Acrylonitrile–Butadiene Rubber/ Reclaimed Rubber—Nylon Fiber Composite

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ABSTRACT: The effect of diphenylmethane diisocyanate (MDI)–polyethyleneglycol (PEG) resin on the cure characteristics and mechanical properties of nitrile rubber/whole tyre reclaim—short nylon fiber composite—was studied. At a constant loading of 5 phr, the resin composition was varied. The minimum torque and (maximum – minimum) torque increased with isocyanate concentration. Scorch time and cure time showed a reduction on introduction of bonding agent. Properties like tensile strength, tear strength, and abrasion resistance increased with increase in MDI/PEG ratio, and these properties are higher in the longitudinal direction of fiber orientation. Compression set increased with isocyanate concentration and the resilience remain unchanged. © 2001 John Wiley & Sons, Inc. Adv Polym Techn 20: 281–288, 2001

Introduction

Short-fiber-reinforced rubber composites have received much attention because of processing advantages and improved mechanical properties. The properties of short-fiber-reinforced composites mainly depend on the type and concentration of fiber, the orientation and distribution of fiber after mixing, the aspect ratio of fiber, and the degree of adhesion between fiber and the matrix.[1–10] Interfacial bond is known to play an important role in composites since this interface is critical in the composite performance. Pukanszky studied the influence of the interfacial bonding on the ultimate tensile properties of the composite.[11] Kondo reviewed the selection of adhesives for bonding short fiber reinforcements in styrene–butadiene rubber

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(SBR) and natural rubber (NR) composites.[12] Bonding of polyester and aramid cord in ethylene–propylene–diene monomer (EPDM) and hydroxylated acrylonitrile–butadiene rubber (HNBR) was developed by Janssen et al.[13] The adhesion of polyester fiber to different matrices was reported by Hirosuke et al.[14] A tri-component dry bonding system based on hydrated silica–resorcinol–hexamethylene tetramine has been successfully used in many short fiber–elastomer composites.[15–21] Suhara et al. have used urethane based bonding agent for short polyester fiber–polyurethane elastomer composite.[22–23] We have reported the effect of urethane based bonding agent on NR/whole tyre reclaim—short nylon fiber composite.[24] In the present work, our aim is to optimize the ratio of diphenylmethane diisocyanate/polyethylene glycol (MDI/PEG) for acrylonitrile–butadiene rubber (NBR)/whole tyre reclaim (WTR)—short nylon fiber composite. A 90/20 blend of NBR/WTR reinforced with 20-phr fiber was selected for this study.

Experimental

MATERIALS USED

Acrylonitrile–Butadiene Rubber was obtained from Apar Polymers Ltd., India. Nylon fibers, procured from SRF Ltd., Madras, were chopped to approximately 6-mm length. Whole Tyre Reclaim was supplied by Kerala Rubber and Reclaims, Mamala, India. The characteristics of reclaim used are given in Table I. Zinc oxide (ZnO) was obtained from M/s. Meta Zinc Ltd., Bombay. Stearic acid was procured from Godrej Soap (Pvt.) Ltd., Bombay, India. Dibenzothiazyldisulfide (MBTS) and 1,2-dihydro 2,2,4-trimethyl quinoline (HS) were obtained from Bayer India Ltd., Bombay. Tetramethyl thiuramdisulfide (TMTD) was supplied by NOCIL, Bombay, India. Sulfur was supplied by Standard Chemical Company Private Ltd., Madras. MDI (4,4′-diphenylmethane diisocyanate) was obtained from BASF South Korea, and PEG (Polyethyleneglycol) with a molecular weight 4000 was obtained from Manali Petrochemicals, Chennai.

