Thermoplastic Elastomers of Butadiene-Acrylonitrile Copolymer and Polyamide. VI. Dynamic Crosslinking by Different Systems

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ABSTRACT: The dynamic crosslinking of butadiene-acrylonitrile copolymer (NBR) with polyamide 6 thermoplastic elastomer are studied. The effect of curing systems and the amount of curing agent are described. It is found that the NBR/PA6 60/40 ratio and phenolic curing system have a significant effect on the physical, mechanical, and thermal behavior of the elastomer. Scanning electron microscopy studies show that in the phenolic cured NBR/PA6 60/40 ratio the rubber phase is still the dispersed phase. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2057–2066, 2000

Key words: thermoplastic elastomers; polyamide; nitrile rubber; dynamic crosslinking; curing systems

INTRODUCTION

Thermoplastic elastomers (TPEs) have undergone an extensive growth in production with the success in commercialization over the past two decades. TPEs can be block copolymers, which contain rubber and resinous molecular systems (such as styrene-butadiene-styrene triblock copolymer[1] and ester or ether-urethane alternating block copolymers,[2] or they can be blends of a rubber–plastic combination such as crystalline polyolefine-ethylene-propylene-diene monomer.[3,4]

Crosslinking or vulcanization is the procedure in which a polymer passes from the plastic state to the elastic state, and the transformation is irreversible. In this reaction linear macromolecules are joined together by intermolecular bridges, thus forming a 3-dimensional network. There are two ways to crosslink the thermoplastic elastomers: static crosslinking and dynamic crosslinking.[5]

The best way to produce thermoplastic compositions, comprising crosslinked elastomer in melt processable plastic matrices, is by dynamic crosslinking, a process of crosslinking the elastomer during its melt mixing with molten plastic.[3,6,7] For TPEs based on rubber plastic, a composition ratio of 60/40 rubber/plastic is often desirable, because these blends are soft and elastic (tension set < 50%).[8]

Dynamic crosslinking can improve properties such as ultimate mechanical properties, fatigue resistance, resistance to attack by fluids, and reduced permanent set.[9] The morphology of uncured and dynamically crosslinked TPEs (rubber/plastic ratio = 60/40) is different and it depends on crosslink density. In the early stages of the dynamic curing process, two cocontinuous phases are generated even in well-defined, dispersed-phase uncrosslinked blends, and, as the curing progresses to completion, a dispersed-phase morphology is always obtained.[10–13] It is quite obvious that the crosslink density of the dispersed
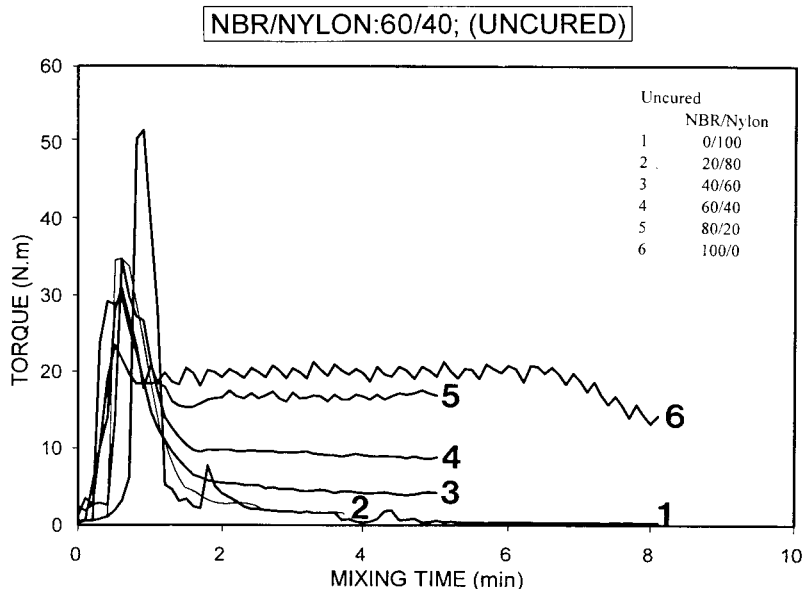
Figure 1 The torque vs. mixing time for uncured NBR/PA6 blends.

rubber phase plays a key role in achieving higher strength.[14]

This study investigated the effect of different systems of curing and the amount of curing agent on mechanical properties, thermal behavior, and the morphology of nitrile-butadiene rubber (NBR)/polyamide 6 (PA6) TPEs.

EXPERIMENTAL

Materials

The elastomer used in this study was butadiene-acrylonitrile copolymer (nitrile, Europrene N3345,

34% AN) obtained from Enichem. Co. (Italy). Poly(ε-caprolactone), nylon 6, and PA6 injection grade ($T_m = 226°C$, density 1.14 g/mL) were obtained from OSM Co. (Poland).

