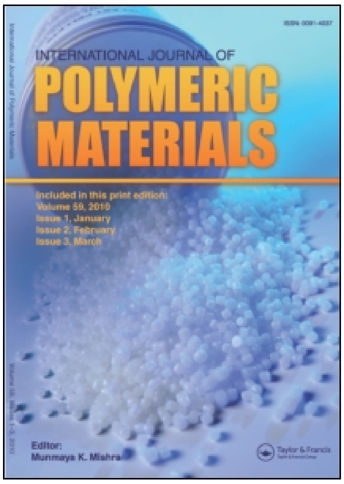

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Mechanical Properties and Morphology of Nitrile Rubber Toughened Polystyrene

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Mechanical Properties and Morphology of Nitrile Rubber Toughened Polystyrene

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Mechanical properties and morphology of blends of polystyrene and finely powdered (uncrosslinked and crosslinked) nitrile rubber were studied with special reference to the effect of blend ratio. Blends were prepared by melt mixing polystyrene and nitrile rubber in an internal mixer at 180°C in the composition range of 0–20 wt% nitrile rubber. The tensile stress/strain properties and impact strength of the polystyrene/nitrile rubber blends were determined using injection molded test specimens. In comparison to the blends with uncrosslinked nitrile rubber, blends with crosslinked nitrile rubber showed higher tensile strength, elongation at break, Young's modulus, impact strength, flexural strength, and flexural modulus. The enhanced adhesion between the dispersed nitrile rubber phase and the polystyrene matrix results in an increase in mechanical properties. Scanning electron micrographs of the fractured surfaces confirm the enhancement in mechanical properties.

Keywords: impact strength, polystyrene, powdered nitrile rubber, toughness

INTRODUCTION

The toughness of most thermoplastics can be considerably enhanced by the incorporation of dispersed rubbery phase. The toughening mechanisms involved are influenced by the properties of the matrix

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material and by the morphology of the blend [1]. The increase in toughness has been attributed to two mechanisms: multiple crazing, which initiates at the rubber particles, and shear yielding [2]. In commercial high impact polystyrene (HIPS) the former dominates because crazing of the polystyrene (PS) matrix occurs readily, as long as the rubber particle diameter is greater than 1 μm [3–4].

Multiphase polymers, in which a soft, rubber-like, toughening phase is combined with a rigid glassy component, offer significant advantages over homogeneous glassy polymers. However, these advantages are obtained only when the properties of the two phases, their morphology, and the quality of the interface between them are carefully chosen or designed to meet certain criteria. The rigid phase should be relatively stiff, with the ability to reach high tensile strains and shear yield stress. Preferably, the shear modulus of the rubber phase should be as low as possible, the rubber should be present as discrete particles, and the level of adhesion between the rubber and rigid phase should be very high [5].

The first definitive observations on toughening mechanisms in multiphase plastics were made by Bucknall and Smith [6]. They demonstrated that the dominant energy absorbing mechanism of deformation in HIPS is multiple crazing in the polystyrene, which is initiated by the rubber particles. Rubber particles have been shown both to initiate and to control craze growth. Under an applied tensile stress crazes are initiated at points of maximum principal strain, which are usually near the equator of rubber particles and then propagate outward normal to the maximum applied stress. Craze growth is terminated when a further rubber particle is encountered, preventing the growth of very large crazes. The result is a large number of small crazes in contrast to a small number of large crazes formed in the same polymer in the absence of rubber particles [7]. Multiple crazing of the PS matrix accounted for the properties such as absorption of energy in impact, stress whitening, yielding, volumetric expansion under tensile strain, and subsequent recovery [8]. When the rubber particles contain rigid polymeric inclusions, the rubber phase forms fibrils, thereby enabling the particle initially to strain-soften, and then to strain-harden. This mechanism promotes craze initiation and stabilizes the crazes mechanically when they have reached a certain total thickness, which is related to the dimensions of the particle [9].