TABLE I
Characteristics of WTR

Parameter	Value
Acetone extract (%)	13
Carbon content (%)	39

PROCESSING

Formulation of the mixtures is given in Table II. The amount of resin used was 5 phr and MDI/PEG ratios used were 0.67:1, 1:1, 1.5:1, 2:1. The mixing was done as per ASTM D 3182 (1989) on a two roll laboratory size mixing mill (150 × 330 mm). Once a smooth band was formed on the roll, the ingredients were added in the following order: reclaimed rubber, fibers, sulfur, MDI–PEG resin, activators, and accelerators. After complete mixing the stock was passed six times through the tight nip and finally sheeted out at a fixed nip gap so as to orient the fibers preferentially in one direction. Schematic representation of fiber orientations in tensile and tear test samples is shown in Fig. 1.

CURE CHARACTERISTICS DETERMINATION

Cure characteristics were determined by Goettfert Elastograph Model 67.85 at 150°C. The machine has two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen was kept in the lower die, which was oscillating through a small deformation angle (±2^0) at a frequency of 50 oscillations/min. The torque transducer on the upper die senses the force being transmitted through rubber. A typical cure curve is shown in Fig. 2.

TABLE II
Formulation of the Mixes

	Mixture No.				
Ingredient (Parts by Weight)	A	B	C	D	E
NBR	90	90	90	90	90
WTR	20	20	20	20	20
Nylon short fiber	20	20	20	20	20
MDI	0	2	2.5	3	3.33
PEG	0	3	2.5	2	1.67

[a] Zinc oxide: 4 phr, stearic acid: 2 phr, HS (1,2-dihydro 2,2,4-trimethyl quinoline): 1 phr, MBTS (dibenzothiazyldisulfide): 0.5 phr, TMTD (tetramethylthiuramdisulfide): 1.8 phr, and sulfur: 0.3 phr are common to all mixes.

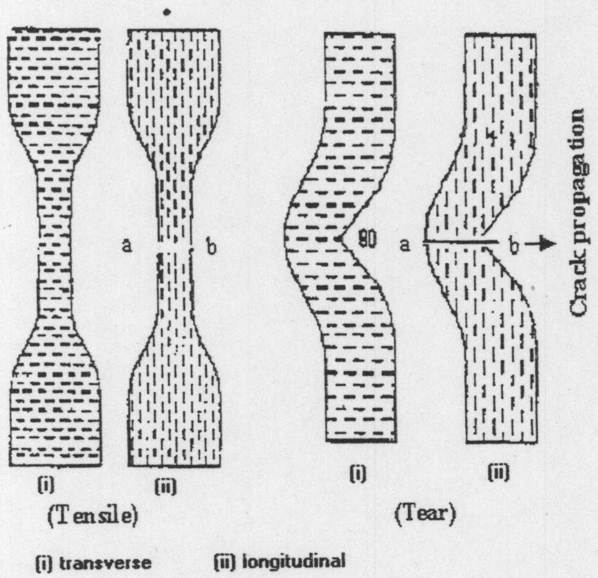

FIGURE 1. Schematic representation of fiber orientation.

Minimum torque (T_{min}) is the lowest torque shown by the mixture at the test temperature before the onset of cure. Maximum torque (T_{max}) is the torque recorded after curing of the mixture is completed. Scorch time (T_{10}) is taken as the time for 10% rise in torque from the minimum torque. The optimum cure time (T_{90}) corresponds to the time to achieve 90% of maximum cure.

VULCANISATION

Test specimens marked with the mill grain direction were vulcanized at 150 ± 2°C and at a pressure of 180 kg/cm^2 in an electrically heated hydraulic press to their respective cure times. For thicker samples sufficient extra cure time was given to obtain satisfactory moldings. Moldings were cooled quickly in water at the end of the curing cycle and stored in a cold dark place for 24 h, and then were used for subsequent property measurements.

