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Morphology and thermal properties of pseudo interpenetrating polymer networks based on natural rubber (*Manihot glaziovii*) and poly(methyl methacrylate)

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Abstract

Pseudo interpenetrating polymer networks were prepared by a sequential method using a high molecular weight natural rubber and poly(methyl methacrylate), PMMA. The thermal properties and morphology were investigated varying the average molar mass between crosslinks ($\bar{M}_c$) and the composition. The extent of crosslinking of natural rubber plays a major role in the transitions domains whatever the sample composition. As the crosslink density decreases, only one T_g value is observed ($\bar{M}_c$ of 500 and 1000 g/mol). Comparison between the pseudo IPNs at different $\bar{M}_c$ values and compositions indicates that there are no significant differences in the thermal stabilities of the materials. Crosslinking and the component composition had a strong effect on the morphological patterns of the samples. For a higher crosslink density ($\bar{M}_c = 142$ g/mol), close and compact phase domains can be seen. The morphologies for lower crosslink densities ($\bar{M}_c$ of 500 and 1000 g/mol) showed fibrillar domains characteristic of the PMMA.

Keywords: Pseudo interpenetrating polymer networks; Natural rubber; Thermal stabilities

1. Introduction

Research into polymeric materials which possess a wide variety of physical properties results in different types of polymeric blends. The understanding of the relationships between structure, morphology and properties assumes great importance. In this connection, the study of the phase separation and morphology of two combined polymers has been an attractive subject of research, especially in the case of Interpenetrating Polymer Networks (IPNs), where specific topological network structures provide smaller domains of phase-separated material. Their miscibility level leads to multiphase polymer blends with a wide variety of ordered structures ranging from a nanometre to a micrometre scale [1]. This class of polymeric materials exibits mechanical and physical properties depending on the morphology and dual-phase continuity, e.g. thermoplastic IPNs [2].

Interpenetrating polymer networks are a unique class of polymers, in which the combination of two polymers in network form are synthesized sequentially or simultaneously. In pseudo IPNs, one of the two components has a linear structure. Changes in the properties are expected to be achieved by combining a glassy polymer with a rubbery one.

IPNs based on a natural elastomer (natural rubber from *Manihot glaziovii*) and synthetic glassy polymer, poly(phenylene oxide), PPO, or a rubbery synthetic polymer, poly(carbonate urethane), PCU, have been produced and analysed [3,4]. Their ultimate-properties performance depend on the relative compositions of the two components and on the natures of the continuous phases of the materials.

The purpose of this work is to study structural peculiarities and thermal properties of sequential pseudo IPNs made of crosslinked natural rubber and poly(methyl methacrylate).

2. Experimental

2.1. Materials

Natural Rubber (NR) from *Manihot glaziovii* was supplied by Prof. Miguel Cunha Filho of the Federal University of Ceará. It was purified and characterized as described in Barros et al. [5]. Divinyl benzene (DVB) was distilled prior

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Table 1
Thermal measurements (DSC) of pseudo IPNs of CNR/PMMA system

Sample	$\bar{M}_c$ (g/mol)	Composition CNR/PMMA(%wt)	T_g (°C)	Sample remarks
LNR	–	–	− 68	TP, LB, rubbery
PMMA	–	–	104[a]	TP, colourless, brittle
CNR/PMMA	142	100/0	− 27.8	TU, PY, brittle
		90/10	− 48.8; 18.8	
		80/20	–[b]; 9.3	
		70/30	− 55.6; 14.6	
CNR/PMMA	500	100/0	− 54	TU,PY, rubbery
		90/10	− 34.5	
		80/20	− 49.3	
		70/30	− 48.4	
CNR/PMMA	1000	100/0	− 60.0	TU, PY, rubbery
		90/10	10.6	
		80/20	11.4	
		70/30	11.6	

TP, transparent; TU, translucent; LB, light brown; PY, pale yellow; LNR, linear natural rubber; PMMA, poly(methyl methacrylate); CNR, crosslinked natural rubber
[a][7]
[b]Broad transition

to use and stored over molecular 4 Å sieves at 18°C. Methyl methacrylate was supplied by Aldrich. It was distilled under vacuum and stored at 18°C. Solubility parameters (δ) of MMA, PMMA and NR are 8.8, 9.1–12.8 and 7.9–8.3 $cal^{1/2}\ cm^{-3/2}$, respectively [6,7]. The other reagents used were of analytical grade.

