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Curing characteristics and mechanical properties of short oil palm fibre reinforced rubber composites

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Curing characteristics and mechanical properties of oil palm fibre reinforced rubber composites have been studied. Modification of fibre surface and use of various bonding systems increased the mechanical properties of oil palm fibre reinforced rubber composites. The presence of bonding agents in composites have prolonged the curing time. However, scorch and curing time were found to be independent of fibre loading and modification of fibre surface. SEM studies show that the bonding between the fibre and rubber matrix is improved when the fibre is treated and used with various bonding agents. © 1997 Elsevier Science Ltd.

(Keywords: curing characteristics; mechanical properties; short-oil palm fibre)

INTRODUCTION

Short fibre elastomer composites are a rapidly growing class of materials because of their improved physical and mechanical properties, easy processability and economic advantages. These materials bridge the gap between elastomers and fibres by combining the stiffness of short fibres with the elasticity of rubber. Short fibre reinforced elastomers have been successfully used in the production of hoses, V-belts, tyre treads, seals, and complex-shaped mechanical goods. The extent of reinforcement is found to depend on the fibre–matrix adhesion, aspect ratio of the fibre in the vulcanizate, fibre dispersion and orientation, nature of matrix, and type of fibres[1–5]. In addition, these fibres offer an excellent opportunity to utilize an abundant source of such materials available from nature[6]. Several cellulosic wastes such as ground wood waste, bark, nut shells, begasse, corncobs, bamboo, and cereal straw have been used as fillers for plastics[7]. One of the most important aspects of composite manufacture is to achieve adequate adhesion between fibres and matrix. The compatibility of hydrophobic polymer and hydrophilic cellulose fibre can be enhanced by the modification of polymer or fibre surfaces. Morrell[8] reported the use of coupling agents to promote the adhesion between the fibre surface and matrix.

The tricomponent system (HRH) consisting of hexamethylenetetramine, resorsinol, and fine-particle hydrated silica generally can be used for most rubber and fibre combinations. Derringer[9] examined the HRH system with various fibres in nitrile and natural rubber. Good bonding was obtained. O'Connors[3] compared the HRH system with RH (resorsinol and hexamethylenetetramine alone) and hexamethoxymethylmelamine (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, modification of the fibre surface was carried out to improve the adhesion between the fibre and matrix. Effects of different loadings and bonding systems on the curing characteristics and mechanical properties of the composites were examined. Ageing resistance and failure mechanism of the composites were also studied.

EXPERIMENTAL

Compounding ingredients and formulation

Tables 1 and *2* show the formulation used in this study. Natural rubber (SMR L) was obtained from Rubber Research Institute of Malaysia (RRIM). Palm oil fibre from the Palm Oil Research Institute of Malaysia (PORIM) chopped to a length of 10 mm was used as the untreated (U) reinforcing fibre. The average fibre filament diameter was 0.1 mm. The chemical composition of the fibres are shown in *Table 3*. Other chemicals such as sulfur, zinc oxide, stearic acid, n-cyclohexylbenthiazyl sulfenamide and silica were all purchased from Bayer (M) Ltd. The Flectol H (poly-1,2-dihydro-2,2,4-trimethylquinoline) was supplied by Monsanto Company, while sodium hydroxide (NaOH) pellet was supplied by Baker Analyzed. Bonding agents used in this study are phenol formaldehyde [Borden Chemical (M) Ltd], hexamethylenetetramine [Fluka Chemical (M) Ltd] and resorsinol formaldehyde [Lianco (M) Ltd].

Fibre treatment

Treated (T) fibre was prepared from the raw palm oil fibre by immersing it in 10% aqueous alkali (NaOH) in reflux equipment at 102°C for 1 h, washing with water was done several times followed by drying. The raw

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Table 1 Formulation of mixes with varying loadings of fibre[a]

	Mix						
	A[b]	B	C	D	E	F	G
Filler		(U)[c]	(T)[d]	(U)	(T)	(U)	(T)
Oil palm fibre	0	15	15	30	30	50	50

[a] Basic recipe: natural rubber (SMR L), 100; zinc oxide, 5; stearic acid, 2; CBS (*N*-cyclo-hexyl-2-benzothiazole sulfenamide, 0.5; sulfur, 2.5; Flectol H, 1.0

[b] Control compound

[c] Contains untreated fibre

[d] Contains treated fibre

Table 2 Formulation of mixes[a]