Curing agents such as phenolic compound (SP-1045, alkyl phenolic resole, yellow color, acid no. 10-30, methylol 7–10%, M.P. 90°C, flash point > 150°C), dicumylperoxide (DCP), and sulfur, and the heat stabilizer Flectol H were used.

Blend Preparation

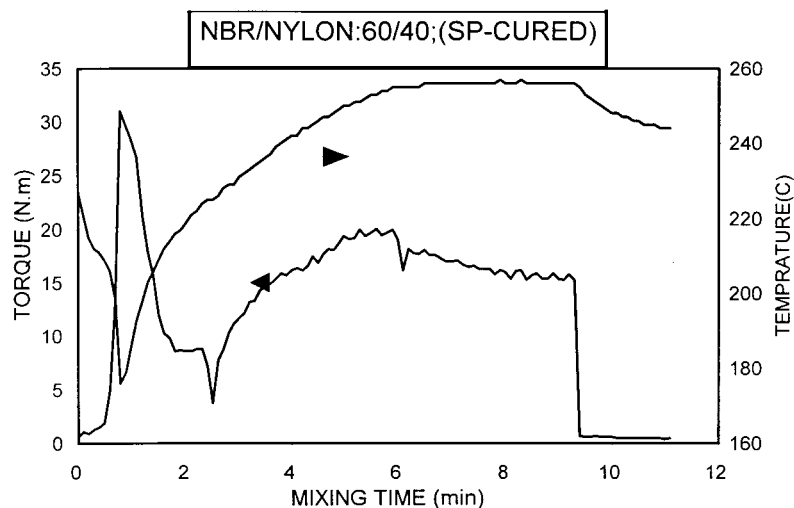The NBR/PA6 blends were prepared by melt mixing in a Haake Buchler Rheomix 750 internal

Figure 2 The torque and temperature vs. mixing time for 60/40 NBR/PA6 blends cured with SP-1045.
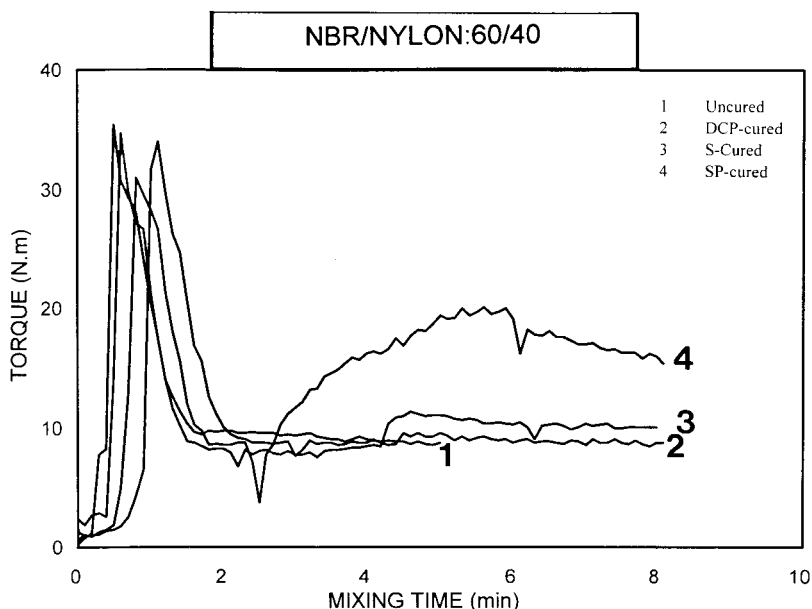
Figure 3 The torque vs. mixing time for cured 60/40 NBR/PA6 with different curing systems.

mixer at 230°C and 80 rpm. For dynamic curing of the blends the curing agent was added and then after constant torque and then the heat stabilizer was added after constant torque and mixing was continued for 1 min. In all compositions 1 phr Flectol H was used as the heat stabilizer.

Mechanical Characterization

The compression molding technique was employed to provide suitable samples for routine tensile testing. At least three and typically five replicate samples were tested for tensile data. Tensile bars conformed to ASTM D-638 and were strained using a crosshead speed of 50 mm/min in an Instron 6025 universal testing machine.

The hardness of the blends was measured according to ASTM D-2240 and D on the durometer scale instrument was selected.

Solvent resistance was measured by immersing the samples in oil with an annealing point of 77°C for 70 h at 125°C in accordance with ASTM D-471. The changes in weight were recorded.