2.2. Preparation of crosslinked natural rubber (CNR)

Purified NR was dissolved in toluene (1% w/v of polymer in solvent). To 50 ml of solution was added an amount of DVB, as crosslink agent, and 4% BPO (% w/w BPO/NR). The average molar mass between crosslinks, $\bar{M}_c$, from the amounts of DVB used, were 142, 500 and 1000 g/mol. This was determined by the equation: $M_c = (m_{NR} \times M_{DVB})/2m_{DVB}$, where: m_{NR} = mass (g) of natural rubber; M_{DVB} = molar mass of DVB; m_{DVB} = mass (g) of DVB.

The solution was homogenized for 1 h. The crosslinking reaction was carried out at 80°C under a nitrogen atmosphere for 48 h.

2.3. Preparation of pseudo IPNs

Proportional amounts of MMA were added to 4 ml of toluene to give the desired w/w% compositions of MMA in relation to NR. The crosslinked NR was immersed in the solution for 36 h. The MMA polymerization reaction was carried out at 80°C for 24 h, under a nitrogen atmosphere using BPO as initiator. The samples were dried under vacuum for 72 h. Sample compositions of 10, 20 and 30 w/w% MMA to NR were prepared.

2.4. Physical measurements

The phase morphology of the samples was examined by scanning electron microscopy (SEM) at 5 kV. A JEOL JSM 840-A electron microscope was used. The samples were fractured after being frozen in liquid nitrogen. The specimens were stuck on a stub, using silver paint and coated with gold (~90 Å) in a Hummer V Sputter coater Mod. SDC 050 Balzers, operating at 40 mV/60 s.

Glass transition temperatures of the materials were obtained by means of a differential scanning calorimeter, Shimadzu DSC-50, operating at a scanning rate of 10°C/min. The measurements were conducted at the temperature range of −150°C to 150°C. Samples of 4.2–6.4 mg were used.

Thermal degradation of the samples was observed by using a thermal analyser, TGA-50 Shimadzu. Experiments were conducted at a temperature range of 25–800°C and a scanning rate of 20°C/min. Samples of 4.5–6.0 mg were used.

3. Results and discussion

Pseudo IPNs of crosslinked NR and linear PMMA were synthesized. The compositions and characteristics of the samples are described in Table 1.

The DSC thermograms obtained for linear NR, crosslinked NR and pseudo IPNs at specified compositions and $\bar{M}_c$ values are shown in Fig. 1. Similar curves are exibited for the pseudo IPNs with $\bar{M}_c$ equal to 142 g/mol and compositions of 90/10, 80/20 and 70/30 (w/w%) [Fig. 1b–d]. Two T_g values were observed inbetween the T_g values of pure NR and PMMA, in the ranges − 48.8 to − 55.6°C and 9.3–18.8°C. One of them, close to the T_g value of NR, is a broad transition of difficult identification. Pseudo IPNs with $\bar{M}_c$ values of 500 and 1000 g/mol showed one T_g value for all the compositions. For the higher crosslink density

