample	Multiple peak analysis data		
	Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR80:PMMA20	27 ^a		
NR70:PMMA30	25	8	12
NR60:PMMA40	27	13	8
NR50:PMMA50	30	20	16

^a Mixed phases.

nent (NR) with a lower T_g thereby increasing the segmental motions of the PMMA polymer chains segments resulting in a lowering of the T_g of the PMMA component.¹⁵

The evidence for improved component mixing from DMTA was further supported by the multiple peak analysis of the derivative complex Cp data (T-MDSC data shown in Table IV). As shown in Figure 3, which illustrates the temperature dependence of dC_p/dT data for the NR50:PMMA50 semi-2 (0.5) IPN, the region between the two glass transitions was differentiated into five regions corresponding to the NR phase, a NR-rich phase, an interphase, a PMMA-rich phase, and the PMMA phase.^{5,17,18} However, there were slight fluctuations observed in the data perhaps due to the choice of the boundaries between the five regions. From the multiple peak analysis data (Table IV and Fig. 3), it can be seen that a considerable amount of interphase content was observed for the semi-2 IPNs with 30–50 wt % PMMA content (Fig. 3). This indicates some enforced mixing probably due to interpenetration of the chain segments and due to crosslinking of the PMMA phase which limits phase separation. It was difficult to differentiate the intermediate region into a NR rich phase, a PMMA rich

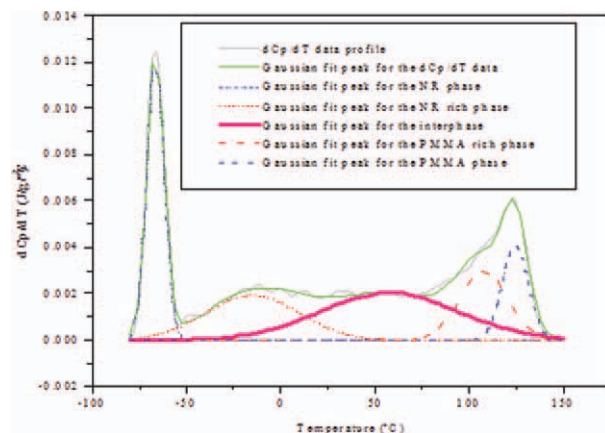


Figure 3 Temperature dependence of dC_p/dT for the NR50:PMMA50 (0.5) semi-2 IPN. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

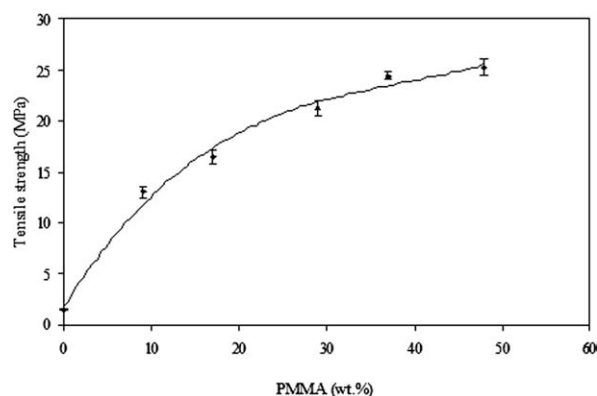


Figure 4 Effect of composition on the tensile strength for the semi-2 (0.5) IPN series

phase and the interphase for the NR80:PMMA20 semi-2 (0.5) IPN. Therefore, in this case these phases will be referred to as a mixed phase. A considerable amount of this mixed phase was found for the semi-2(0.5) IPN with the 20 wt % PMMA.

Effect of composition on stress–strain behavior

Tensile data

Dependencies of the tensile properties on the composition of the semi-2 (0.5) IPNs are illustrated in Figures 4 and 5. It is evident that the tensile strength of these compositions has increased with increasing the PMMA content. Dramatic increases in the 300 and 500% moduli were also observed in these semi-2 IPNs, when the PMMA content was between 30 and 50 wt % (Fig. 5). Therefore, the improved tensile properties thus obtained may be ascribed to the interpenetration and reinforcement effects imparted by the glassy crosslinked PMMA phases.