Numerous studies were carried out to investigate the toughening of PS by the effects of dispersed rubber phase variables such as rubber concentration, particle size, shape, spatial packing of the rubber particles, and the degree of functionalization. However, there were few studies concerned with crosslinking of the rubber phase. Bucknall

[10] reported that crosslinking of rubber particles is desirable because during impact the rubber phase is subjected to a very large tensile strain giving craze-like structure. A moderate degree of crosslinking allows the rubber particles to reach high strain by fibrillation and at the same time renders mechanical strength to the fibrils. Dao [11] found that crosslinked ethylene propylene diene terpolymer (EPDM) is more effective as an impact modifier for polypropylene than uncrosslinked EPDM. Crosslinking increases the rubber viscosity, which will affect the blending process and particle size of rubber. The particle size, in turn, strongly influences the impact behavior of the blends [12]. Crosslinked EPDM did not seem to have any effect on the impact properties of polyamide 6/EPDM blends [13]. Mehrabzadeh and Buford [14] studied the effect of crosslinking on the impact properties of polyamide 11/NBR blends. They found that static and dynamic crosslinking do not significantly improve the impact strength.

The main objective of this work was to prepare toughened thermoplastic polymer by blending PS with nitrile rubber (NBR) in a finely powdered form and to evaluate mechanical properties and morphology of the resulting blend.

EXPERIMENTAL

Materials

Polystyrene of density 1.05g/cm^3 and melt flow index of 10 g/10 min was supplied by M/s LG Polymers, Mumbai, India. Powdered nitrile rubber was purchased from Gujarat Apar Polymers Ltd., Mumbai, India.

Uncrosslinked NBR (P6423): Acrylonitrile content $= 33\%$, density $=$ 1.0 g/cm^3 and Mooney viscosity $(1+4)$ 100°C $= 80$.

Crosslinked NBR (P3383): Acrylonitrile content $= 33\%$, density $=$ 1.0 g/cm^3 and Mooney viscosity $(1+4)$ 100°C $= 60$.

Methods

Preparation of Blends

PS/NBR blends with 5, 10, 15, and 20 wt% of NBR were prepared by melt mixing in a Thermo Haake Rheocord 600 internal mixer at a temperature of 180°C and rotor speed of 40 rpm for 10 min. The hot mix was sheeted out using a two-roll mill and granulated. The test specimens were prepared using a semiautomatic plunger type injection molding machine at a barrel temperature of 180°C. The blends of uncrosslinked

NBR were designated as P_{100}, $P_{95}L_5$, $P_{90}L_{10}$, $P_{85}L_{15}$, $P_{80}L_{20}$ and crosslinked NBR were designated as $P_{95}X_5$, $P_{90}X_{10}$, $P_{85}X_{15}$, $P_{80}X_{20}$. The subscripts indicate the amount of PS and NBR, respectively, in the blend.

Determination of Mechanical Properties

Izod impact strength (unnotched) was measured according to ASTM D-256 using a Zwick impact tester. Measurements were done at room temperature. The tensile properties were determined on an Universal Testing Machine (Shimadzu) at a crosshead speed of 50 mm/min. Specimens for tensile testing were prepared according to the ASTM D-638 method. The flexural strength and flexural modulus were evaluated at a 5 mm/min. crosshead speed and a span length of 50 mm as per ASTM D-790.

Scanning Electron Microscopy (SEM)

The morphologies of the fractured surface of tensile specimens were examined by SEM. All the samples were coated with a thin layer of gold in a sputtering unit before taking scanning electron micrographs using the Cambridge Stereoscan S 360 Scanning Electron Microscope.

RESULTS AND DISCUSSION

Mechanical Properties

The effects of the crosslinking of the rubber on the mechanical properties are given in Table 1.

TABLE 1 Mechanical Properties of PS/NBR Blends

Sample code	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (J/m)
P_{100}	39.43	1.99	2.87	68.0	3.20	124
$P_{95}L_5$	30.2	2.67	2.54	56.2	2.51	174
$P_{90}L_{10}$	24.03	2.80	2.16	49.2	2.26	210
$P_{85}L_{15}$	16.91	2.37	1.96	40.5	2.14	185
$P_{80}L_{20}$	14.63	2.18	1.45	34.6	2.04	143
$P_{95}X_5$	34.95	3.07	2.76	58.1	2.84	189
$P_{90}X_{10}$	29.57	3.39	2.40	50.4	2.66	274
$P_{85}X_{15}$	23.84	2.78	2.10	42.4	2.41	235
$P_{80}X_{20}$	17.59	2.51	1.76	36.6	2.34	157