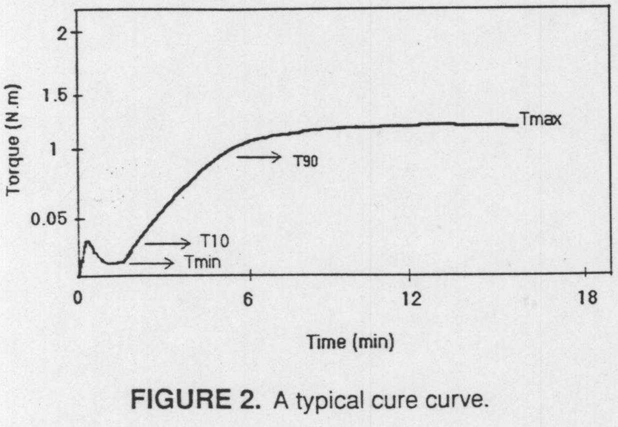

FIGURE 2. A typical cure curve.

PROPERTY MEASUREMENTS

The vulcanizates were tested for different mechanical properties according to ASTM standards. Tensile properties were measured using a Zwick UTM Model 1445 according to ASTM D 412 (die E). The test speed was 500 mm/min. Tear test was done on Zwick UTM as per ASTM D 624 (die C). The grip separation speed was 500 mm/min. Abrasion resistance of blends was measured using DIN abrader as per DIN 53516 and the values were expressed as volume loss per our. Compression set at constant strain was measured according to ASTM D 395-86 method B. Samples with 6.25-mm thickness and 18-mm diameter were compressed to constant strain (25%) and kept for 22 h in an air oven at 70°C. At the end of the test period the test specimens were taken out, cooled to room temperature for 30 min and the final thickness was measured. The compression set in percentage was calculated as follows:

$$\text{Compression set}\,(\%) = \frac{T_i - T_f}{T_i - T_s} \times 100$$

where T_i and T_f are the initial and the final thickness of the specimen, and T_s is the thickness of the space bar used.

Resilience was measured according to ASTM D 2832-88. For ageing resistance, samples were aged in an air oven for 48 h at 70°C (ASTM D 573-88). The properties were measured 24 h after the completion of ageing.

Results and Discussion

CURE CHARACTERISTICS

The minimum torque values of the composites increased with increase in isocyanate concentration with a marginal reduction at higher isocyanate concentration (Fig. 3). The increased minimum torque indicates a marginal loss in the processability of the composites. The increase in stock viscosity is arising from a low level of urethane resin formation during the processing stage. Similar results have been reported earlier.[24]

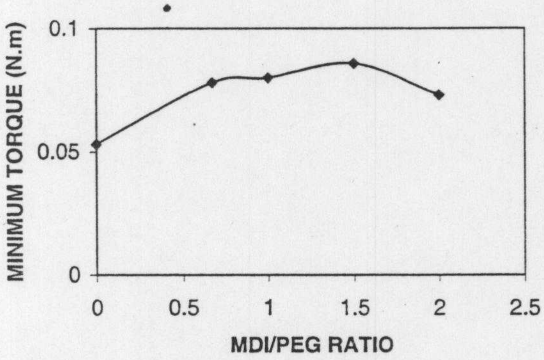

FIGURE 3. Variation of minimum torque with MDI/PEG ratio.

A plot of (maximum – minimum) torque values with isocyanate concentration is given in Fig. 4. The (maximum – minimum) torque values increase with increase in isocyanate concentration with a marginal reduction at higher MDI/PEG ratio. This indicates a more restrained matrix arising from better fiber–matrix bonding in presence of urethane resin. The reduction at higher isocyanate concentration can be attributed to less effective utilisation of monomer functionalities.

Scorch time showed a reduction from 2.25 to 1.95 min on the introduction of bonding agent (Fig. 5). The cure time is decreased from 5.55 to 5.1 min in presence of urethane resin (Fig. 6). Beyond a MDI/PEG ratio of 0.67:1 both the scorch time and the cure time tend to stabilize. This indicates that the presence of isocyanate group is interfering with the sulfur cross-linking reaction. The cure rate values are found to decrease with increase in MDI/PEG ratio (Fig. 7).