Table I   Physical and Mechanical Properties of 60/40 NBR/PA6 Blends

	Properties					
Curing System	Shore D Hardness	Volume Swelling in Oil (%)	Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Permanent Set (%)
Uncured	35	15.9	125	5.2	47	—
DCP cured (1 phr DCP)	34	16.1	118	5.0	56	41
Sulfur cured (standard system)	36	15.4	144	5.9	80	25.4
Phenolic cured (1.3 phr SP-1045)	42	13.5	140	12.7	222	32.8

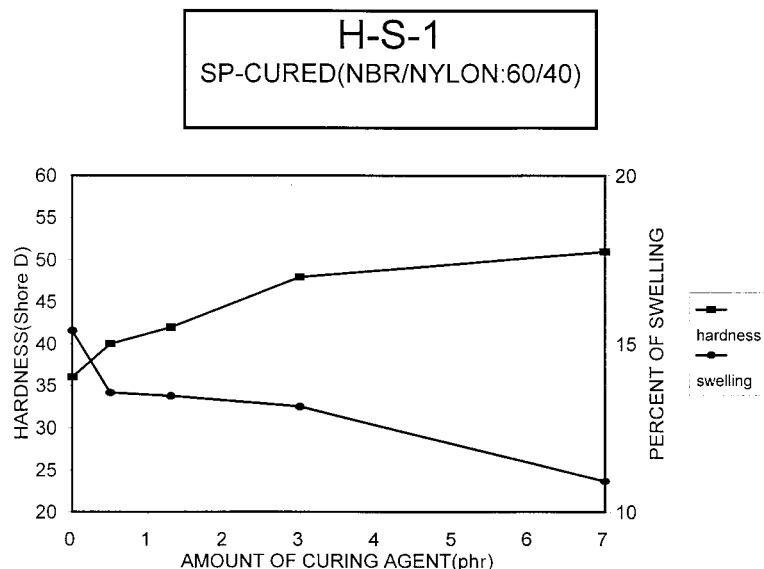## H-S-1
SP-CURED(NBR/NYLON:60/40)

Figure 4 The effect of the amounts of SP-1045 on the hardness and swelling of 60/40 NBR/PA6 blends.

The permanent set of the samples was measured according to ASTM D-412 by a tensile instrument at a constant speed of 50 mm/min.

Thermal Behavior

Dynamic mechanical properties tests of the samples were performed using $30 \times 10 \times 1$ mm compression molded test pieces and employing a PL-DMTA system equipped with liquid nitrogen cooling facilities, which allowed testing to be completed over the temperature range at 1 Hz and 10°C/min.

The notched Izod fracture surface of the samples at low temperature was studied by using scanning electron microscopy (SEM) with a Cambridge stereoscan S360.
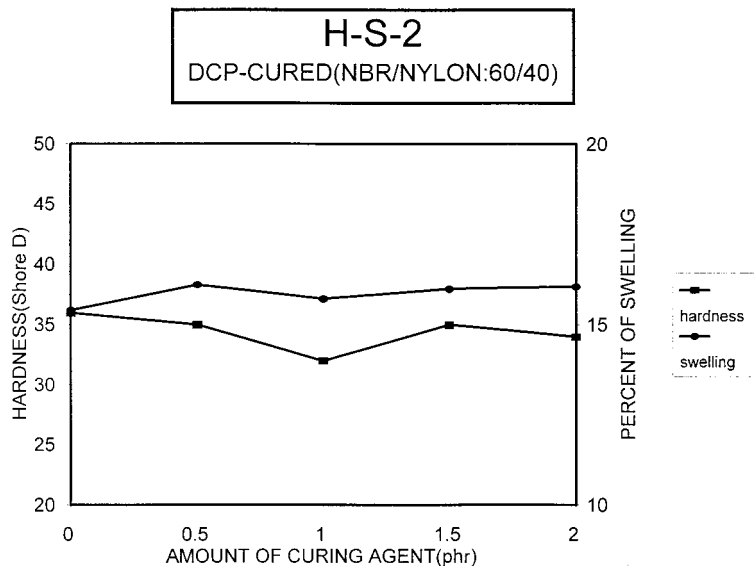
H-S-2
DCP-CURED(NBR/NYLON:60/40)

Figure 5 The effect of the amounts of DCP on the hardness and swelling of 60/40 NBR/PA6 blends.
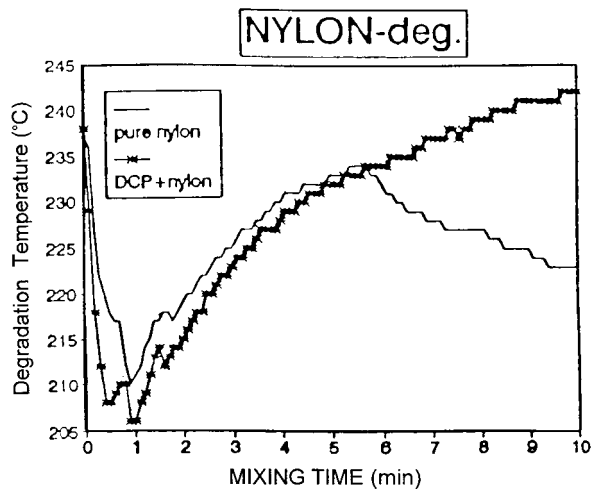
Figure 6 The effect of DCP on the degradation of PA6.