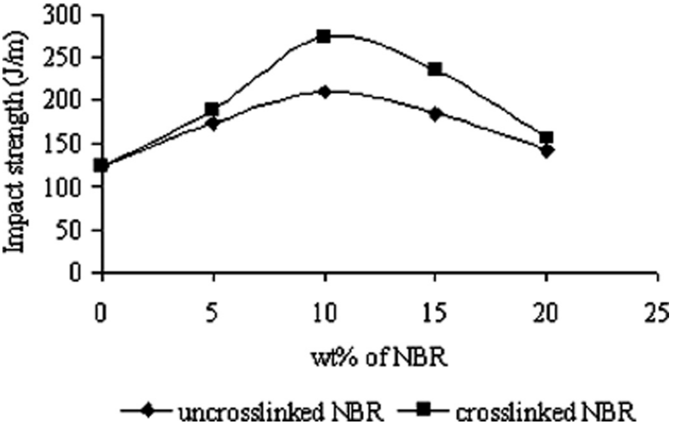

FIGURE 1 Variation of impact strength with wt% of NBR.

Impact Strength

The variation of Izod impact strength (unnotched) of the blends with NBR content is shown in Figure 1. The impact strength increases as the NBR content increases from 0 to 10% in both blend systems. This is attributed to the fact that rubber domains act as stress concentration sites for dissipation of impact energies by controlling and promoting matrix deformation. The addition of rubber leads to relaxation of the stress concentration due to release of constrains of strain by Poisson's contraction between voids at the PS-NBR interfaces. As a result nucleation of catastrophic cracks at the sites of crazes is suppressed and impact strength is improved.

The low impact strength for blends of PS and uncrosslinked NBR compared with blends of PS and crosslinked NBR is due to the coalescence of rubber domains during static cooling. This gives rise to irregularly sized rubber domains that are larger than the critical size desired for impact toughening. The size enlargement and shape irregularity result in a reduction of stress concentration sites and interfacial adhesion.

In the blends with crosslinked NBR, the crosslinked structure of rubber particles inhibits the chance of rubber cohesion during cooling and also the interfacial adhesion is increased by physical interlocking.

Flexural Strength and Flexural Modulus

The flexural strength and flexural modulus results are given in Table 1 and variations of flexural strength and flexural modulus with rubber

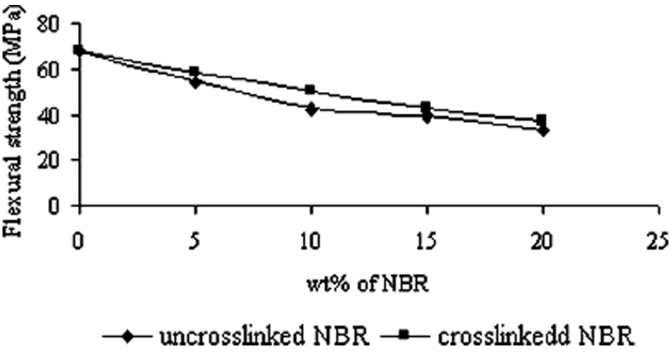

FIGURE 2 Variation of flexural strength with wt% of NBR.

content are shown in Figures 2 and 3. Flexural strength and Flexural modulus show a negative trend. This is mainly caused by poor interfacial adhesion. The decrease in flexural strength with increased rubber content indicates an elastomeric nature of the blend. The blends with crosslinked NBR have higher flexural strength and flexural modulus than the corresponding blends with uncrosslinked NBR. The crosslinked structure enhances the interfacial adhesion. This is accompanied by an increase in flexural strength and flexural modulus.

Tensile Strength and Young's Modulus

The results of tensile strength and Young's modulus of various blends are given in Table 1 and variations with rubber content are shown in

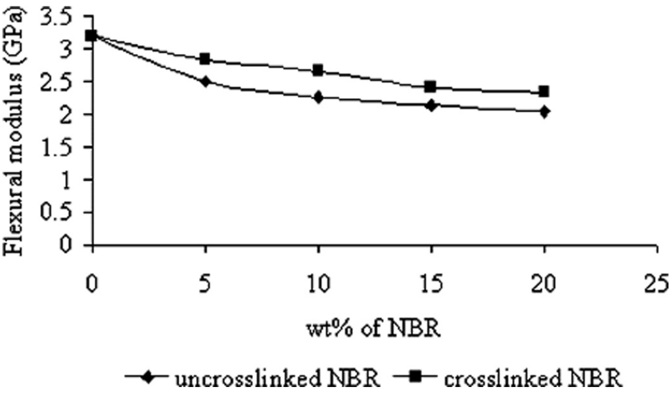

FIGURE 3 Variation of flexural modulus with wt% of NBR.