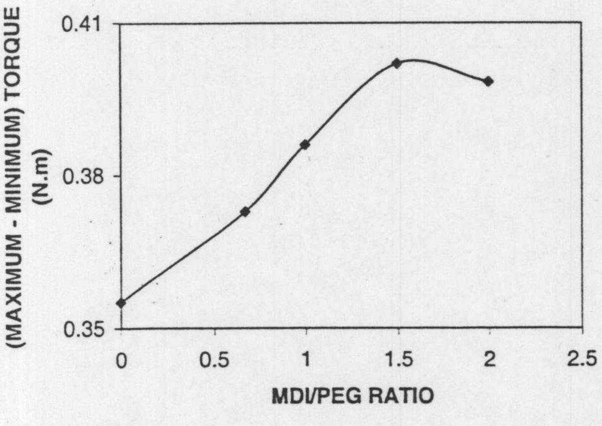

FIGURE 4. Variation of (maximum – minimum) torque with MDI/PEG ratio.

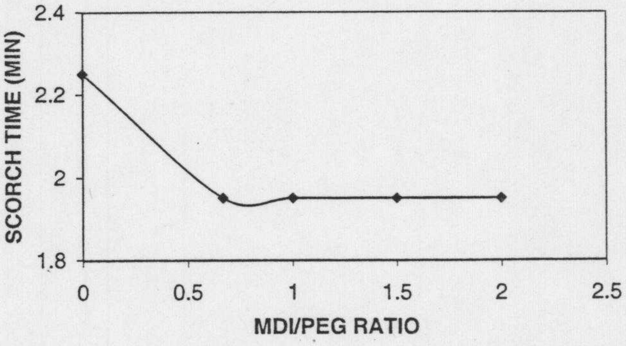

FIGURE 5. Variation of scorch time with MDI/PEG ratio.

MECHANICAL PROPERTIES

A plot of tensile strength vs. MDI/PEG ratio is shown in Fig. 8. The tensile strength in both the orientation direction increases with isocyanate concentration. The interfacial bond formed facilitates better load transfer to the fibers and results in higher tensile values. At any MDI/PEG ratio, the tensile strength is higher in the longitudinal direction. In the longitudinal direction, the fibers are more effective in restraining the matrix and hence better tensile values are obtained.

Elongation at break values of the composite with different MDI/PEG ratios are shown in Fig. 9. The elongation at break values are not much affected by the presence of the bonding agent. In all cases the elongation values are higher in the transverse direction.

The tear strength in both the orientation direction shows an improvement with increasing MDI/PEG ratio (Fig. 10). The improvement in tear strength

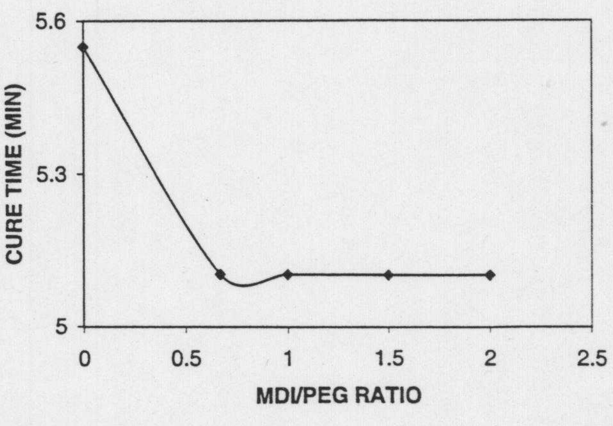

FIGURE 6. Variation of cure time with MDI/PEG ratio.