RESULTS AND DISCUSSION

Mixing

Figure 1 shows the torque versus time for uncured NBR/PA6 blends with different NBR content. It can be seen that increasing the NBR content increases the torque. The torque and temperature versus time of the 60/40 NBR/PA6 cured

Table II Comparison of Tensile Properties of 60/40 NBR/PA6 Blends at 25 and 125°C

Phenolic Cured at	Properties		
	Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
25°C	140	12.7	222
125°C	32	4.3	112

with SP-1045 samples are shown in Figure 2. It should be noted that the curing increases the torque because of the formation of crosslinking and increasing the viscosity causes better mixing.[15] Also, it can be seen that the temperature increases because of the increasing viscosity and generation of friction heat during the mixing. Figure 3 shows the torque versus time for uncured and cured NBR/PA6 60/40 blends with different curing systems. It is clear that the phenolic compound increases the torque more than the other curing agent and causes better curing and consequently better physical and mechanical properties.
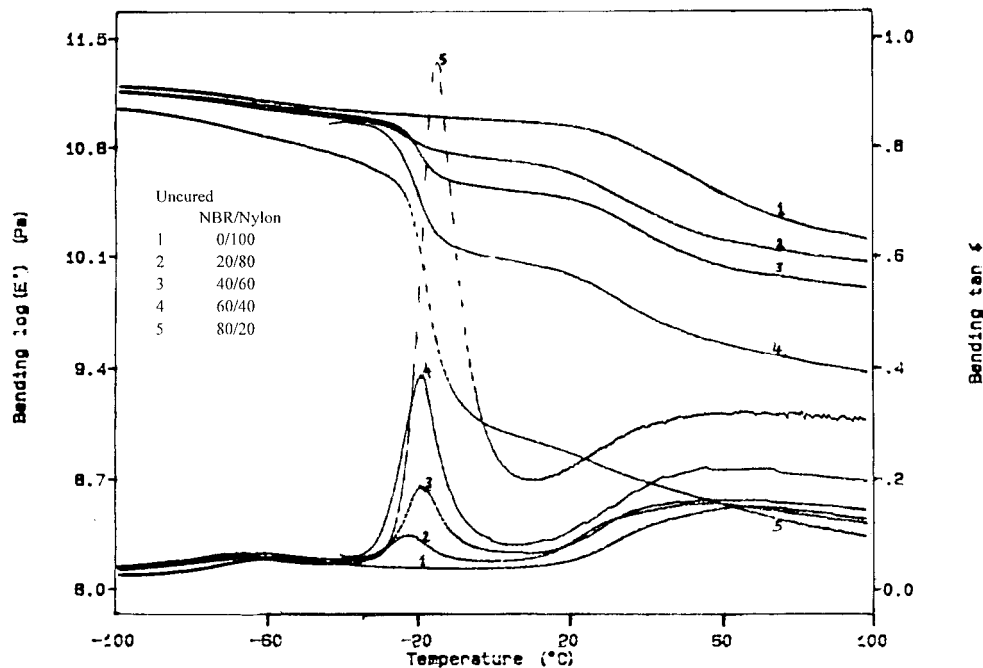

