

Effect of Crosslinking on Polyamide 11/Butadiene–Acrylonitrile Copolymer Blends

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ABSTRACT: The effect of crosslinking of polyamide 11 and butadiene–acrylonitrile copolymer (nitrile rubber) was studied. The effect of static and dynamic crosslinking on blending are described. Static and dynamic crosslinking do not significantly improve impact strength of low-rubber-content PA11/NBR blends. For blends with dynamic crosslinking and high rubber contents, mechanical properties including impact strength improve. Thermal behavior of crosslinked PA11/NBR blends were studied by DSC and DMA. SEM was used for investigation of the effect of crosslinking on particle size and particle size distribution, phase morphology, and fracture surface morphology. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1605–1611, 1997

Key words: polymer blends; polyamide; nitrile rubber; crosslinking; particle size

INTRODUCTION

Crosslinking, or vulcanization, is the procedure in which a polymer passes from the plastic state to the elastic state, and it is an irreversible transformation. In this reaction linear macromolecules are joined together by intermolecular bridges, thus forming a three-dimensional network.

There are two ways to blend thermoplastics with crosslinked rubber.

Static Crosslinking

In this process the rubber is crosslinked conventionally; that is, the rubber with curative, accelerator, and other additives are mixed in a mixer, banbury, or a two-roll mill at low temperature (~70°C) and then press-cured in a hot press. Cured rubber is then converted to a powder and blended in a mixer or extruded into the molten

thermoplastic. The pelletized material can be subsequently molded or extruded.

Dynamic Crosslinking

In this method the rubber and thermoplastic are premixed, with the curative and other additives then added. The rubber crosslinks *in situ* to give typically a form of semi-interpenetrating polymer network, which is subsequently capable of being molded or extruded. It is convenient to follow the progress of crosslinking by monitoring mixing torque or mixing energy requirement during mixing. After the mixing torque or energy curve goes through a maximum, mixing can be continued somewhat longer to improve fabrication of the blend.

Crosslinking, especially dynamic crosslinking, is widely used for thermoplastic elastomers (high rubber content) by Coran and Patel^{1–4} and Coran, Patel, and Williams.⁵ He suggests that in thermoplastic elastomers, crosslinking of the rubber gives composition with improved mechanical properties (compared to those of uncured or

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slightly crosslinked compositions). Much of the improvement in the mechanical properties of the dynamic crosslinked thermoplastic elastomers are attributed to the stabilization of the rubber particulate morphology, which would result from crosslinking.

Only a small amount of crosslink formation is required for a large improvement in tension set.⁶ The effect of the curatives on tension set is widely variable.⁴ The reason for variation of the effect on tension set is not understood, but it could be related to the extent whereby curatives promote molecular linkages between the polyamide and rubber, rather than cure the rubber.

Coran and Patel¹ reported that tensile strength improves rather continuously as the crosslink density of the rubber phase increases, but the compositions remain fabricable as thermoplastics even at high rubber crosslink densities. However, only small changes in the stiffness of the compositions occur, with great changes in the extent of cure. Young's modulus can even decrease slightly as a result of crosslinking. The improved strength could arise from a more favorable micromorphology, which may be associated with more highly crosslinked rubber particles.

Sabet and Patel⁷ also state that the crosslinking density of the dispersed rubber phase plays a key role in achieving higher strength.

There has been little experimental work done in which the influence of the crosslinked rubber upon the impact behavior of blends is studied. Dao⁸ found that a lightly crosslinked EPDM rubber is slightly more effective as an impact modifier for polypropylene than uncrosslinked EPDM. The crosslinking increases the rubber viscosity, which will affect the blending process and thus the rubber particle size. The particle size, in turn, strongly influences the impact behavior of the blends.⁹ However, lightly crosslinking EPDM did not seem to have any effect on the impact properties of polyamide 6/EPDM blends.¹⁰

