



Mechanical and Morphological Properties of Short Nylon Fibre Reinforced NR/SBR Composites: Optimization of Interfacial Bonding Agent

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ABSTRACT

Nylon short fibres were incorporated in NR/SBR rubber matrix with and without a bonding system on a two-roll mill mixer. A dry bonding agent consisting of resorcinol, hexamethylene tetramine and hydrated silica (HRH) was chosen as the interfacial-bonding agent for this composite system. The effect of bonding agent content on the microstructure, mechanical and morphological properties of the composites was investigated. Samples were vulcanized at 150°C using a hot press after determination of the curing characteristics. The cure and scorch times of the composites decreased with increasing bonding agent concentration, while the maximum torque values showed an increasing trend. The bonding agent not only provided a shorter curing time but also enhanced the mechanical properties of the composite. The scanning electron microscopy (SEM) of the composite fracture surfaces implied that the presence of bonding agent has led to the breakage of fibres and less dark holes indicating the pull out of fibres without bonding agent. The results of anisotropic swelling studies, carried out to analyze fibre/matrix interactions and also orientation of the fibres, showed that the restriction to swelling is higher for the composites containing bonding agent. Furthermore, the preferential orientation of the fibres was observed to be in the milling direction. For composites prepared with short fibres and different loading levels of bonding agent, the dependence of the storage modulus (G') on angular frequency followed a clear non-terminal behaviour.

Key Words:

NR/SBR composites;
short nylon fibre;
dry bonding agent;
mechanical properties;
morphology.

INTRODUCTION

Although elastomers are popular for their rubber-like elasticity, high flexibility and abrasion resistance, but their applications are confined due to the low strength and stiffness. For compensating these drawbacks, elastomers are often reinforced with short fibres, so that the composites of this type can be a useful engineering material. These composites possess the strength

and stiffness of the fibres and also the elasticity of the matrix [1].

Recently short fibre reinforced rubbers have gained a remarkable importance due to some advantages; for instance, easy processability, anisotropy in technical properties, stiffness, damping and enormous flexibilities in product design [2-8]. Short fibres can be incorporated directly into the rubber

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compounds along with other additives; so the produced composites would be amenable to standard rubber processing techniques of extrusion, calendaring and various types of moulding operations [9,10].

The properties and performance of short fibre-reinforced rubber composites depend on several factors such as the nature, aspect ratio (L/D), orientation and concentration of fibres as well as the adhesion strength of the fibre/matrix [11]. Chemical nature of the fibres and the matrix and also the presence of a bonding system determine the extent of interfacial adhesion and thus the strength of the composites [12-17].

One of the most important aspects of composite fabrication is to achieve adequate adhesion between fibres and matrix. If the fibres are not bonded properly with the rubber matrix, they would slide past each other under the tension deforming the matrix; thereby the strength properties of the composite would be reduced. Natural fibres such as cotton, cellulose, etc., have short whiskers protruding from the surface, which help to give a physical bond when mixed with rubber [18-20]. Glass, nylon, polyester and rayon have smooth surfaces and adhesion of these fibres to the rubber matrix is comparatively poor. These synthetic fibres have chemically unreactive surfaces which must be treated to form a bond with the rubber. Kubo et al. [21] proposed a three-layer model composed of fibres, adhesive agents, and elastomers to explain the adhesion between elastomers and fibres. According to Kubo et al. [21], the bonding mechanism between the fibre layer and the adhesive agent layer varies with each fibre and the adhesion between the bonding agent and the elastomer is established after vulcanization of the elastomer. The unsaturated bonds in the system are bonded by cross-linking reactions of the elastomer [22].

The effects of bonding agent and alkali treatment on the mechanical properties of coir-fibre-reinforced NR composites have been studied by Geethamma et al. [12] and Arumugam et al. [23]. They showed that using various bonding systems increased the interfacial adhesion between the coir and natural rubber as well as the modification of fibre surface. Setua et al. [24] studied the effect of bonding agent in

short silk fibre reinforced polychloroprene rubber composites and found that the adhesion between the fibre and the matrix was complete only when all the three components of the bonding system were present together. Seema et al. [25] reported the use of epoxy based bonding agent to promote the adhesion between nylon fibre and NBR matrix. Ghoreishy et al. [26] described the properties of short nylon fibre reinforced natural rubber composites in the presence of HRH dry bonding system.