	Mix						
Bonding agents	B[b]	H (U)[c]	I (T)[d]	J (U)	K (T)	L (U)	M (T)
Phenol formaldehyde (PF)	0	10	10	0	0	0	0
Resorsinol formaldehyde (RF)	0	0	0	5	5	5	5
Silica (Sil)	0	0	0	2	2	2	2
Hexatetramine (Hexa)	0	0	0	0	0	5	5

[a] Basic recipe: natural rubber (SMR L), 100; zinc oxide, 5; stearic acid, 2; CBS (*N*-cyclo-hexyl-2-benzothiazole sulfenamide, 0.5; sulfur, 2.5; Flectol H, 1.0, oil palm fibre, 15

[b] Control compound (filled with untreated fibre but without bonding agents)

[c] Contain untreated fibre

[d] Contain treated fibre

Table 3 Chemical composition of palm oil fibre

Moisture content	10.4%
Holocellulose	68.3%
α-Cellulose	41.9%
Lignin	13.2%
Pentosan	20.3%
Hot water solubles	13.4%
Alkali solubles	29.9%
Alcohol benzene solubles	3.2%
Ash	3.6%

fibres were first chopped to 10 mm before immersing it in 10% aqueous alkali. The purpose of heating fibre in aqueous alkali is to reduce the lignin content on the fibre surface and to improve the adhesion between fibre and rubber matrix.

Sample preparation

Mixing was carried out on a laboratory size (160 × 320 nm) two roll mixing mill (Model XK-160) in accordance to the method described by the American Society for Testing and Materials (ASTM), designation D 3184-80. The respective cure times at 140°C as measured by t_{90} were then determined using a Monsanto Rheometer, model MDR 2000. The scorch times, torque, elastic modulus, etc., can also be determined from the rheometer rheograph.

Measurement of tensile, tear strength and hardness

The various rubber compounds were compression moulded at 140°C according to their respective t_{90}, into test specimen sheets. Dumb-bell and crescent test pieces according to ISO 37 and ISO 34, respectively, were then cut out. Tests were carried out using a Monsanto Tensometer, T10 according to BS 903: Part A2 and BS 903: Part A3, respectively, at 500 mm min^{-1} cross-head speed. The test for hardness was carried out by using the Shore type A Durometer according to ASTM 2240. All tests were conducted at room temperature (25°C). Ageing test was carried out at 70°C for 48 and 168 h in a cell type ageing oven.

Scanning electron microscopy

Examination of the fracture surface was carried out using a scanning electron microscope (SEM) model Leica Cambridge S-360. The objective was to form some idea of the mode of fracture. The fracture ends of the tensile and tear specimens were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrical charging during examination.

RESULTS AND DISCUSSION

Effect of fibre loading and modification of the fibre surface

Table 4 shows that scorch and curing time are found to be independent of fibre loading. It can be seen that curing time is not affected by modification of the fibre except compounds C and G which show the curing time decreases. However, the maximum and minimum torque values depend on fibre loading. There is a gradual increase in maximum and minimum torque values with increase in fibre loading. This is due to the increase in stiffness and hardness of composites[10]. Maximum and minimum torque values are also unaffected by aqueous alkali treatment.

Table 5 shows that tensile and tear strengths decrease abruptly at 15 phr fibre loading. When fibre loading is increased further, these properties decrease again slowly. An increase in hardness is observed with increased fibre loading. It can be seen that tensile strength, tear strength and hardness of composites filled with treated fibre are higher than untreated fibre at similar loading. To obtain good fibre reinforcement in rubber composites, the adhesion between the rubber and the fibre is very important. From these results, it is clear that the aqueous alkali treatment of palm oil fibre improves the fibre adhesion to rubber matrices. Since palm oil fibre has hydroxyl groups on its surface, it is expected the pretreatment with aqueous alkali will give a better adhesion between the fibre and the rubber matrix.