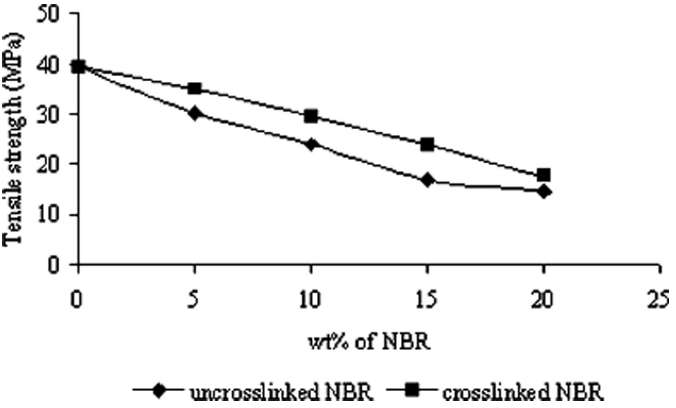

FIGURE 4 Variation of tensile strength with wt% of NBR.

Figures 4 and 5. The tensile strength and Young's modulus are lower than that of pure PS, and blends with crosslinked NBR display higher values than blends with uncrosslinked NBR. This is due to better interfacial adhesion between PS matrix and crosslinked NBR.

Elongation at Break

The variation of elongation at break with rubber content is shown in Figure 6. Blends with crosslinked NBR have higher elongation at break. This is because the craze fibrils are stabilized by molecular entanglements and can sustain high stresses for long periods.

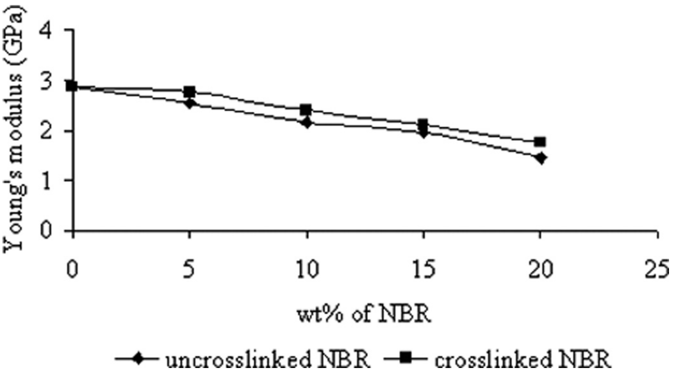

FIGURE 5 Variation of Young's modulus with wt% of NBR.

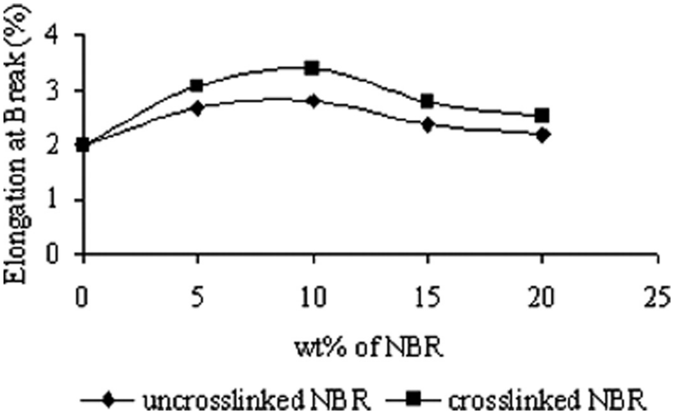

FIGURE 6 Variation of elongation at break with wt% of NBR.

In unvulcanized systems the molecular entanglements are unable to prevent rapid flow and fracture in response to applied stress.