Compared to adhesive dipping which is mostly used for continuous fibres, the tri-component dry bonding system consisting of resorcinol (or a resorcinol derivative), hexamethylene tetramine (hexamine), and fine particle hydrated silica (HRH) can be used to achieve adhesion between short fibre and the rubber matrix. Derringer [27] examined the HRH system with various fibres in nitrile and natural rubber so that good bonding would be obtained. O'Connor [28] compared the HRH system with RH (resorcinol and hexamethylene tetramine alone) and hexamethoxy methyl melamine (HMMM) alone in various short fibre natural rubber composites. He found that the RH system worked best with carbon fibre while HMMM showed some bonding with Kevlar. In the present study, the effect of different loading levels of bonding agent HRH on the curing characteristics, mechanical properties, morphology and rheological behaviour of the NR/SBR composites prepared with 30 wt% of nylon short fibre were investigated. Fibre-matrix adhesion has been analyzed by scanning electron microscopy studies and anisotropic swelling measurements.

EXPERIMENTAL

Materials

Natural rubber (SMR-20) with ML (1+4) at 100°C = 65 (Malaysia) and styrene-butadiene rubber (SBR 1502) with ML (1+4) at 100°C = 54 (Bandar-Emam Petrochemical Company, Iran) were used in this study. Nylon 66 fibres in yarn form were obtained from Iran Saba Fibre Co., with 1260 denier and diameter of 0.18 mm which were chopped to approximately 6 mm in length. *N*-Cyclohexyl-2-benzothiazyl sulphenamide (CBS), sulphur (S), zinc

Table 1. Samples and their ingredient compositions.

Ingredients	B ₀ F ₀ (1)	BF ₀ (2)	BF ₃₀ (3)	B ₀ F ₃₀ (4)	B _{1/2} F ₃₀ (5)	B ₂ F ₃₀ (6)
NR	40	40	40	40	40	40
SBR	60	60	60	60	60	60
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Resorcinol	0	2.5	2.5	0	1.3	5
Hexamine	0	1.6	1.6	0	0.8	3.2
Silica	0	5	5	0	2.5	10
Fibre	0	0	30	30	30	30
CBS	0.8	0.8	0.8	0.8	0.8	0.8
Sulphur	2	2	2	2	2	2

B: bonding agent, F: fibre

oxide (ZnO) and stearic acid from Bayer Company, Germany, were used for curing system. A combination of resorcinol, $d = 2.36 \text{ g/cm}^3$, hexamethylene tetramine, $d = 1.33 \text{ g/cm}^3$ and hydrated silica (Vulcasil S), $d = 2 \text{ g/cm}^3$, used as the bonding agent between rubber and fibre were supplied by Lanxess Company (Germany).

Preparation

The sample formulations employed in this study are reported in Table 1. The composite materials were prepared in a two-roll mill model (Polymix 200L, England) at a roll speed of 50 rpm and temperature of 50°C. The nip gap, mill-roll speed ratio, mixing time and temperature, and sequence of mixing were kept constant for all compounds. The orientation of the fibre in non-cured compound was achieved in rolling direction by passing the sample through a controlled nip. The rolling direction was kept unchanged for all the samples to promote better fibre orientation (as shear forces occurring during milling operations orientating most of the fibres along the grain direction). The sheeted rubber compound was conditioned at room temperature for 24 h before vulcanization.

Characterization

Zwick rheometer (Germany), model 4308, was used to determine cure characteristics data for composites at 150°C according to ASTM D 2084. The samples were vulcanized at 150°C in a hydraulic press 25 ton (Davenport Ltd., England) under 180 kg/cm² pressure for a time, based on data obtained from a rheometer.