Czvikovszky *et al.*[11] reported that the surface of fibre can be modified by aqueous alkali treatment at elevated temperature, and this was found to improve its adhesion properties significantly. According to Zadorecki and

Table 4 Cure characteristics of oil palm natural rubber composites with varying loadings of fibre[a]

	Mix						
	A	B	C	D	E	F	G
Cure characteristics		(U)	(T)	(U)	(T)	(U)	(T)
Max. torq. (Nm)	7.1	10.0	9.8	12.2	14.1	16.1	16.7
Min. torq. (Nm)	0.6	0.4	0.3	0.3	0.4	0.6	0.5
Cure time, t_{90} (min)	19.6	17.5	14.6	16.1	15.8	16.1	14.9
Scorch time, t_2 (min)	18.6	6.1	4.6	5.2	5.4	4.7	4.6

[a] Monsanto rheometer at 140°C

Flodin[12], fibre treatment can be used to prevent the debonding at the fibre interface since it can form covalent bonds between the rubber matrix and fibre. Strong adhesion between treated fibre and rubber matrix due to treatment of fibre resulted in higher shear strength at the fibre/matrix interface. The applied stress is transferred from the matrix to the stronger fibre by shear stress at the fibre/matrix interface[13]. Stronger force must be used to overcome the shear strength interface which resulted in higher tensile strength.

The value of elongation at break (EB) shows a reduction with increasing fibre loading. Initially elongation at break decreases abruptly when 15 phr of fibre is used. However, further decrease in elongation at break with increasing fibre loading was only gradual. Increased fibre loading in the rubber matrix resulted in composites becoming stiffer and harder. This will reduce composites resilience and toughness and lead to lower resistance to break. Flink *et al.*[14] and Akhtar *et al.*[15] also reported similar observations.

Figure 1 shows that elongation at break for compounds with treated fibre is lower than compounds with untreated fibre at similar loading. This is due to better strength and stiffness achieved from strong adhesion between fibre and rubber matrix. Consequently, the toughness of the composites is reduced, resulting in lower elongation at break. Higher toughness is obtained from weak interfacial adhesion as shown by lower elongation at break for compounds filled with untreated fibre. Weak interfacial bonding resulted in an energy adsorption mechanism, i.e. bond breakage at the fibre/matrix interface and pull out fibre caused higher toughness in the composites (*Figure 2*). *Figures 2a* and *b* shows SEM for compounds B and D with 15 and 30 phr of untreated fibres. The fractured surface shows many holes remaining after the fibres are pulled out from the matrix when stress is applied, while *Figure 2c* shows the presence of short broken fibres on the surface for compound with 30 phr of treated fibre. When stress is applied the fibres broke due to the stronger adhesion between fibre and matrix.

Table 5 shows the modulus at 100 and 300% elongation increase with increasing loading of fibres in composites. For treated fibre the enhancement is found

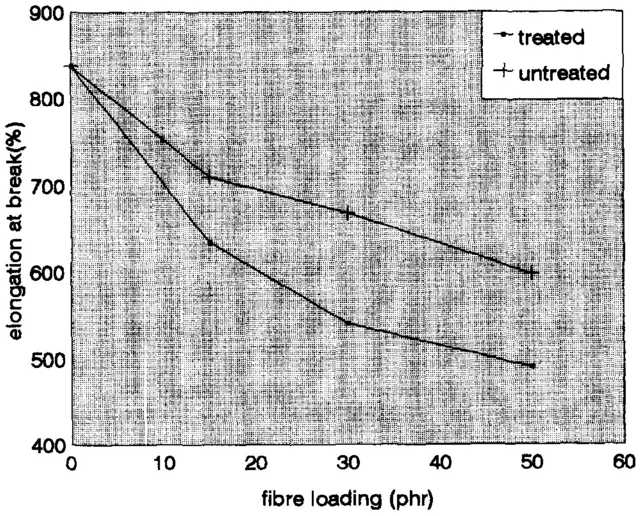

Figure 1 Relationship between elongation at break and fibre loading for treated and untreated fibre