Tinker^{11,12} showed that an optimum crosslink density in natural rubber (NR) (*cis*-1, 4-polyisoprene) exists for impact modification of polypropylene. This impact modification is attributed to the crosslinking of the rubber phase and also the formation of block or graft copolymers at the interface when bismaleimides (crosslinker) were mixed with NR and PP. In these blends the mechanism is probably more complex, since bismaleimides are also known to react with PP and form crosslinked structures.¹³

Xanthos and Dagli¹⁴ believe that blends con-

taining crosslinkable constituents may be compatibilized through the addition of suitable curatives, and the compatibilizing copolymers are formed *in situ*. It is believed that phase separation in these systems is inhibited by the presence of an intercrosslinked morphology with good interface bonding. Such morphology is assumed to be present in various "cure compatible" blends such as SBR/BR, NR/BR, etc.,¹⁵ based on components having approximately equal cure rates. Good properties may be also obtained by a slow overall rate of cure that favors overlapping and interdiffusion.¹⁶

EXPERIMENTAL

The thermoplastic used throughout was a natural grade of polyamide 11, Rilsan, BMV. This is a fine particle size, white, unmodified injection molding grade, provided by Atochem S.A., France.

The butadiene-acrylonitrile (nitrile) elastomers employed were Nipol 1052 (33% AN), Krynac 19.65 (19% AN), Nipol 1411 (38% AN, crosslinked powder), the products provided by Nippon Zeon Co. Ltd., Japan.

Blend Preparation

Blends were prepared by a melt mixing technique using a Haake 600 internal mixer followed by a Johns CF 550 injection molding machine.

The polyamide 11 was dried to remove moisture for 18 h at 60°C and the rubber slab was pelletized using a Crompton Parkinson granulator before using.

Conditions for the injection molding of blends were held constant for the measurement of mechanical properties of the samples.

Mechanical Characterization

The injection molding procedure employed a four-cavity mold, two cavities providing suitable samples for routine tensile and impact testing. At least three and typically five replicate samples were tested for both tensile and impact data. Tensile bars conformed to ASTM D-638, Type II and were strained using a crosshead speed of 50 mm/min⁻¹ in an Istron 1115 universal testing machine.

Impact bars 60 × 12 × 6 mm (thin bars) and 55 × 14 × 10 mm (thick bars) were sharp notched (2.5 mm) using a razor blade rather than em-

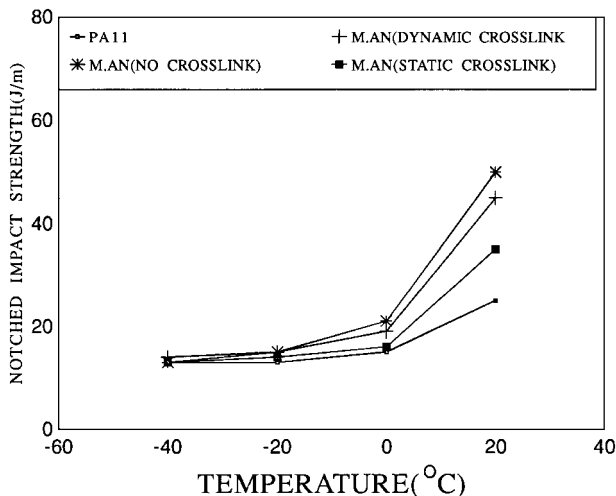


Figure 1 Effect of static and dynamic crosslinking on notched charpy impact strength in PA11/NBR: 80/20 blends.

employing the 45° notch specified in ASTM D 256. Impact testing was performed in a Zwick 5102 pendulum machine (for thin bars) and Satec System Inc. model SI-ID3 pendulum machine with a 33.9 J head (for thick bars).

The rubber particle size and particle size distribution of the blends are measured by an image analyser (Optomax system) from SEM micrographs of the fracture surface.