Stress-strain measurements were carried out by using a tensile testing machine, HIWA 200 (Iran), at a crosshead speed of 500 mm/min Dumb-bell shaped samples of a 2 mm thickness were cut along (longitudinal) and across (transverse) the grain direction. Mechanical properties were determined according to ASTM D412. The hardness was measured at room temperature using a shore-A hardness Tester (Zwick Company, Germany) according to ASTM D2240. Resilience was determined at 28°C using Resilience Tester Frank (Germany) according to ASTM D1054. Abrasion loss was measured with the Frank Abrasion Tester (Germany) as ASTM D5963. Anisotropic studies were carried out using rectangular samples which were cut with dimensions (10×25×2 mm) from the tensile sheets in both directions. They were weighed then swollen in toluene at room temperature for 2 days. The morphology of cryogenically fractured composite surfaces was observed under a Cambridge Stereoscan 360 (England) scanning electron microscope (SEM). The rheological characterization of samples was carried out using a stress-controlled rheometer (RPA 2000, USA); experiments were performed at a temperature of 80°C and in the frequency range of 0.01-30 Hz.

RESULTS AND DISCUSSION

The results of rheometric studies for the compounds are given in Figure 1; and, the cure characteristics of

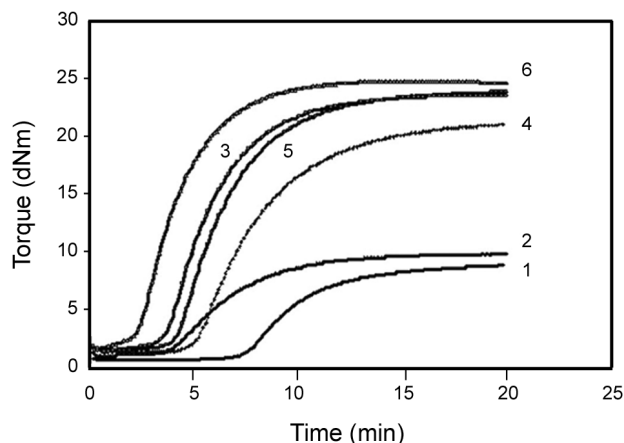


Figure 1. Rheographs of composites prepared with 30 phr fibre and different bonding agent ratios at 150°C (Numbers on the curves represent composite compounds).

the compounds are summarized in Table 2. Figure 2 shows that the minimum and maximum torques of compounds increased with the incorporation of nylon fibre and/or the bonding system. Figure 3 shows the effect of HRH bonding system concentration on cure characteristics of the composites prepared with 30 wt% of short fibre. Here, a reduction is observed in the scorch time and cure time with increased concentration of bonding agent.

It can be observed that addition of bonding agent to the gum compound (compound 2) resulted in lower scorch time and optimum cure time and yet caused no significant change in the cure rate in comparison with compound 1, possibly due to the presence of silica and resorcinol in the bonding system which may have retarded the cure process [7,29-31]. Addition of fibres into the pure matrix (compound 4) lowered the scorch time and optimum cure time as well as an increase

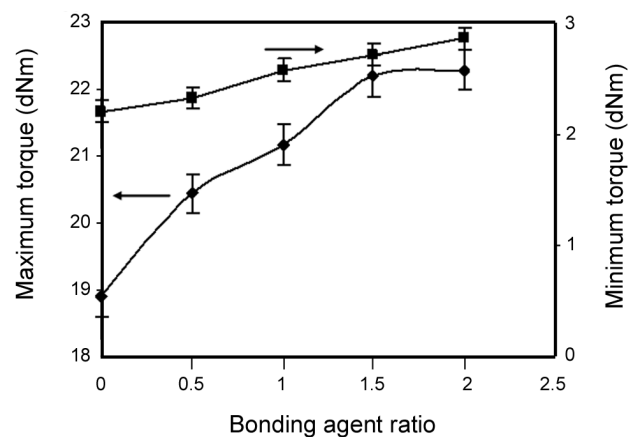


Figure 2. Variation of maximum and minimum torques with bonding agent ratio.

in the optimum cure rate of the composites in comparison with the compound 1 which could be ascribed to the presence of amine groups on the fibres surface which itself, has a role in the sulphur curing process of NR/SBR rubber [7,29].