Figure 7 The storage modulus and tan δ traces of uncured NBR/PA6 blends.
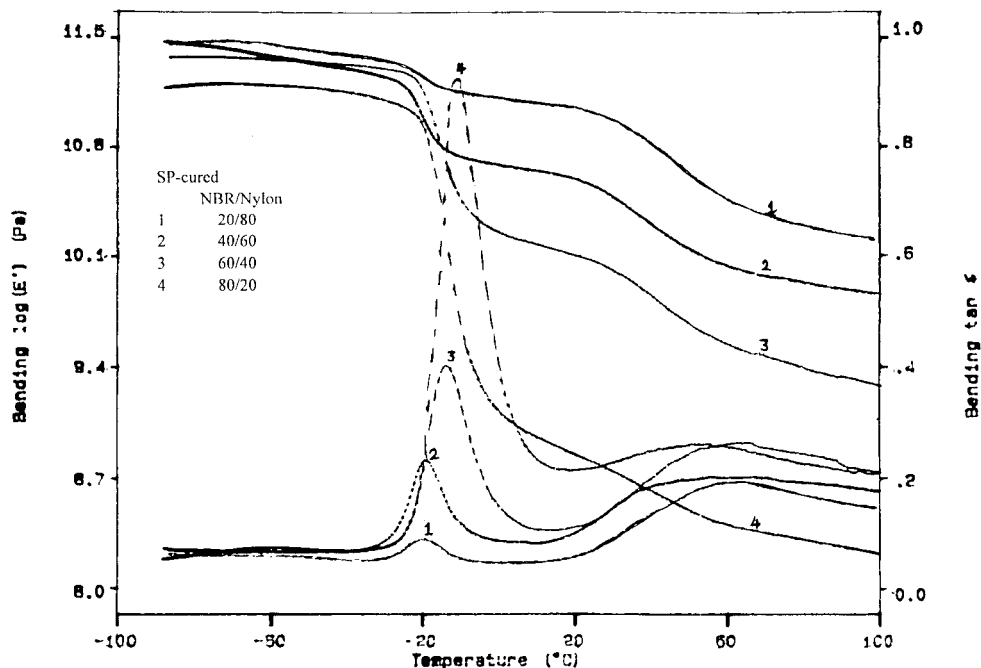
Figure 8   The storage modulus and tan δ traces of phenolic-cured NBR/PA6 blends.

Physical and Mechanical Properties

Table I shows the physical and mechanical properties of the 60/40 NBR/PA6 uncured and cured

with different curing systems. It can be seen that cured blends compared to uncured blends have higher hardness, tensile strength, and elongation, lower modulus and swelling, and better perma-
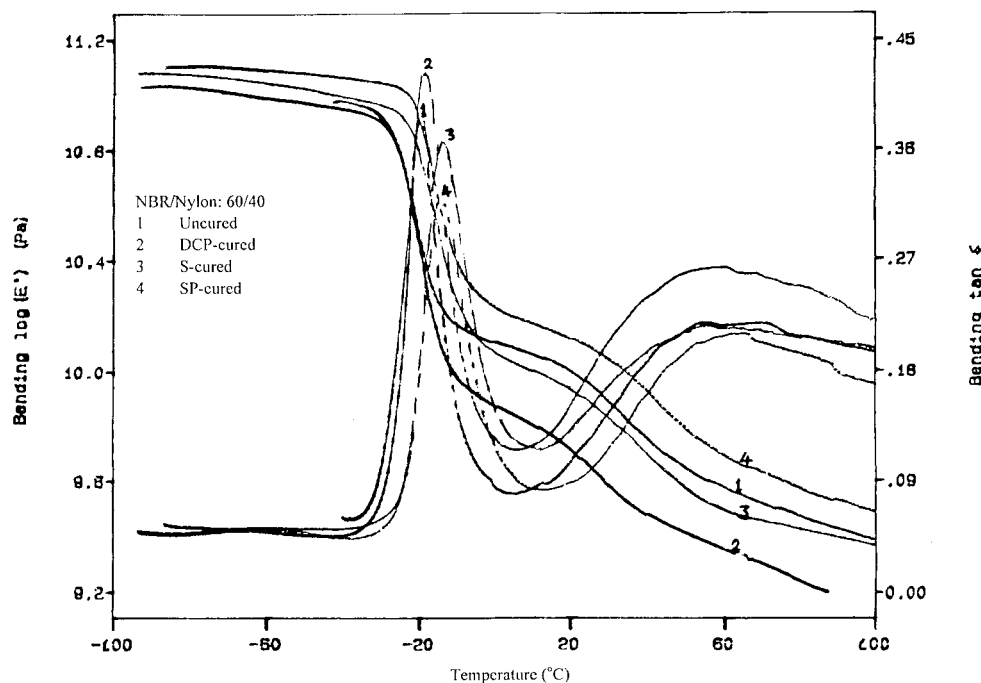

