

Interfacial activity of natural rubber-g-poly(methyl methacrylate) in incompatible natural rubber/poly(methyl methacrylate) blends

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Summary

Blend of natural rubber and poly(methyl methacrylate) (NR/PMMA) has been made compatible by the addition of graft copolymer of natural rubber and poly (methyl methacrylate) (NR-g-PMMA). The interfacial activity of the graft copolymer is studied as a function of concentration of the graft copolymer by following the morphology of the blend using optical and scanning electron microscopies. Domain size of the dispersed phase is decreased sharply by the addition of small amount of copolymer followed by a levelling off at higher concentration. Improvements in mechanical properties is noted with the addition of graft copolymer. Attempts have been made to correlate the morphology and properties.

Introduction

Industrially important thermoplastic elastomers can be developed by blending natural rubber and poly (methyl methacrylate). These materials combine the excellent processability characteristics of PMMA and the elastic properties of NR. In addition they exhibit good damping properties and weather resistance. These materials can be successfully used for the fabrication of automobile components. Since the polymer pair is highly incompatible, the properties of the resulting blends can be improved by the addition of a graft copolymer with segments that are chemically identical to NR and PMMA. Fundamentally compatibilization of this system draws special attention since the incompatible NR/PMMA blend has a very sharp interface and poor physical and chemical interactions across the phase boundaries.

Several studies have been carried out on the interfacial activity of copolymers in heterogeneous polymer blends. These include the work of Molau et al. (1,2,3) Riess et al. (4,5) and Patterson et al. (6). Teyssie and coworkers (7,8) have investigated the influence of polymeric emulsifiers on a large number of incompatible polymer blends. Recently, Thomas and Prud'homme(9) have studied the compatibilizing effect of block copolymers in heterogeneous polystyrene/poly(methyl methacrylate) (PS/PMMA) blends.

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In the present paper we report on the interfacial activity of natural rubber-g-poly (methyl methacrylate) (NR-g-PMMA) in heterogeneous natural rubber/poly(methyl methacrylate) blends.

Experimental

Poly(methyl methacrylate) (PMMA) is prepared by polymerising methyl methacrylate using benzoyl peroxide in our laboratory. Natural rubber (NR, ISNR-5 grade) was supplied by Rubber Research Institute of India, Kottayam.

Graft copolymer of NR and PMMA was prepared in our laboratory by polymerising methyl methacrylate in the presence of rubber latex using a redox initiator consisting of cumene hydroperoxide and tetra ethylene pentamine. NR latex particles are swollen with methyl methacrylate which is then polymerised at room temperature for about 24 hrs. The graft is purified by fractional precipitation method. Free PMMA and NR are removed using acetone and petroleum ether, respectively. The purified graft copolymer is dried in vacuum oven. The amounts of grafting efficiency and PMMA grafted were 60 and 25% respectively. These values were obtained gravimetrically as reported earlier (10). Grafting was confirmed by the separation of high molecular weight component from GPC eluate. The IR and H'NMR spectroscopic studies further confirm the formation of graft copolymer. The IR spectrum of the graft copolymer shows intense absorption at 1730 cm^{-1} and 1140 cm^{-1} corresponding to $>\text{C}=\text{O}$ and $(\text{C}-\text{O})$ group in the methacrylate chain along with characteristic absorption of the NR group. The H'NMR spectrum obtained at 90 MHz shows chemical shifts at 1-2, 3-4, and 4.6 to 4.8 corresponding to alkyl, OCH_3 and vinyl protons respectively. H'NMR analysis indicated that the per cent of MMA grafted on to NR backbone is 26% which is in agreement with the gravimetric determination.

Dynamic mechanical spectroscopy studies of the graft copolymer showed two transitions corresponding to natural rubber (-50°C) and polymethyl-methacrylate (135°C). This suggests that the copolymer is sufficiently phase separated and can be located at the interface. The molecular weight determination of NR, PMMA and NR-g-PMMA by viscometry method (Table 1) supports the above observations.

Natural rubber and poly (methyl methacrylate) in the ratio 60/40 were blended together in toluene with and without the addition of graft copolymer. The solvent was allowed to evaporate for two days at room temperature. The films were further dried under vacuum at 80°C for two weeks followed by heating at 120°C for 48 hours to remove the last traces of solvents. The morphology of the blend was examined by optical and scanning electron microscopies. The mechanical properties of the blends were studied according to ASTM test methods.