When fibres and the dry bonding agents are added to the matrix simultaneously (compound 3), although the maximum torque value is increased but the scorch time and optimum cure time are decreased. The cure rate is also increased with respect to the compound containing either the fibre or dry bonding system (compounds 4 and 2). This observation suggests that the amine groups present in the bonding agent (hexamine) and also in nylon fibres (generated from the degradation of fibres at the curing temperature of rubber [7]) establish an alkaline pH medium which accelerates the curing reaction of the sample. In fact, the concentration of amine groups in this compound is high enough to neutralize the retarding effect of

Table 2. Cure characteristics of composites.

Sample	Maximum torque (dNm)	Minimum torque (dNm)	Cure time (t_{90}) (min)	Scorch time (t_5) (min)	Cure rate (dNm)/(min)
1	7.92	1.05	13.80	7.25	1.06
2	8.80	1.51	10.61	3.91	1.08
3	21.17	2.57	8.32	3.25	3.26
4	18.90	2.20	12.58	5.12	2.51
5	20.44	2.32	10.39	4.20	3.04
6	22.29	2.86	7.31	2.20	3.80

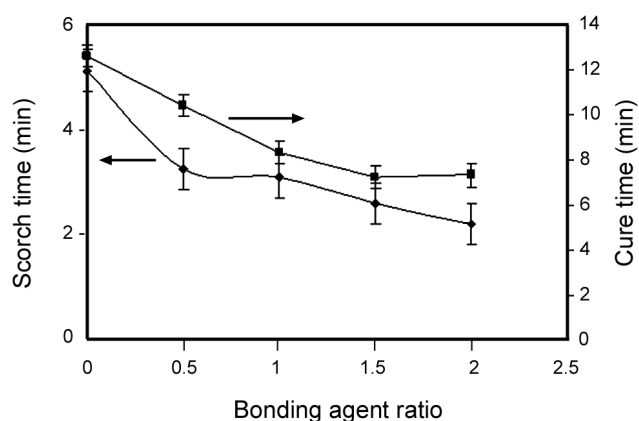


Figure 3. Variation of cure time and scorch time of composites with bonding agent ratio.

silica.

In contrast, the interaction between the fibre and the matrix in the presence of a bonding system is established during the curing reaction when resorcinol-formaldehyde resin is formed. This material migrates to the rubber-fibre interface and results in an efficient and stable bonding between the two components. The concentration of the HRH bonding system was optimized by determining the mechanical properties of compositions with different proportions of resorcinol, hexamine and silica (i.e., 2.5/1.6/5, 1.3/0.8/2.5, 5/3.2/10 parts by weight) at a 30 phr fibre concentration (Table 1). The results of mechanical properties are summarized in Table 3. It can be easily observed from Figure 4 that the presence of fibre resulted in a marked anisotropy in

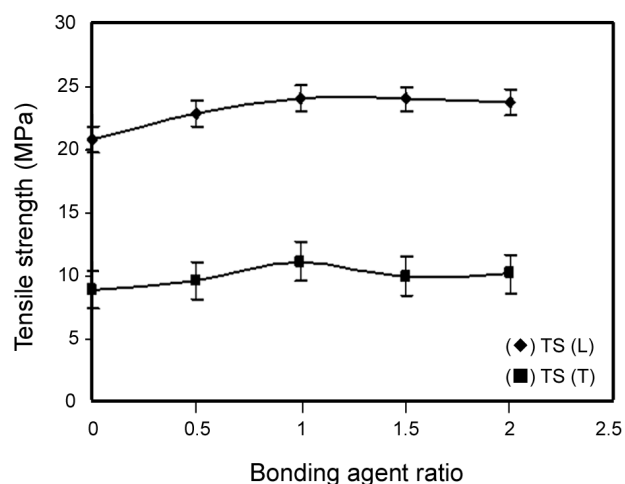


Figure 4. Variation of tensile strength of composites with bonding agent ratio.

tensile properties of the composites. In transverse direction, the mechanical properties of the compounds improved very slightly. In addition, it is observed that the nylon fibre in the absence of a suitable bonding agent (compound 4) cannot reinforce the matrix in comparison with the compound containing bonding agent (compound 3). It is noticed that the increase of tensile strength in the longitudinal direction is much higher than that of the transversal direction which shows the anisotropic behaviour of these composites. It is also clear that with twice as much bonding agent (compound 6) present, the tensile strength of compound 6 shows a little change compared to compound 5; and still the abrasion and resilience properties are not improved.