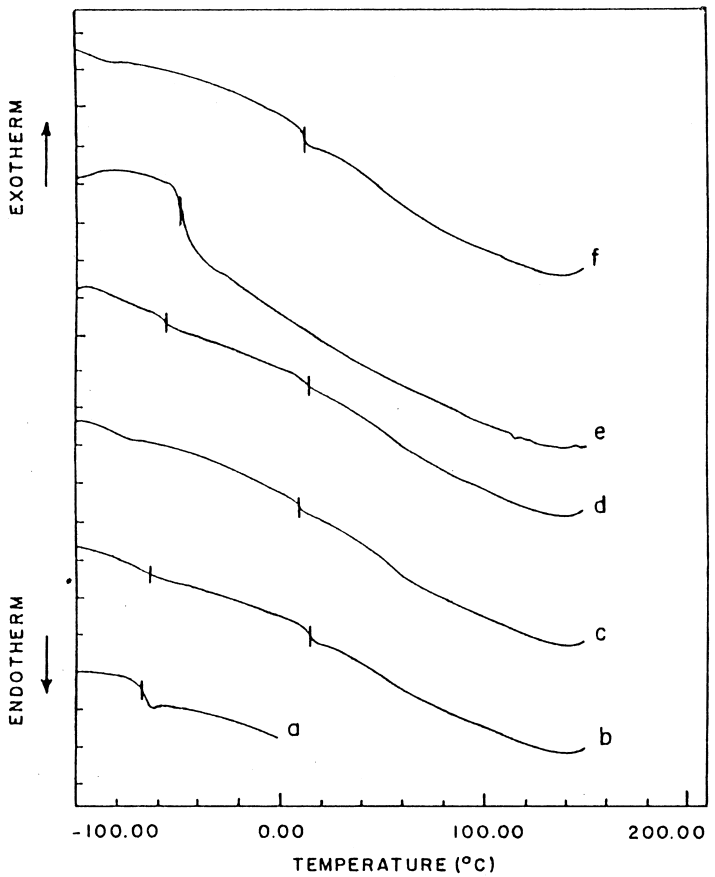

Fig. 1. DSC curves. (a) NR. Pseudo IPNs of CNR and PMMA at %wt compositions: (b) 90/10, $\bar{M}_c = 142$ g/mol; (c) 80/20, $\bar{M}_c = 142$ g/mol; (d) 70/30, $\bar{M}_c = 142$ g/mol; (e) 80/20, $\bar{M}_c = 500$ g/mol; (f) 70/30, $\bar{M}_c r = 1000$ g/mol.

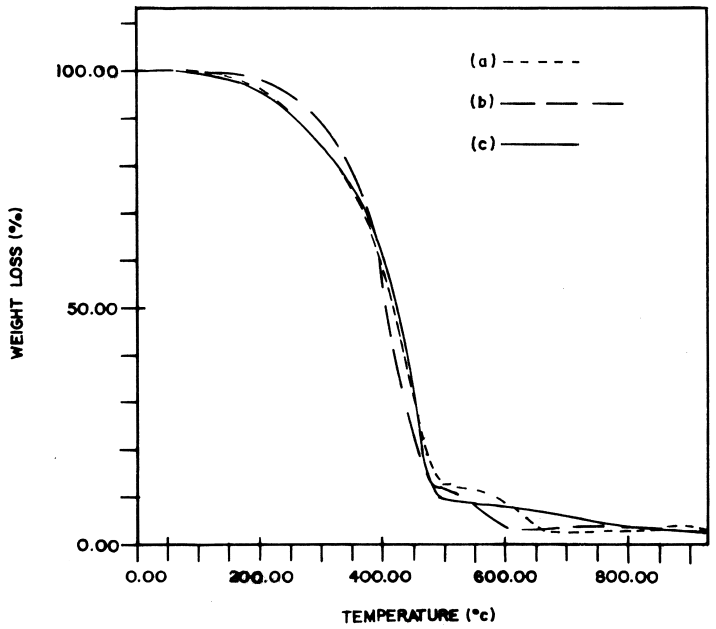

Fig. 2. Thermograms. Pseudo IPNs of CNR and PMMA. (a) 70/30, $\bar{M}_c = 142$ g/mol, (b) 70/30, $\bar{M}_c = 500$ g/mol, (c) 70/30, $\bar{M}_c = 1000$ g/mol.