Table 1. Characteristics of the materials used

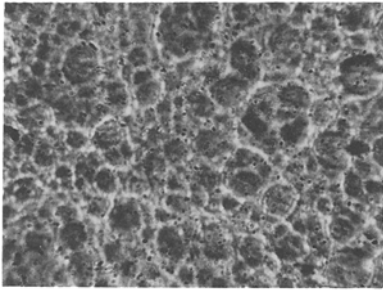
Materials	Density g/cc	Solubility Parameter (Cal/cm ³)	Intrinsic Viscosity (dl/g)	Molecular Weight (Mw)
NR	0.90	7.75	4.35	8.05 x 10 ⁵
PMMA	1.185	11.802	0.42	2.09 x 10 ⁵
NR-g-PMMA	-	-	3.2	8.76 x 10 ⁵

Results and discussion

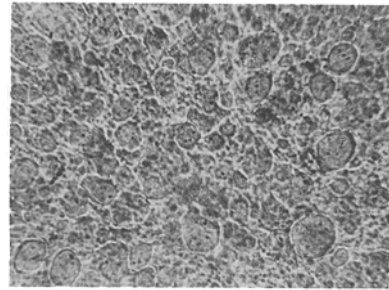
The interfacial activity of a copolymer in a binary blend depends on the molecular weight, concentration, composition and conformation of the copolymer at the interface. The interfacial activity of the NR-g-PMMA is evident from the reduction in the domain size of the dispersed phase as shown by the optical and scanning electron micrographs. Figure 1 a,b,c and d show the optical micrographs of 60/40 NR/PMMA blend with 0 2.5 3 and 5% of the graft copolymer respectively. It is seen that the domain size of the dispersed PMMA phase decreases with the addition of graft copolymer. The scanning electron micrographs of the fracture surface of 60/40 blends (cryogenically fractured) containing 0 and 5% of copolymer are given in Figures 2 a and b respectively. No evidence of interfacial adhesion is seen in the blend containing no copolymer. Interestingly the domain size is very large in this case. The interfacial adhesion between dispersed PMMA phase and natural rubber matrix is improved by the addition of copolymer.

It can be noticed from the photographs that the poly(methyl methacrylate) dispersed in the rubber matrix are almost spherical in shape. The domain size is measured from the optical and electron photomicrographs. About 100 domains were selected at random for the diameter measurements. The domain size distribution curve is given in Figure 3. A high degree of polydispersity is evident by the large width of the distribution curve of zero percent graft copolymer. The average size of the domain is about 32.2 μ m (Table 2). It is seen that the polydispersity decreases with the increase of graft copolymer concentration which is evident by the decrease in the width of the distribution curve. The standard deviation values also support the large particle size distribution for blends having no graft. The average domain size is analysed as a function of graft copolymer concentration. Figure 4 shows the plot of

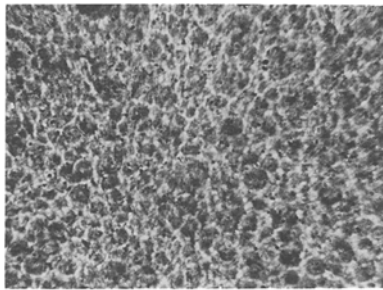
Fig.1. Optical micrographs of 60/40 NR/PMMA blends containing (a) 0% (b) 2.5% (c) 3% and (d) 5% graft copolymer.



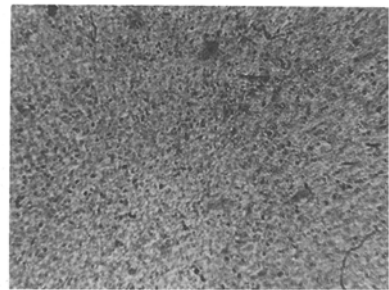
(a)



(b)

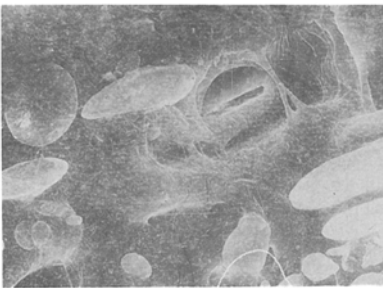


(c)

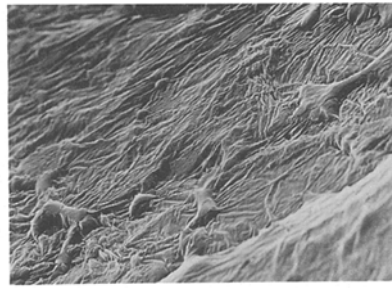


(d)

Fig.2. Scanning electron micro graphs of 60/40 NR/PMMA blends containing (a) 0% and (b) 5% graft copolymer.