Table 3. Mechanical properties of composites.

Sample	Tensile strength (MPa)	Elongation-at-break (%)	Hardness (Shore A)	Resilience (%)	Abrasion (%)
1	5.01	456.8	47	71	25.6
2	5.97	462.1	48	70	25.0
3	L 24.0	24.9	87	55	18.0
	T 11.1	40.4			
4	L 20.7	30.6	86	59	27.0
	T 8.8	78.1			
5	L 22.8	23.3	87	61	22.7
	T 9.6	45.9			
6	L 24.7	26.5	88	57	23.9
	T 10.1	64.5			

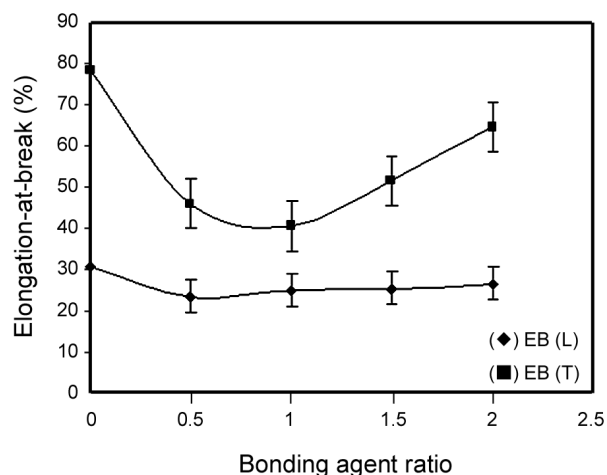


Figure 5. Variation of elongation-at-break of composites with bonding agent ratio.

Thus, it can be concluded that an optimum concentration of a bonding system should be considered with the ratio of 2.5 resorcinol, 1.6 hexamine, 5 silica parts by weight.

Figure 5 shows the dependence of elongation-at-break versus the bonding agent concentration in the composites under study. It is clear that the addition of fibres leads to a sharp decrease in the elongation-at-break in both directions. On the other hand, the longitudinal elongation is lower than the transverse one for all concentrations of bonding agent, which indicates that the fibres are well oriented in the rubber matrix in the mill direction. Table 3 shows that the elongation-at-break of the compound prepared with bonding agent is lower than the compounds prepared without any bonding agent under similar fibre loading. This is due to the higher interfacial strength and stiffness achieved as the result of strong bonding forces established between the fibres and the rubber matrix. An increasing trend in the hardness values of composite samples was also observed. It can be seen that the hardness of composites containing nylon fibres and also bonding agent is higher than that of compounds prepared without bonding agent under similar fibre loading. Therefore, the adhesion between the rubber and the fibre plays a very important role in obtaining good fibre reinforcement in the rubber composites. A continuous decrease in the resilience was observed with increasing the bonding agent concentration in all the composites (Table 3). In fact,

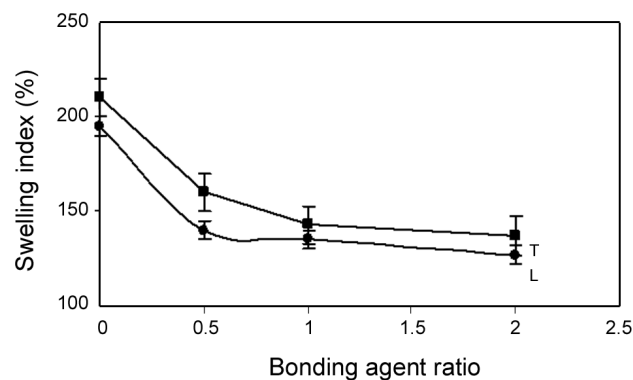


Figure 6. The dependence of both longitudinal (L) and transversal (T) swelling index of composites with different bonding agent ratios.

resilience is a measure of the elasticity of the composite which is affected by the degree of bonding interactions. For instance; when the concentration of the bonding agent is increased, the energy is more dissipated at the fibre/matrix interface, hence the resilience of composites is reduced.