Figure 9   The storage modulus and tan δ traces of cured and uncured 60/40 NBR/PA6 blends.
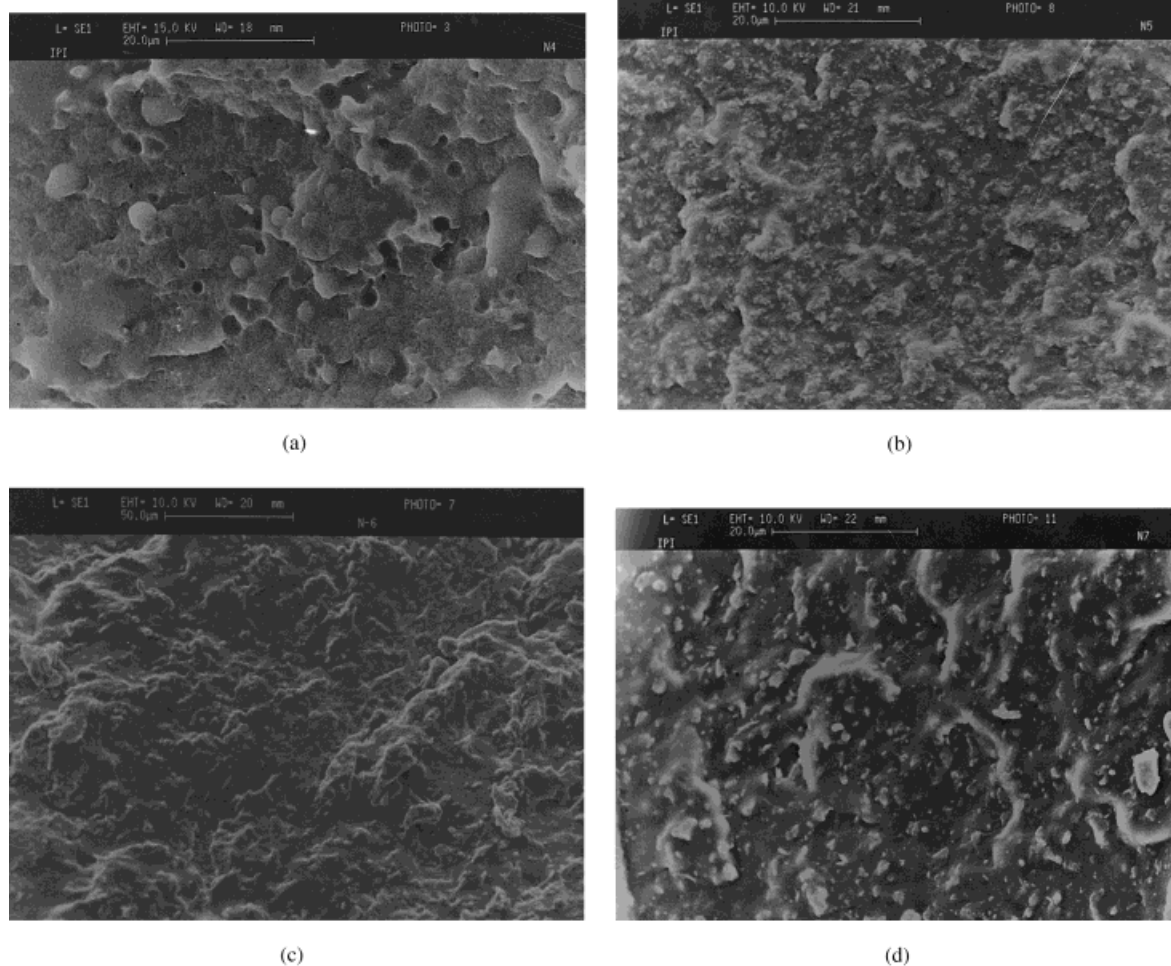
Figure 10   An SEM micrograph of the fracture surface of NBR/PA6 blends at ratios of (a) 20/80, (b) 40/60, (c) 60/40, and (d) 80/20.

nent set. It should also be noted that among the curing systems the phenolic compound curing system has good elongation at break of about 3 times more than other systems, which is important in TPEs, and this system has better tensile strength, hardness, and volume swelling in oil compared to other systems. From Table I we can conclude that the phenolic compound curing system is better than the others, and we suggest this curing system for the preparation of NBR/PA6 TPEs.

Figures 4 and 5 show the effect of the amount of curing agent on hardness and swelling for phenolic and peroxide systems, respectively. It can be seen that increasing the amount of phenolic compound increases the hardness and decreases the swelling (Fig. 4) whereas in the peroxide curing system increasing the amount of DCP causes no