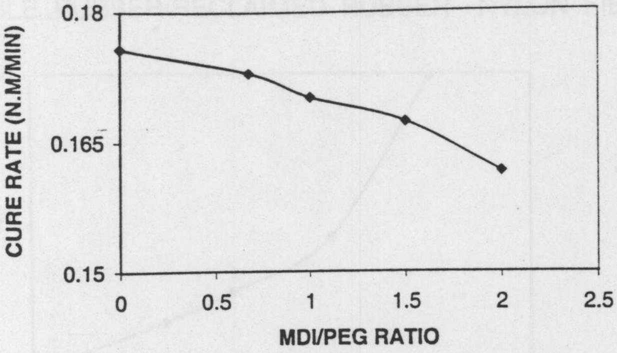

FIGURE 7. Variation of cure rate with MDI/PEG ratio.

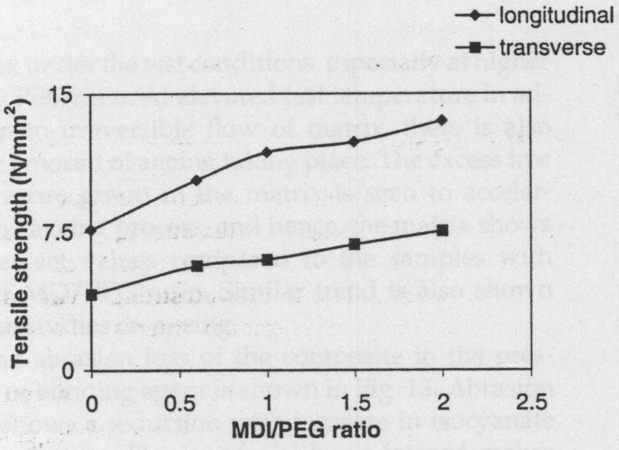

FIGURE 8. Variation of tensile strength with MDI/PEG ratio.

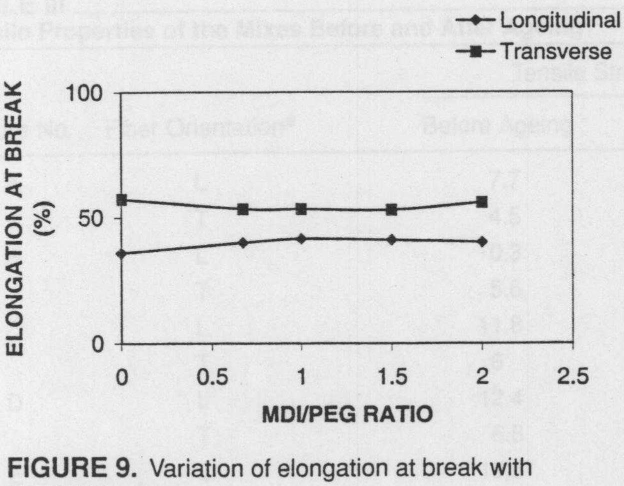

FIGURE 9. Variation of elongation at break with MDI/PEG ratio.

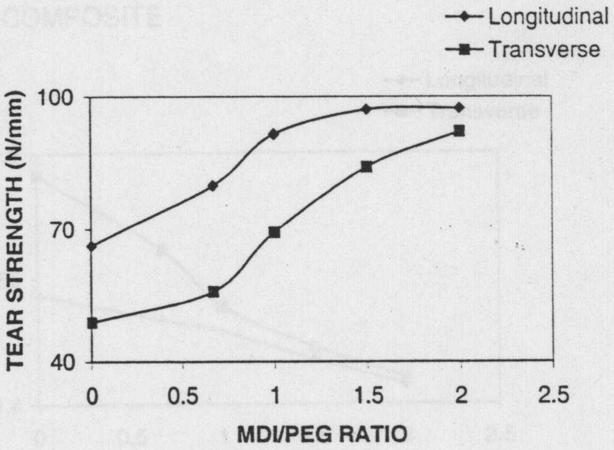

FIGURE 10. Variation of tear strength with MDI/PEG ratio.

further confirms a better fiber–matrix bonding in the presence of urethane resin. The tear strength values are higher in the longitudinal direction in all cases. The growing crack easily passes through the fiber–matrix interface when the fibers are in transverse direction and the improvement in interfacial strength is less prominent in this case.