The abrasion loss of the fibre filled compound was observed to be lower than that of the unfilled compound as given in Table 3. This might be due to the more restrained matrix of the composite so that fibres do not detach from the matrix easily.

The anisotropic solvent swelling behaviour of all the composites indicated that the restriction to swelling is higher for composite containing bonding agent. This indicates that the bonding agent improves the interfacial bond strength between the fibre and matrix. Solvent swelling studies also confirm the preferential orientation of the fibres in the milling direction because it is restricted in the longitudinal direction more than in the transverse direction. This could be concluded from the lower swelling index in the longitudinal direction as shown in Figure 6.

Scanning electron microscopy (SEM) results of composite samples 3 and 4, i.e. the samples with and without bonding agent respectively, are presented. Figure 7 shows the cryogenically fracture surface of the compound 4 in longitudinal direction (L). Long de-bonded fibre ends pulled out of the matrix show poor matrix/fibre bonding strength as well as several dark holes remaining in the matrix surface after failure. However when the bonding agent is introduced, the morphology of the fracture surface

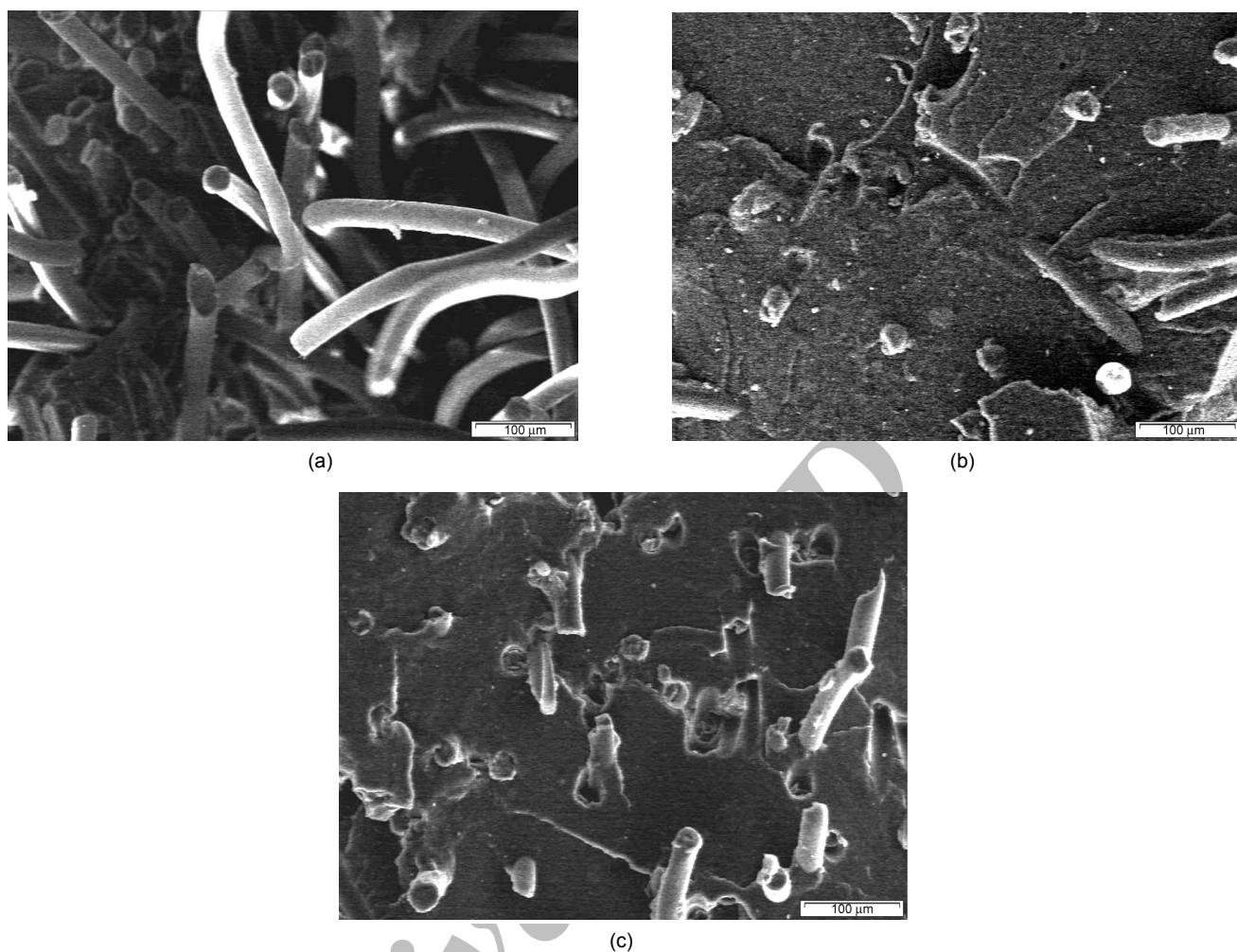


Figure 7. SEM Photomicrographs of the composites: 4 (a) in longitudinal direction without bonding agent, 3 (b) in longitudinal and 3 (c) in transversal direction with bonding agent (Magnification 200 \times).

(compound 3) is changed. The presence of short broken fibres on the surface due to the stronger adhesion between fibre and matrix can be seen from Figure 8b when stress is applied. These observations also confirm the orientation of fibres in the milling direction as well. Figure 7c illustrates the SEM photomicrograph of the tensile fracture surface for the sample 3 which has been cut in the transverse direction (T). Here, fibres mostly appear to lie parallel to the fracture surface, indicating the preferential orientation of the fibres in the opposite direction.