Hysteresis data

Energy losses during the cycling tests of these semi-2 (0.5) IPNs are listed in Table V. The amount of energy dissipated as heat markedly increased with increasing PMMA content. This trend is possibly

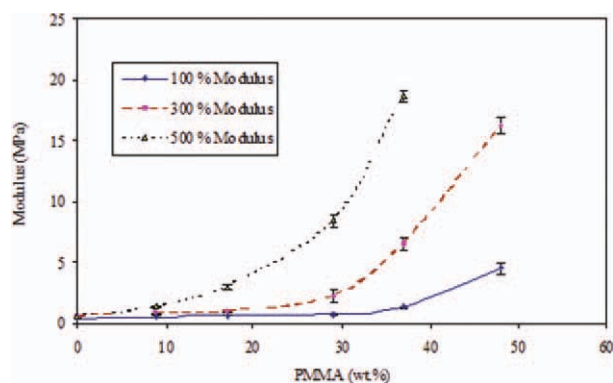


Figure 5 Effect of composition on the 100, 300, and 500% moduli of the semi-2 (0.5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

associated with the break down of the PMMA phases²¹ which tends to occur to the greatest extent in the first cycle. The amount of energy loss decreased with increase in the number of cycles.

Effect of the level of crosslinking in the PMMA component on dynamic and mechanical properties

Dynamic properties

The effects of the level of crosslinking of the PMMA component on the dynamic properties are listed in Table VI. The crosslinking of the PMMA component does not have much influence on the T_g -NR. Nevertheless, when the MDSC data shown in Table VII is considered, the amount of NR component in the interphase tends to increase considerably with increasing crosslinker level in the PMMA component and this suggests that the crosslinking of the PMMA apparently increases the extent of mixing with the NR component.

The effect of extent of crosslinking on the PMMA component has two different influences on the miscibility of the PMMA component depending on the PMMA content in the semi-2 IPN. One of the trends is that as the crosslinker level of the PMMA component increased the T_g -PMMA of the samples with 20–30 wt % of PMMA apparently increased. The

TABLE V
Energy Loss and Hysteresis Behavior of the Semi-2 (0.5) IPN Series

Sample composition NR/PMMA (wt %)	Cycle 1		Cycle 2		Cycle 3	
	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
100/0 ^a	0.57	0.45	–	–	–	–
90/10	0.12	0.31	0.03	0.11	0.02	0.07
80/20	0.22	0.51	0.13	0.33	0.09	0.24
70/30	0.44	0.96	0.28	0.72	0.25	0.73
60/40	1.34	2.8				
50/50	7.03	5.3				

^a Natural rubber treated under the same condition. HL-Hysteresis behavior was calculated as the ratio of the energy lost to the energy recovered in each cycle.

TABLE VI
Dynamic Mechanical Data For the Semi-2 IPNs Prepared with Different EGDM Levels

Sample	NR T_g (°C)	$\tan \delta$ NRmax	PMMA T_g (°C)	$\tan \delta$ PMMAmax
NR90:PMMA10 semi-2 (0.5)IPN ^a	-48	1.8	—	—
NR90:PMMA10 semi-2 (1.5)IPN	-48	1.9	—	—
NR80:PMMA20 semi-2 (0.5)IPN	-46	1.8	—	—
NR80:PMMA20 semi-2 (1.5)IPN	-47	1.9	173	0.3
NR70:PMMA30 semi-2 (0.5)IPN	-46	1.4	160	0.3
NR70:PMMA30 semi-2 (1.5)IPN	-46	1.6	178	0.2
NR60:PMMA40 semi-2 (0.5) IPN	-46	1.1	159	0.3
NR60:PMMA40 semi-2 (1.5)IPN	-45	0.8	156	0.4
NR50:PMMA50 semi-2 (0.5)IPN	-48	0.7	154	0.4
NR50:PMMA50 semi-2 (1.5)IPN	-49	0.5	150	0.5