The resilience values (Fig. 11) remain constant in the presence of urethane resin. The resilience test relates to the elasticity of the matrix at very low strain levels. The constant resilience values indicate that the elasticity of the composite at very low extensions is not affected by the presence of bonding agent as there is less chance for the load to be transferred to the fibers at low strain levels.

The compression set increases with increase in isocyanate concentration (Fig. 12). The increased compression set indicates an increased flow of

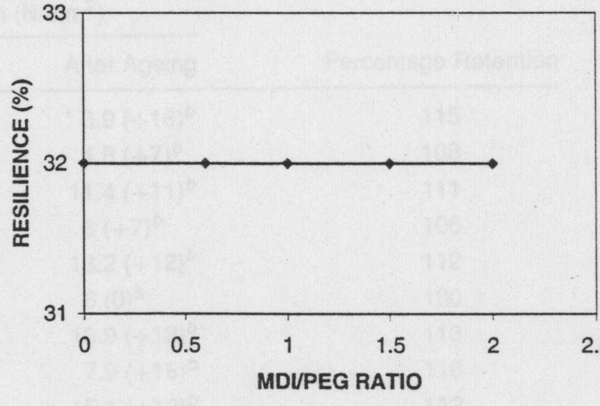

FIGURE 11. Variation of resilience with MDI/PEG ratio.

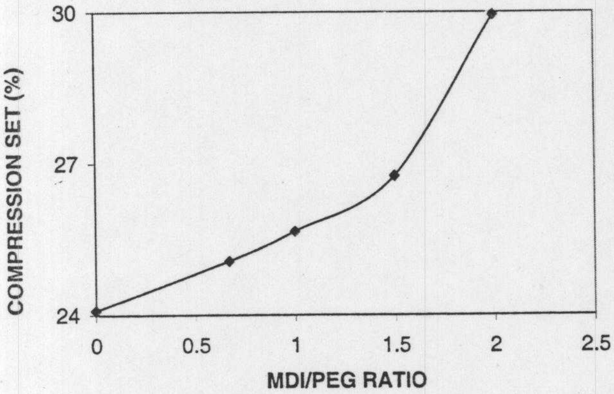

FIGURE 12. Variation of compression set with MDI/PEG ratio.

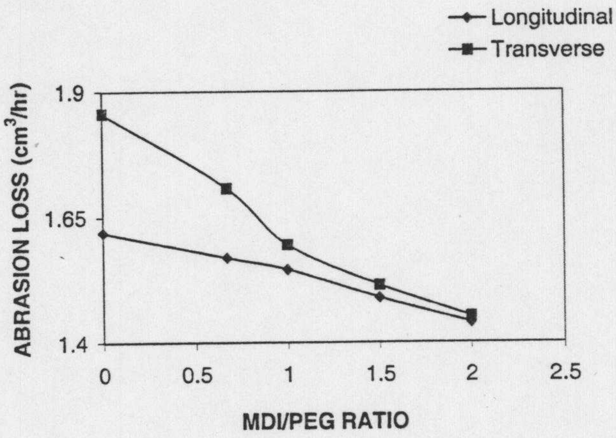

FIGURE 13. Variation of abrasion loss with MDI/PEG ratio.

matrix under the test conditions, especially at higher MDI/PEG ratio. At elevated test temperature in addition to irreversible flow of matrix, there is also some amount of ageing taking place. The excess free isocyanate group in the matrix is seen to accelerate the ageing process, and hence, the matrix shows higher set values compared to the samples with lower MD/PEG ratio. Similar trend is also shown by the studies on ageing.