changes in swelling and the hardness decreases. This is probably due to the degradation of PA6 by DCP at high temperature. Figure 6 shows the effect of DCP on the degradation of PA6. It can be seen that the addition of 0.5 phr of DCP to the PA6 increases the temperature by increasing the mixing time, which is probably because of the degradation of PA6 by DCP. In the sulfur curing system, because of the coagulation of rubber particles and the break down of the polysulfur to monosulfur, the modulus increases[14] but it has weaker tensile properties than the phenolic curing system. In the phenolic curing system the SP-1045 also acts as a functionalizer, reacts with PA6, increases the viscosity of the PA6, and improves the mixing. As a result, the particle size and particle size distribution decrease, thus improving the mechanical properties.
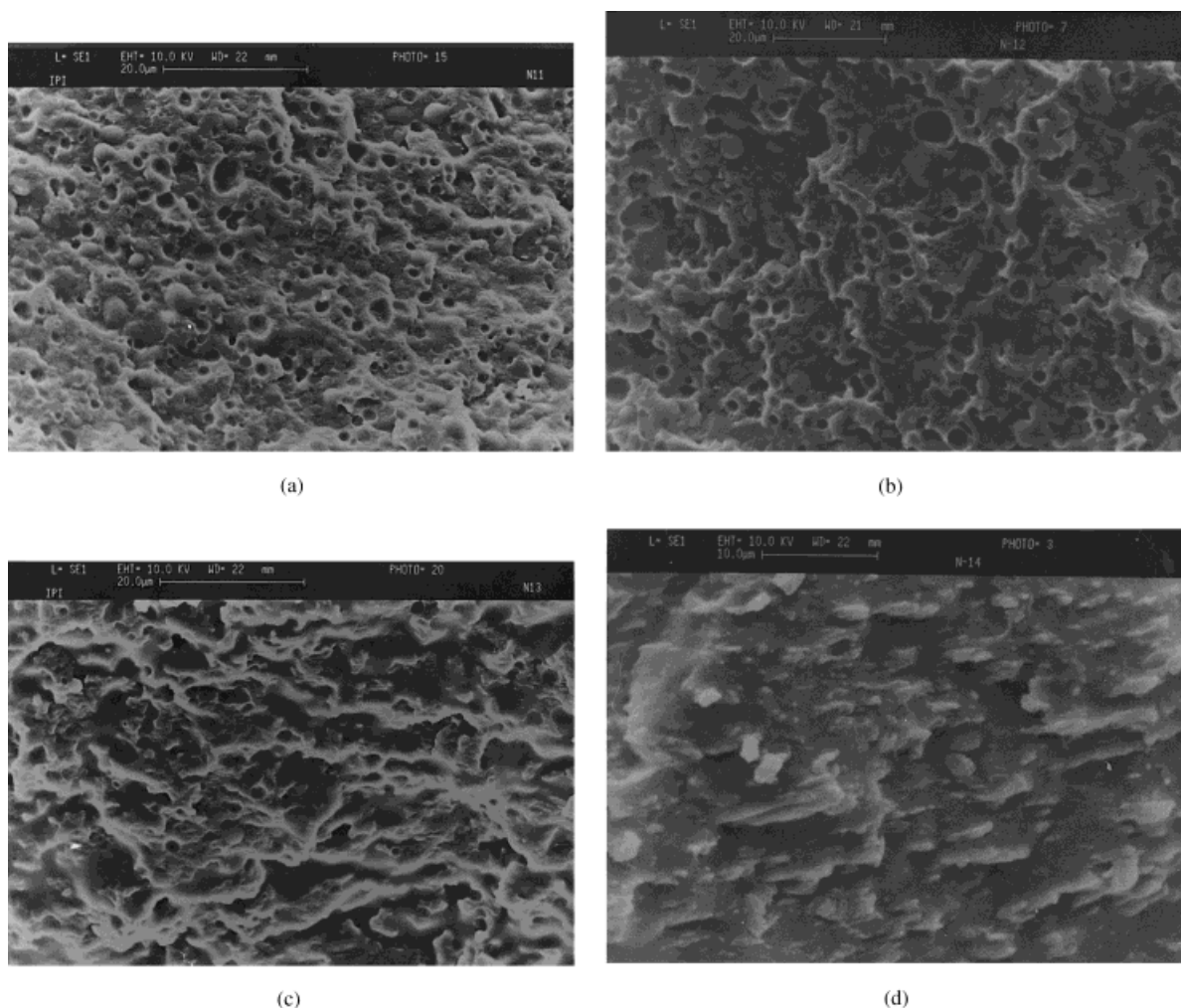
Figure 11 An SEM micrograph of the fracture surface of phenolic-cured NBR/PA6 blends at the ratios of (a) 20/80, (b) 40/60, (c) 60/40, and (d) 80/20.

**Performance in Oil and at High Temperature**

The oil resistance of 60/40 NBR/PA6 elastomer cured with the phenolic compound (SP-1045) is good (Table I). Table II shows the comparison of tensile properties of the NBR/PA6 60/40 blend at 25 and 125°C. It can be seen that phenolic cured samples, compared to other curing agents, still have good tensile properties at 125°C.