^a Values given in the parenthesis refer to the EGDM level.

chances for grafting of PMMA are usually higher at lower levels of PMMA, but the extent of grafting may be retarded because of the competing crosslinking of the PMMA component resulting in an increase in the T_g -PMMA.²²

However, in the samples with high PMMA content, where homo-polymerization is facilitated, such a trend is not observed for the shift of the T_g -PMMA. The decrease of T_g -PMMA with increase of the crosslinker level in the semi-2 IPNs with 40–50 wt % PMMA was ascribed to the improved mixing with the NR component as was evident from the interphase fractions calculated from MDSC data (Table VII). These results clearly indicate that the NR component in the interphase region significantly increased with increase of the crosslinking level in

TABLE VII
Multiple Peak Analysis Data For the Semi-2 IPNs Prepared with Different EGDM Levels

Sample	Multiple peak analysis data		
	Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR70:PMMA30 semi-2 (0.5)IPN	25	8	12
NR70:PMMA30 semi-2 (1.5)IPN	31	18	3
NR50:PMMA50 semi-2 (0.5) IPN	30	20	16
NR50:PMMA50 semi-2 (1.5) IPN	28	27	0.5

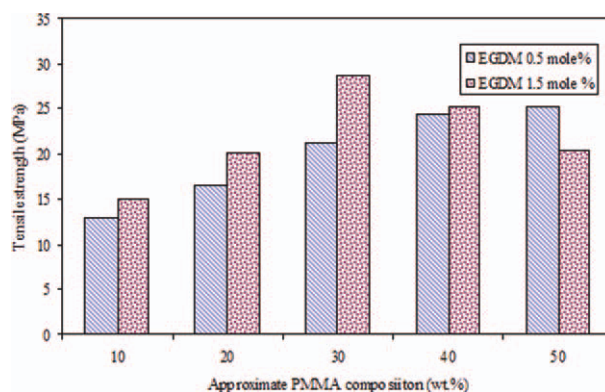


Figure 6 Effect of crosslinker level in the PMMA component on the tensile properties of the semi-2 IPNs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PMMA phase and were significantly higher than for the semi-2 IPNs with lower PMMA content. The significantly higher level of the NR component in the interphase facilitates the mobility of PMMA polymer chains which results in the lowering of the T_g -PMMA in the semi-2 IPNs with higher PMMA content.^{13–16}

Tensile properties

As shown in Figure 6, the tensile properties of the semi-2 IPNs increased with crosslinker level, with the exception of the NR50:PMMA50 sample. This behavior is ascribed to the increased number of effective network chains due to the crosslinking of the PMMA component with higher EGDM levels. As a result, in addition to the strain-induced crystals present in the NR phase,²¹ applied load will also be borne by the crosslinked PMMA polymer chains, thus requiring a higher force for tensile rupture.^{23,24} In addition, the improved tensile properties may be ascribed to the reinforcement caused by the hard, crosslinked PMMA domains dispersed in the continuous NR matrix. The observed decreasing trend of tensile strength of the NR50:PMMA50 sample with increasing EGDM level was attributed to the presence of highly crosslinked PMMA domains¹, which may restrict not only the formation of strain-induced NR crystals, but also retard the efficiency of the stress distribution in the matrix.^{23,24}

CONCLUSIONS

DMTA results clearly indicated that the semi-2 IPNs possessed two glass transitions indicating a phase-separated nature in these materials. Nevertheless, DMTA and MDSC data clearly showed that a considerable amount of component mixing has occurred due to the crosslinking of the PMMA component.

The extent of component mixing increased with the level of crosslinker in the PMMA phase. The modulus, tensile strength and hysteresis increased with increase of PMMA content in the semi-2 (0.5) IPNs. Increased degree of crosslinking of the PMMA component also improved the tensile properties of the semi-2 IPNs, with the exception of the NR50:PMMA50 composition.

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