Morphology

Figure 7 shows the SEM image of the fractured surface for unmodified PS. It contains plane areas with sharp brittle fracture in various

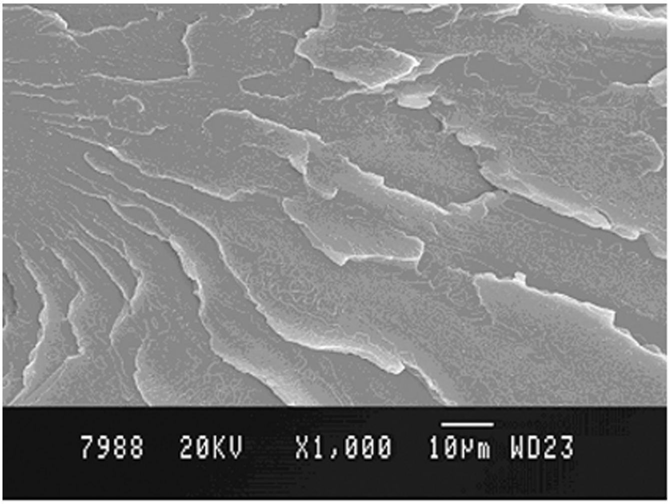

FIGURE 7 Scanning electron micrograph of pure polystyrene.

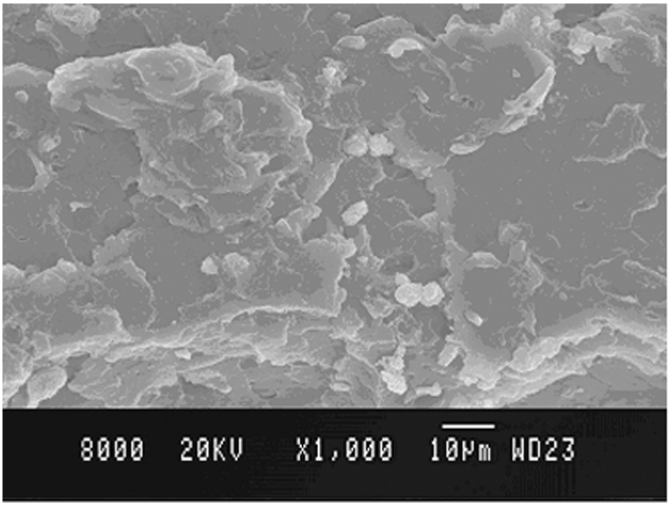

FIGURE 8 Scanning electron micrograph of 90/10 PS/NBR (uncrosslinked) blend.

planes. The SEM image of the 90/10 PS/NBR (uncrosslinked) blend is given in Figure 8. In this system the rubber particles exist as irregularly shaped domains in the PS matrix. The fracture surface

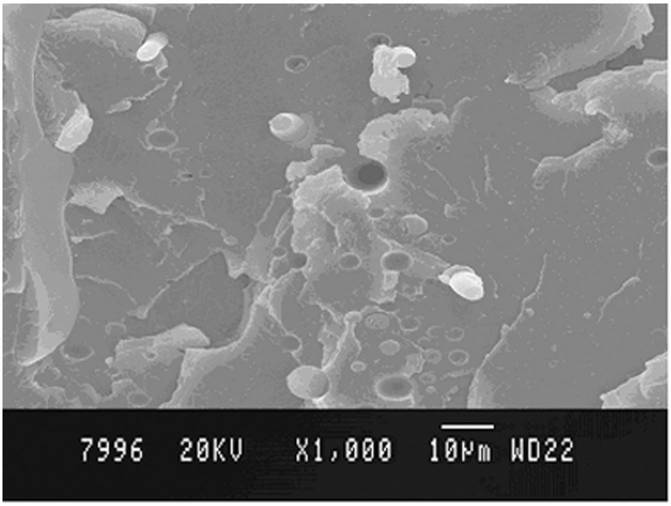

FIGURE 9 Scanning electron micrograph of 90/10 PS/NBR (crosslinked) blend.

observation of 90/10 PS/NBR (crosslinked) blend by SEM (Figure 9) reveals that the crosslinked rubber particles exist as dispersed spherical domains with fine morphology. The 3-dimensional network structure of crosslinked NBR strengthens the interfacial adhesion and hence the impact strength.

CONCLUSION

Impact strength, toughness, and elongation at break of brittle PS could be improved by the addition of crosslinked NBR. The possible toughening mechanism is the deformation of the brittle matrix and rubber particles induced crazes. The high interfacial activity of crosslinked rubber particles reduces the size of the dispersed phase and provides a more uniform particle size distribution. A small amount of PS/NBR graft copolymer may be produced on the interface and 3-dimensional network structure of crosslinked NBR strengthen the interfacial adhesion. The increased interfacial adhesion permits the interaction of the stress concentration sites leading to multiple crazing in the PS matrix.

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