Thermal Behavior

Dynamic mechanical properties of the blends were performed using 23 × 10 × 4 mm injection-

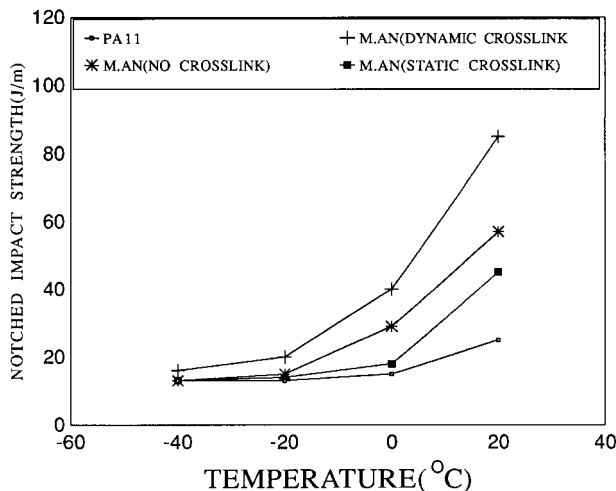


Figure 2 Effect of static and dynamic crosslinking on notched charpy impact strength PA11/NBR: 60/40 blends.

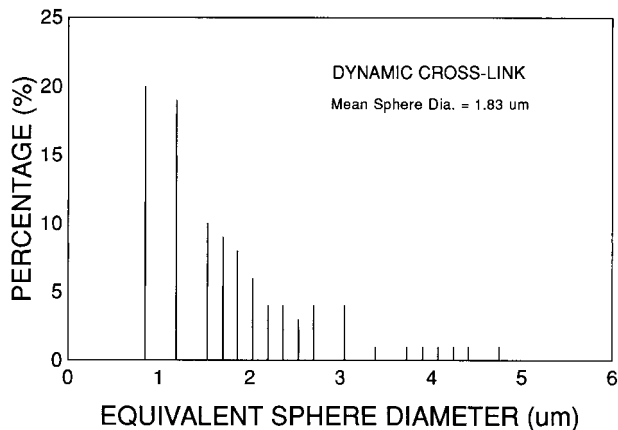


Figure 3 Effect of dynamic crosslinking on rubber particle size and particle size distribution of PA11/NBR(M.AN): 80/20 blends.

molded test pieces by using a DuPont 983 DMA and series 2100 analyzer. The DMA system possessed liquid nitrogen cooling facilities (LNCA II), which allowed testing to be completed over the temperature.

RESULTS AND DISCUSSION

The charpy notched impact strength for both static and dynamic crosslinked blends are shown for 80/20 and 60/40 blends of PA 11 and medium AN nitrile rubbers (i.e., 1052 and 1411) in Figures 1 and 2. In the former case simple blends (no crosslinking) and dynamic crosslinked blends show similar toughness, but at higher rubber content the dynamically vulcanized blend is superior.

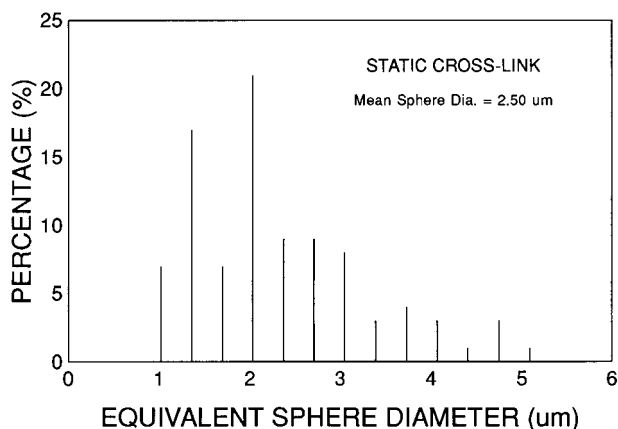


Figure 4 Effect of static crosslinking on rubber particle size and particle size distribution of PA11/NBR(M.AN): 80/20 blends.