The abrasion loss of the composite in the presence of bonding agent is shown in Fig. 13. Abrasion loss shows a reduction with increase in isocyanate concentration. The interfacial bond formed makes the matrix more stiff and resists the debonding of fiber from the matrix resulting in higher abrasion resistance. The abrasion resistance is higher in the longitudinal direction in all cases. This is in agreement with the results reported earlier.[25]

AGEING RESISTANCE

Table III shows the retention of tensile properties of the composites before and after ageing. There is minor improvement in the tensile strength of all the mixtures after ageing. This improved strength values indicates an improved fiber–matrix interfacial bond after ageing.

The tear properties of the composites are given in Table IV. The retention values are around 100 at lower MDI/PEG ratio. However, at higher isocyanate concentration the retention values are found

TABLE III
Tensile Properties of the Mixes Before and After Ageing

		Tensile Strength (N/mm^2)		
Mixture No.	Fiber Orientation[a]	Before Ageing	After Ageing	Percentage Retention
A	L	7.7	8.9 (+16)[b]	115
	T	4.5	4.8 (+7)[b]	108
B	L	10.3	11.4 (+11)[b]	111
	T	5.6	6 (+7)[b]	106
C	L	11.8	13.2 (+12)[b]	112
	T	6	6 (0)[b]	100
D	L	12.4	13.9 (+12)[b]	113
	T	6.8	7.9 (+16)[b]	116
E	L	13.5	15.1 (+12)[b]	112
	T	7.5	7.8 (+14)[b]	105

[a] L: longitudinal orientation; T: transverse orientation.
[b] Percentage change.

TABLE IV
Tear Properties of the Mixes Before and After Ageing

		Tear Strength (N/mm)		
Mixture No.	Fiber Orientation[a]	Before Ageing	After Ageing	Percentage Retention
A	L	66.3	87.2 (+32)[b]	132
	T	49	49.6 (+1)[b]	100
B	L	80	72.6 (−9)[b]	91
	T	56	55.3 (−1)[b]	99
C	L	91.5	91.9 (+0.4)[b]	100
	T	69.3	67.4 (−2.7)[b]	97
D	L	97.1	70.4 (−28)[b]	73
	T	84.2	45.3 (−46)[b]	54
E	L	97.5	74.3 (−24)[b]	76
	T	92.2	37.1 (−60)[b]	40

[a] L: longitudinal orientation; T: transverse orientation.
[b] Percentage change.

TABLE V
Elongation at Break Values of the Mixes Before and After Ageing

		Elongation at Break (%)		
Mixture No.	Fiber Orientation	Before Ageing	After Ageing	Percentage Retention
A	L	30.2	35.1 (+16)[b]	117
	T	57.3	95.4 (+67)[b]	166
B	L	40.3	42.7 (+6)[b]	107
	T	53.5	55.9 (+5)[b]	105
C	L	41.9	41.4 (−1)[b]	99
	T	53.5	64.6 (+21)[b]	121
D	L	41.3	39.2 (−5)[b]	95
	T	53	44.1 (−17)[b]	83
E	L	40.3	42.5 (+6)[b]	106
	T	56	37 (−34)[b]	66

[a] L: longitudinal orientation; T: transverse orientation.
[b] Percentage change.

to be reduced. Higher level of MDI in the matrix leaves many free isocyanate group which may be contributing to the reduced tear resistance of the composite. Since the micromechanism of failure under tensile and tear conditions are different the test results are not parallel with respect to the isocyanate concentration.

The percentage retention of the elongation at break values is found to be less than 100 in the presence of bonding agent (Table V). The lower values of retention is exhibited by mixtures containing higher isocyanate concentration. This suggests a possible acceleration of the ageing process by the free isocyanate groups.

Conclusions

Introduction of short fibers to NBR/WTR blends affect the cure characteristics and mechanical properties. Properties such as tensile strength, tear strength, and compression set increase with increasing MDI/PEG ratio. The tensile and tear strengths are higher in the longitudinal direction of fiber orientation. Abrasion resistance increases in the presence of bonding agent and this property is higher in the longitudinal direction. Resilience is unchanged in presence of bonding agent. The processability is adversely affected by the bonding agent.

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