Figure 8 shows the elastic moduli (G') and complex viscosity (η^*) of composites prepared with different concentrations of bonding system as a function of angular frequency. The increase in the storage modulus and complex viscosity are found for

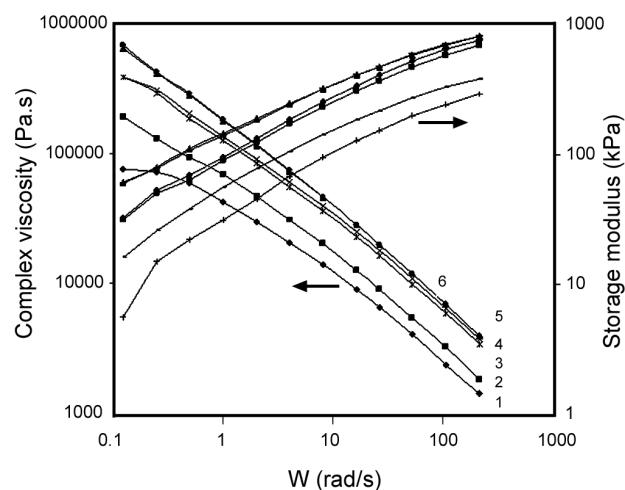


Figure 8. Complex viscosity and storage modulus as a function of frequency of composites with different bonding agent ratios.

all composites. The gum compound exhibited a viscosity that approaches the Newtonian behaviour towards the low frequencies; while the viscosity of all other composites clearly showed a shear thinning behaviour over the entire range of shear rates studied here. As it is predicted the rheological behaviour of both compounds 3 and 6 are quite similar.

CONCLUSION

The cure characteristics, mechanical and morphological properties of nylon fibre reinforced NR/SBR composites have been investigated. The introduction of fibre or dry bonding system into the compound reduced the optimum cure time and also the scorch time while the maximum torques and cure rate showed an increasing trend. The NR/SBR composites displayed anisotropy in mechanical properties due to the preferential orientation of nylon fibres in the milling direction (longitudinal). In the samples prepared with fibres and the bonding agent, mechanical properties were higher in the longitudinal direction compared to the transverse direction. The anisotropy in the properties of the composites as well as the strong bonding of the fibre to the matrix in the presence of the dry bonding system was confirmed by SEM studies. The increase in the storage modulus and complex viscosity were found to be larger in the composites prepared with short fibres containing bonding agent.

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