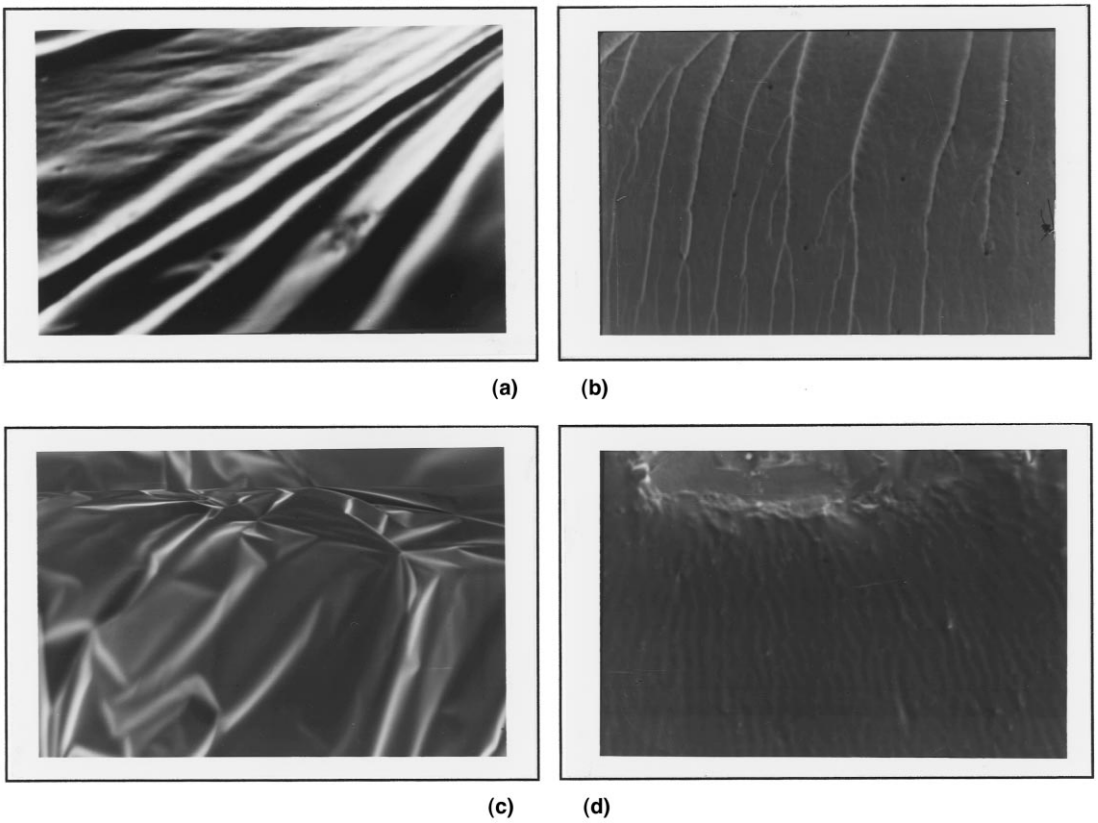

Fig. 3. SEM of linear NR (LNR) and crosslinked NR (CNR). (a) LNR; (b) CNR, $\bar{M}_c = 142$ g/mol; (c) CNR, $\bar{M}_c = 500$ g/mol; (d) CNR, $\bar{M}_c = 1000$ g/mol.

($\bar{M}_c = 500$ g/mol), the T_g is close to that of NR (Fig. 1e). However, pseudo IPNs of the lower crosslink density ($\bar{M}_c = 1000$ g/mol) showed T_g values much higher, 10.6–11.6°C (Fig. 1f). The single glass transitions found for the pseudo IPNs with $\bar{M}_c$ values of 500 and 1000 g/mol are indications of compatibility in these systems [8].

Degradation curves are shown in Fig. 2. Two broad decomposition curves under helium, for the samples with $\bar{M}_c$ values of 142 and 500 g/mol, were observed (Fig. 2a,b). The first step of the decomposition process starts at a temperature of ca. 120°C and is complete at 500°C. The second starts at ca. 505°C and is complete at ca. 750°C. The first step was interpreted as the decomposition of the pseudo IPN and the second as the degradation of small structural products of the rubber decomposition [7]. The degradation curves for the samples with a $\bar{M}_c$ value of 1000 g/mol showed one decomposition step which started in the temperature range of 130–160°C and was complete at 485–495°C.

3.1. Morphological studies of pseudo IPNs

Photo-micrographs of linear and crosslinked NR, linear PMMA and pseudo IPNs of NR/PMMA into the compositions of 90/10, 80/20 and 70/30 (w/w%) and $\bar{M}_c$ values of 142, 500 and 1000 g/mol are shown in Figs 3–7. Linear and crosslinked NR showed smooth and wave-like morphologies which were independent of crosslink density (Fig. 3). Pure PMMA presented a wave-like morphology with some fibres (Fig. 4).

The analysis of the pseudo IPNs micrographs evidenced differences in their morphological patterns, especially with respect to changes in the crosslink density of the samples (Figs 5–7). A more compact and smaller phase domain was observed for the samples with an $\bar{M}_c$ value of 142 g/mol, for all compositions (Fig. 5). As the crosslink density decreased, a wave-like and smooth morphology became clear ($\bar{M}_c$ of 500 and 1000 g/mol).

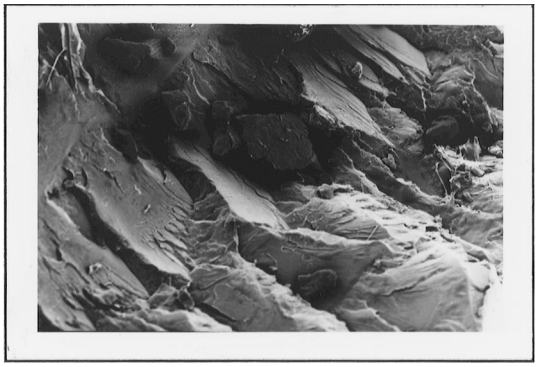

Fig. 4. SEM of linear PMMA.