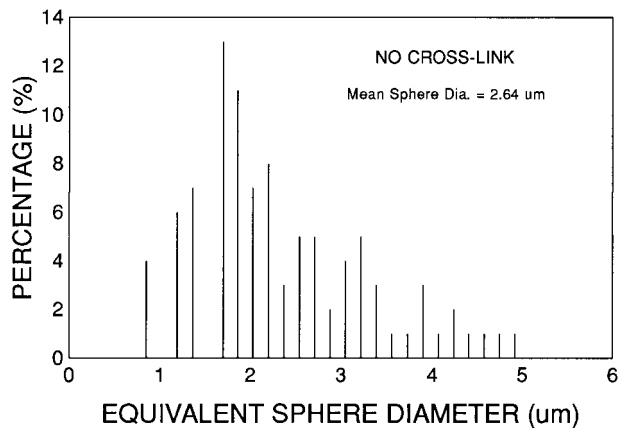


Figure 5 Rubber particle size and particle size distribution of PA11/NBR(M.AN): 80/20 blends.

The statically crosslinked blend is tougher than the polyamide alone, but lower than the simple blend, as shown in Figure 2.

In the case of static crosslinking, Yongsok¹⁷ postulated that the impact strength of Nylon 6 and crosslinked SBS rubber blends can be improved only with a moderate degree of crosslinking, while at low and high degrees of crosslinking, the impact strength decreases.

Effect of Crosslinking on Rubber Particle Size

The rubber particle size and particle size distribution of the PA11/NBR (M.AN): 80/20 dynamic crosslinked, static crosslinked and without any crosslinked blends were measured by using an image analyzer from SEM micrographs of fracture surface at room temperature (Figs. 3–5, respectively). It can be seen that the crosslinking decreases the particle size due to the prevention of

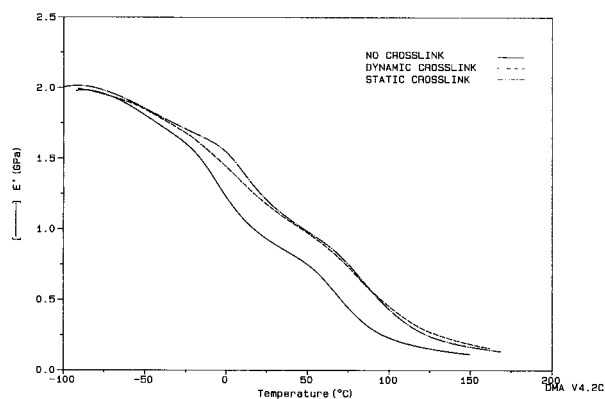


Figure 6 Effect of static and dynamic crosslinking on storage modulus of PA11/NBR(M.AN): 80/20 blends.

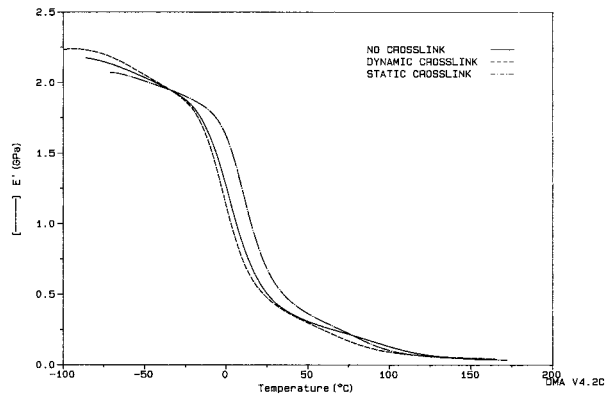


Figure 7 Effect of static and dynamic crosslinking on storage modulus of PA11/NBR(M.AN): 40/60 blends.

rubber coalescence, but the dynamic crosslinking has more effect on particle size, which is reflected in the high impact strength.

Effect of Static and Dynamic Crosslinking on Thermal Behavior

As described before, there are two ways to make crosslinked blends, static and dynamic crosslinking. Figure 6 shows the DMA trace of storage modulus for no crosslink, static, and dynamic crosslinking PA11/NBR(M.AN): 80/20 blends. It can be seen that crosslinking increases the modulus. However, the modulus in static crosslinked blends increases more especially between -25 to 25°C . This correlates with a decrease in the impact strength (Fig. 1). In low rubber content the modulus is more effective in impact strength.