Thermal Behavior

Figures 7 and 8 show the storage modulus and tan δ traces of uncured and phenolic cured NBR/PA6 blends, respectively. As shown in Figure 7, the modulus of the 60/40 NBR/PA6 blend is much lower than the 40/60 NBR/PA6. This means that with this composition the phase inversion from PA6 to NBR occurs because the modulus of the NBR is much lower than nylon. In SP-cured samples (Fig. 8), however, this inversion occurs because of the composition ratio of 60/40 NBR/PA6. This, we can conclude that in this ratio (60/40 NBR/PA6) the NBR is still a dispersed phase, and this is one of the reasons that the SP-cured 60/40 NBR/PA6 sample has good properties. These results correlate with the mechanical properties and morphology observations.

The traces of tan δ in Figures 7 and 8 show the shifts of the glass-transition temperature (T_g) values of NBR and PA6 toward each other and there are more of these shifts in SP-cured samples (Fig. 8), which indicates cured samples with better miscibility.
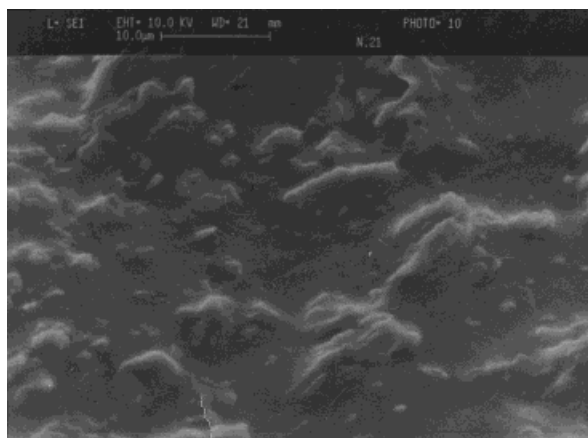
(a)
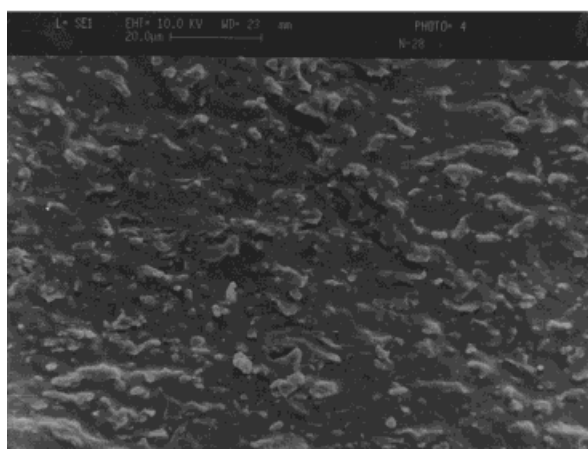
(b)

Figure 12 An SEM micrograph of the fracture surface on 60/40 NBR/PA6 blends that were (a) DCP cured and (b) sulfur cured.

In Figure 9 the storage modulus and tan δ traces results of uncured and cured 60/40 NBR/PA6 blends are presented. It can be seen that the modulus of SP-cured samples is higher than other samples. On the other hand, the shifts of the T_g values of NBR and PA6 toward each other are more than other samples, which means better miscibility and compatibility. DCP causes degradation and reduces the modulus.

Morphology

The notched fracture surface of uncured and cured samples was studied by using SEM. Figures 10 and 11 show SEM micrographs of the fracture surface of uncured and phenolic-cured NBR/PA6 samples, respectively. The figures show that the rubber particle size is reduced by curing and rubber particle size distribution shows improvement over the uncured samples. On the other hand, in uncured samples the phase inversion occurs at about a 60/40 NBR/PA6 ratio where a cocontinuous phase can be seen.

In SP-cured samples with a 60/40 NBR/PA6 ratio the rubber phase still dominates the dispersed phase and the inversion phase occurs at a higher ratio of NBR. Figure 12 shows the SEM micrograph of DCP-cured and sulfur-cured 60/40 NBR/PA6 blends. It can be seen that in DCP-cured samples the morphology is almost a cocontinuous (similar to uncured samples) phase and in the sulfur-cured sample the morphology is characterized by dispersion of large particles (agglomeration particles) in the PA matrix because of the agglomeration of rubber particles.

CONCLUSION

In general, dynamic crosslinking in TPEs increases the torque and causes better mixing. With the 60/40 NBR/PA6 composition, which is a good ratio for a TPE, dynamic crosslinking produces a significant improvement in tensile properties, hardness, swelling in oil, permanent set, and high performance temperature. We found that the phenolic curing system is better than other curing systems such as the DCP and sulfur curing systems. The dynamic mechanical studies showed the partial miscibility of NBR/PA blends and more reduction of modulus at phase inversion from the PA phase to the NBR phase. The SEM micrographs of the fracture surface of the samples showed that the phase inversion of the NBR/PA blends occurred at a ratio of more than 60/40 and with this ratio the NBR was still the dispersed phase.

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