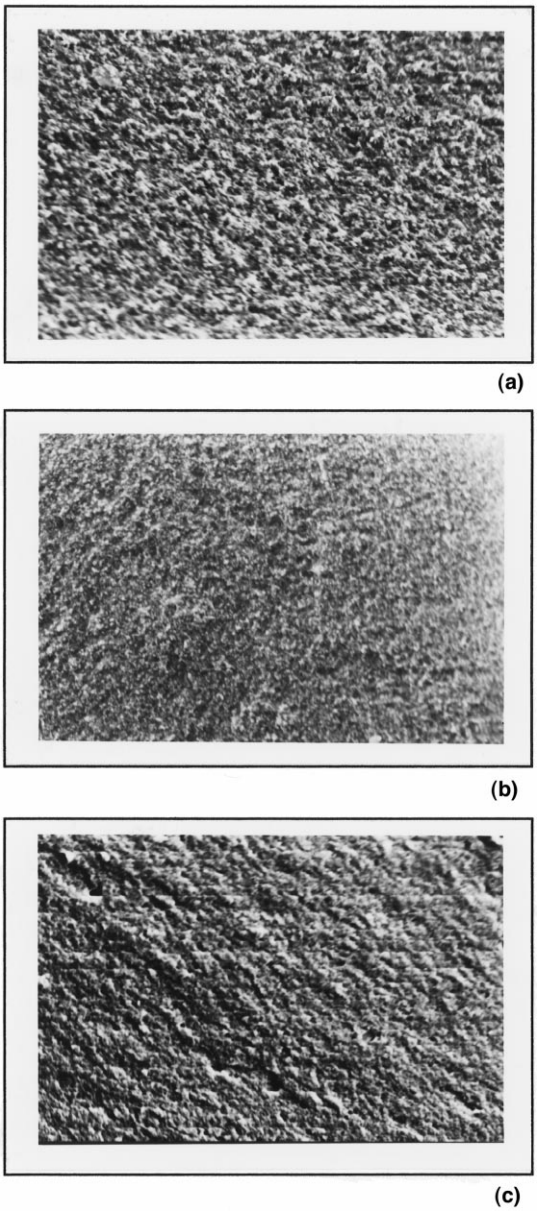

Fig. 5. SEM of pseudo IPNs (CNR/PMMA, $\bar{M}_c = 142$ g/mol). (a) 90/10; (b) 80/20; (c) 70/30.

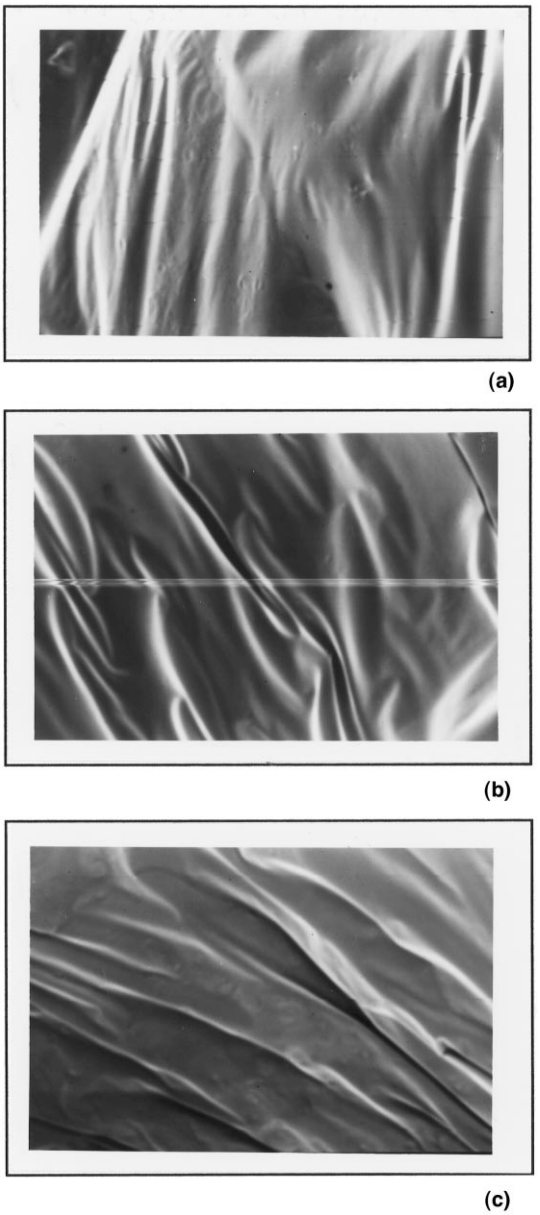

Fig. 6. SEM of pseudo IPNs (CNR/PMMA, $\bar{M}_c = 500$ g/mol). (a) 90/10; (b) 80/20; (c) 70/30.