Figure 7 shows the DMA storage modulus

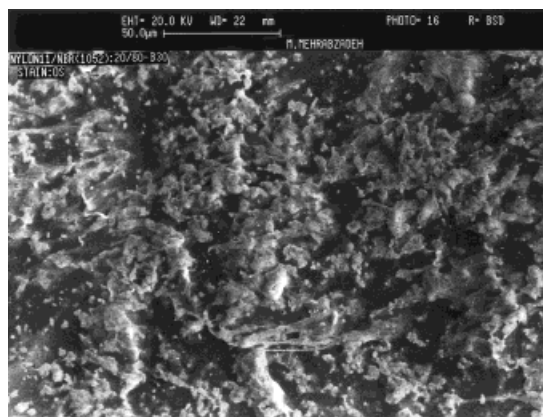


Figure 8 SEM micrograph of PA11/NBR(M.AN) (1052): 20/80 blends, uncrosslinked stained with 2% OSO_4 solution.

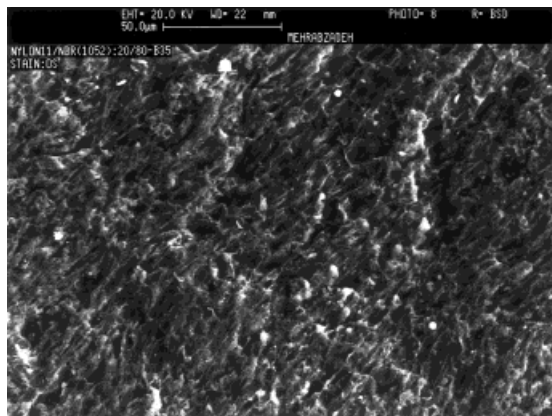


Figure 9 SEM micrograph of PA11/NBR(M.AN)-(1052): 20/80 blends, dynamically crosslinked with SP-1045, stained with 2% OSO_4 solution.

traces for crosslinked PA11/NBR(M.AN): 40/60 blends. It can be seen that at high rubber content (>60%) the static crosslinking still increases the modulus, but dynamic crosslinking decreases the modulus, with an associated increase in impact strength. Coran and Patel¹ have also reported that the modulus can decrease slightly as a result of dynamic crosslinking.

Effect of Crosslinking on Phase Morphology

Static and dynamic crosslinked and uncrosslinked blends, with low rubber content, have similar morphologies, but in high rubber content blends the phase morphology is different.

For these experiments, the blends were made of PA11/NBR.M.AN(1052): 20/80 by a Haake internal mixer at 210°C and 60 rpm with and with-

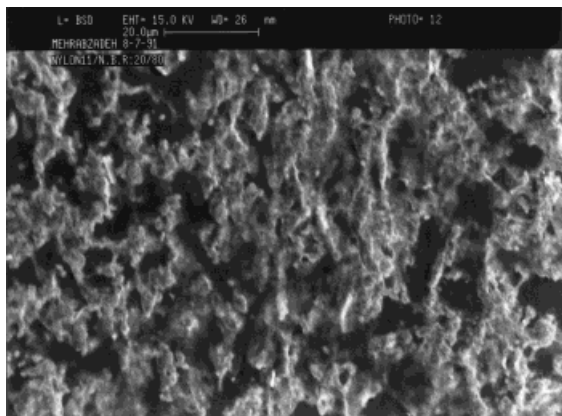


Figure 10 SEM micrograph of PA11/NBR(1411): 20/80 blends, stained with 2% OSO_4 solution.