(a)



(b)

average size of the domains versus weight percent of the graft copolymer. It can be noticed that the addition of 1% graft copolymer causes a domain size reduction of 60%. Addition of another 1.5% makes only a further reduction of 24% and the size of the domains finally gets levelled off at high concentrations. The levelling point for 60/40 NR/PMMA is about 3% which is evident from Figure 3. This saturation point represent the concentration of the graft copolymer required to saturate unit volume of the interface. Further addition of the the copolymer will be useless since it does not modify the interface anymore.

Table 2. Domain size of dispersed phase.

% of graft copolymer	Average size(μ m)	Standard Deviation
0	32.2	15.19
1	13.7	4.02
2.5	10.3	4.37
3	9.8	3.57
5	9.1	3.65

The mechanical properties of the blend also vary with the graft copolymer concentration. Properties like modulus, tensile strength, elongation at break etc are given in Table 3. Modulus shows an average increase of 150% by the addition of 2.5% graft copolymer. The values then decrease showing the saturation point. Tensile strength also increases sharply till the interface is saturated followed by a levelling off. Further addition makes only a little change in mechanical properties. The improved mechanical properties are associated with the strong interfacial interaction between the PMMA domains and natural rubber matrix which is evident from the morphology of the blend. However, the elongation at break did not show any regular trend with graft copolymer concentration.

Figure 3 Distribution curve of 60/40 NR/PMMA Based from 100 particles

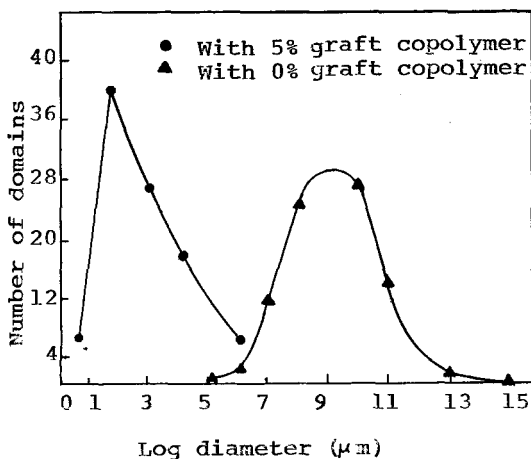


Figure 4 60/40 NR/PMMA

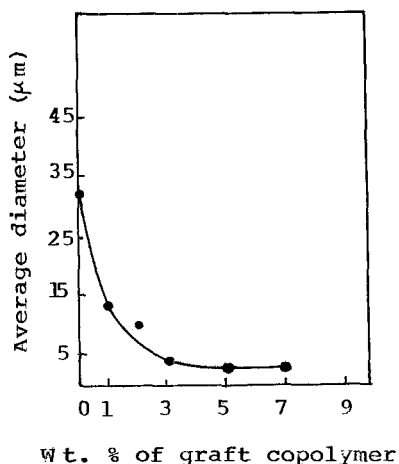


Table 3. Mechanical properties of the blends.

% of graft copolymer	Stress at 50 % elongation N/mm ²	Stress at 100 % elongation N/mm ²	Stress at 130% elongation N/mm ²	Tensile strength N/mm ²	Elongation at break (%)
0	1.05	1.41	1.70	3.98	362
1	1.07	1.54	1.96	6.97	429
2.5	2.55	3.92	4.55	7.43	262
3	1.18	1.95	2.56	7.81	381

Conclusion

The interfacial activity of natural rubber-g-poly(methyl methacrylate) (NR-g-PMMA) in natural rubber /poly(methyl methacrylate)(NR/PMMA) blends has been studied. Addition of a few percent of the copolymer reduces the size of the dispersed PMMA phase followed by a levelling off at higher concentrations. SEM analysis of the fracture surfaces of the compatibilized blend showed improved interfacial interaction between the phases. The mechanical properties of the blends are also improved by the addition of the graft copolymer. Further studies are in progress to analyse the conformation of the copolymer at the interface.

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