The morphological features were also dependent on the proportion of the linear component in the samples. This was evident in the samples of lowest crosslink density ($\bar{M}_c = 1000$ g/mol) where fibrils were observed dispersed in the continuous CNR phase. The fibrils are more compact and uniformly distributed at the highest PMMA composition (30%; Fig. 7). No distinct morphological features depending on sample composition were observed for $\bar{M}_c$ values of 142 and 500 g/mol (Figs 5 and 6).

4. Conclusions

Pseudo IPNs made of a high molecular weight natural elastomer and a plastomer (PMMA) showed differentiated morphologies, glass transition temperatures and thermal decomposition behaviours. It can be seen that the extent of crosslinking of the natural elastomer plays a major role in determining the transition domains whatever the sample composition. As the crosslink density decreases, only one T_g is observed ($\bar{M}_c$ of 500 and 1000 g/mol).

The degradation temperature is independent of the crosslink density and sample composition, although two decomposition steps for samples of $\bar{M}_c$ values of 142 and 500 g/mol can be seen.

Crosslinking and the component compositions had a strong effect on the phase morphological patterns of the samples. The morphologies of pseudo IPNs were similar

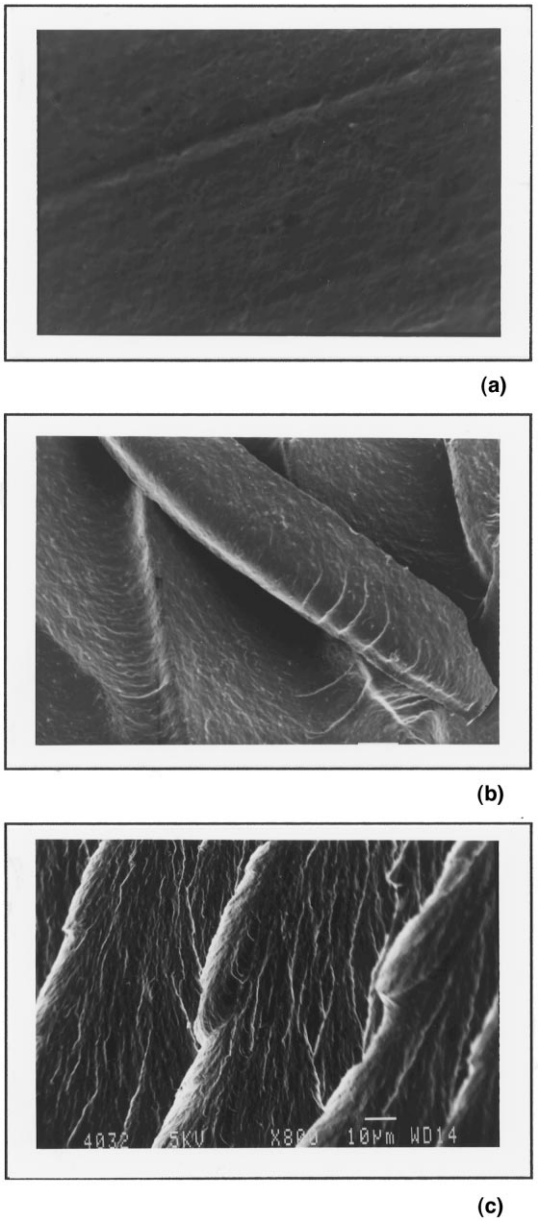

Fig. 7. SEM of pseudo IPNs (CNR/PMMA), $\bar{M}_c = 1000$ g/mol). (a) 90/10; (b) 80/20; (c) 70/30.

to those presented previously in the literature [9]. For higher crosslink densities ($\bar{M}_c$142 g/mol), compact phase domains can be seen. For lower crosslink densities ($\bar{M}_c$ of 500 and 1000 g/mol), the morphologies were characterized by fibrillar domains of the disperse phase characteristic of the plastomer component. A finer disperse phase becomes more evident for the sample of low crosslink density ($\bar{M}_c$ = 1000 g/mol) at the highest PMMA composition (70/30, w/w% NR/PMMA).

There is some indication that the reaction crosslink initiator does not affect the morphology, as compared to literature data for a similar system [9].

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