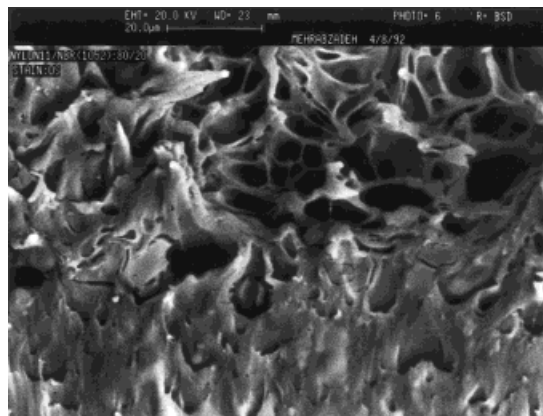


Figure 11 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 80/20 blends, uncrosslinked, at notch tip.

out SP-1045 as the crosslinking agent. The specimens for SEM were thin films.

Figures 8 and 9 show the differences between the phase morphology of uncrosslinked and dynamically crosslinked blends. It can be seen from Figure 8 (uncrosslinked) that there are two distinct phases, where the PA11 phase is the continuous phase. In Figure 9, the NBR and PA11 phases are cocontinuous.

Comparing Figure 9 with Figure 10 (when the blend has been statically crosslinked) shows that with static crosslinking, at high rubber content, the NBR phase is still the disperse phase and PA11 is predominantly the continuous phase. The cocontinuous phase in dynamically crosslinked blends can be reason for impact improvement in high rubber level blends.

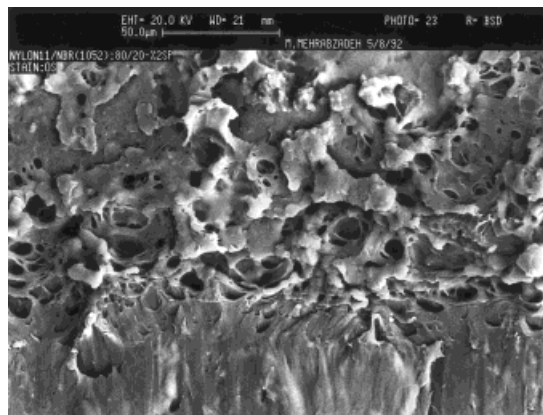


Figure 12 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 80/20 +2% SP-1045 blends, partially crosslinked, at notch tip.

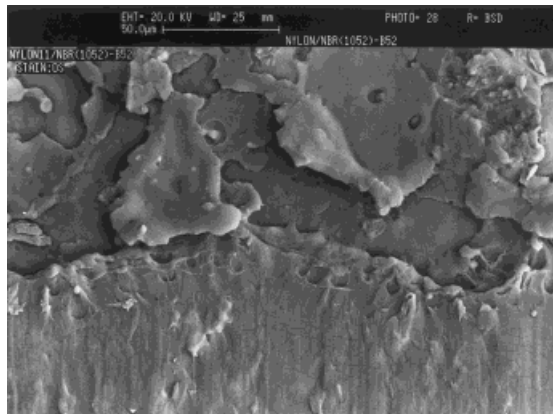


Figure 13 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 80/20 +2% DCP blends, static crosslinked, at notch tip.

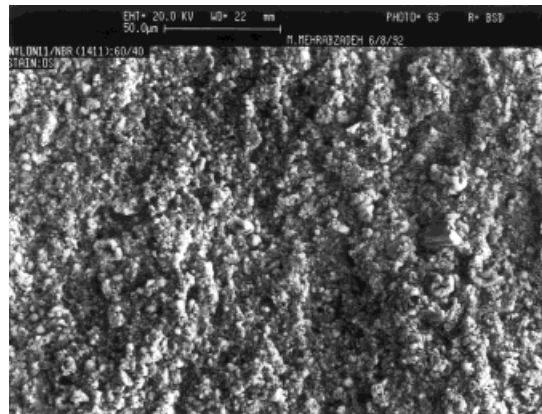


Figure 15 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 60/40 blends, static crosslinked.

Effect of Crosslinking on Impact Fracture Morphology

For the study of the effect of crosslinking on fracture surface morphology, dimethylol phenolic resin (SP-1045) and dicumyl peroxide (DCP) were used for dynamically crosslinked NBR in the blends at low and high crosslink density, respectively.

Figures 11 and 12 show SEM micrographs of PA11/NBR(M.AN): 80/20 and PA11/NBR(M.AN) + 2% SP-1045, which is partially crosslinked. It can be seen that by partially crosslinking, the voiding and cavitation, and even matrix drawing (Fig. 12), compared to the uncrosslinked blend (Fig. 11), decrease. By further crosslinking (with DCP) the fracture surface morphology is characteristic of brittle

fracture (Fig. 13). These morphologies are correlated with impact strength results. Crosslinking in low rubber content blends decreases the impact strength.

At high rubber content, the fracture surface morphology is quite different. Figures 14–16 show the SEM micrographs of PA11/NBR(M.AN): 60/40 with no, static, and dynamic crosslinked blends, respectively. It can be seen that voiding, cavitation, and matrix drawing occur in uncrosslinked blends (Fig. 14), but in static crosslinking (Fig. 15) there is no more cavitation or matrix drawing and so with poor impact strength. On the other hand, in dynamic crosslinked blends (Fig. 16) there are large cavities and high matrix yielding and drawing, which might be a tough

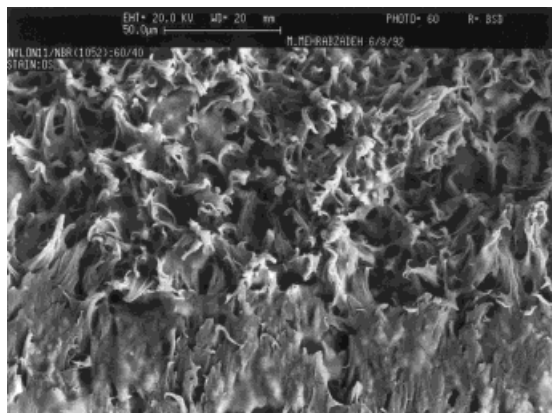


Figure 14 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 60/40 blends, uncrosslinked.

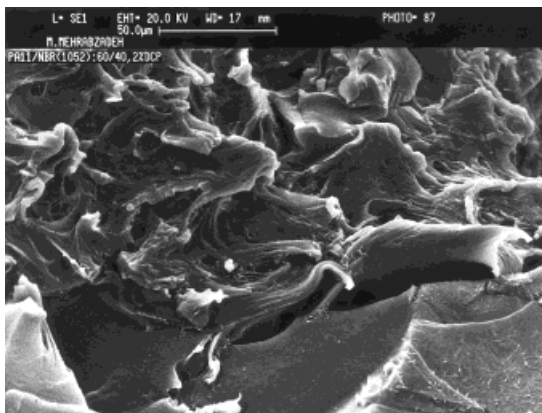


Figure 16 SEM micrograph of charpy impact fracture surface of PA11/NBR(M.AN): 60/40 blends, dynamic crosslinked.

fracture surface, which correlates with an improved impact performance.

CONCLUSION

Static and dynamic crosslinking do not significantly improve impact strength of low-rubber-content PA11/NBR blends. For blends with dynamic crosslinking and high rubber contents mechanical properties including impact strength improve.

In general, crosslinking can improve the oil swelling resistance. It also decreases the rubber particle size in PA11/NBR blends.

Generally, crosslinking increases the T_g of NBR and a similar trend was also observed in cross-linked PA11/NBR blends. DMA results show that by increasing crosslinking, blend storage modulus increases.

Static and dynamic crosslinking both increase the storage modulus of low-rubber-content PA11/NBR blends, but dynamic crosslinking of high-rubber-content (60%) blends slightly decreases the storage modulus.

Crosslinking of rubber in low-rubber-content PA11/NBR blends leads to a decrease in rubber particle size and morphology is now characteristic of brittle fracture. However, with high rubber contents and for dynamically crosslinked blends there are large cavities and high matrix yielding and drawing. This may be a consequence of the cocontinuous phase structure.

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