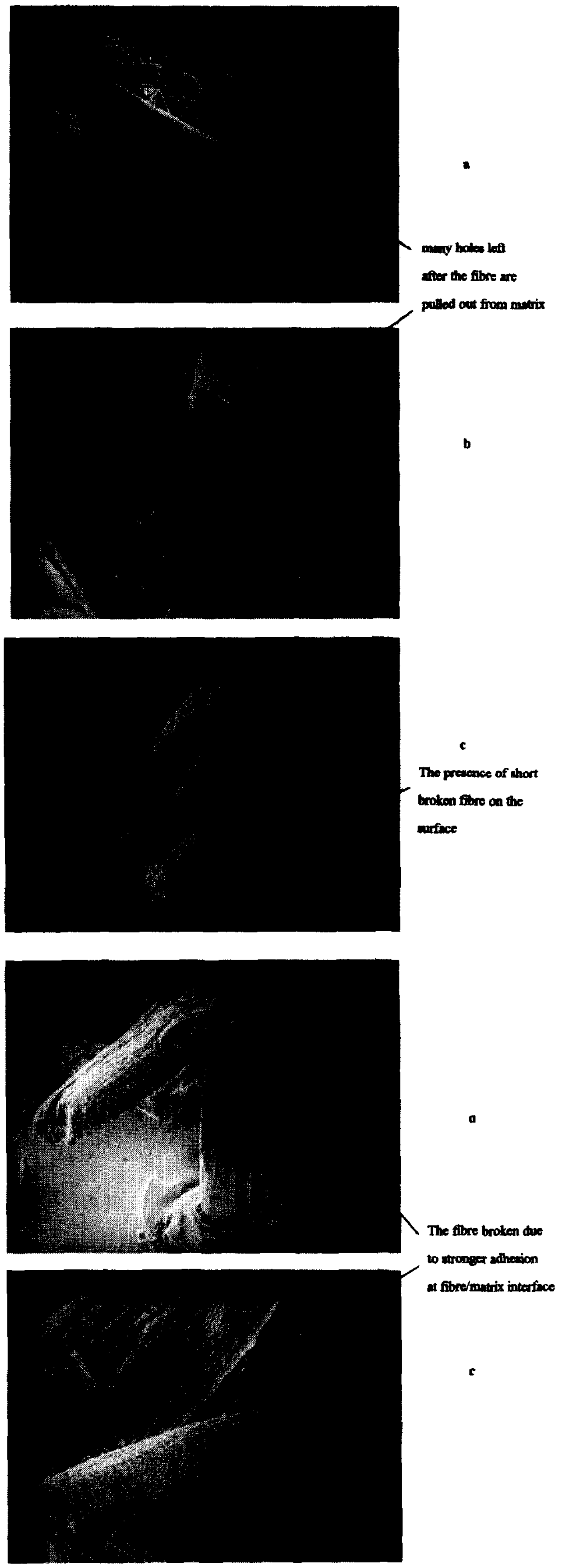

Figure 2 SEM micrographs for oil palm reinforced natural rubber composites: (a) control compound (B) with 15 phr (untreated fibre/mag. ×50); (b) compound D with 30 phr (untreated fibre/mag. ×40); (c) compound E with 30 phr (treated fibre/mag. ×170); (d) compound K with 15 phr [treated fibre/bonding agent (RF : Sil), 5 : 2/mag. ×171]; (e) compound M with 15 phr [treated/bonding agent (RF : Sil : Hexa), 5 : 2 : 5/mag. ×169]

Table 5 Properties of vulcanizate containing varying loadings of fibre

Test	Mix A	 B (U)	 C (T)	 D (U)	 E (T)	 F (U)	 G (T)
Tensile strength (MPa)	21.3	8.3	9.5	5.5	8.5	3.6	5.4
(1) after ageing (48 h)	27.4	9.3	9.5	5.9	8.6	4.5	6.0
(2) after ageing (168 h)	26.9	7.6	8.0	4.9	8.4	4.0	5.2
Elongation at break (%)	838	710	634	668	541	598	491
(1) after ageing (48 h)	824	622	573	557	523	516	478
(2) after ageing (168 h)	777	655	587	610	536	546	517
Modulus at 100% elongation (MPa)	0.7	1.2	1.5	1.4	2.0	1.6	1.8
(1) after ageing (48 h)	0.9	1.4	1.7	1.6	2.1	1.9	2.0
(2) after ageing (168 h)	0.8	1.3	1.5	1.3	2.0	1.6	1.7
Modulus at 300% elongation (MPa)	1.4	1.5	2.1	1.6	2.4	1.8	2.1
(1) after ageing (48 h)	2.0	2.1	2.3	1.8	2.6	2.2	2.5
(2) after ageing (168 h)	1.8	1.9	2.2	1.7	2.3	2.0	2.1
Tear strength (kN m^{-1})	51.0	32.8	39.6	33.5	36.7	26.2	31.6
(1) after ageing (48 h)	60.3	33.9	40.6	40.7	41.0	35.6	32.8
(2) after ageing (168 h)	55.6	30.1	38.2	39.5	39.3	27.2	30.1
Hardness (shore A)	43	55	60	64	68	74	76

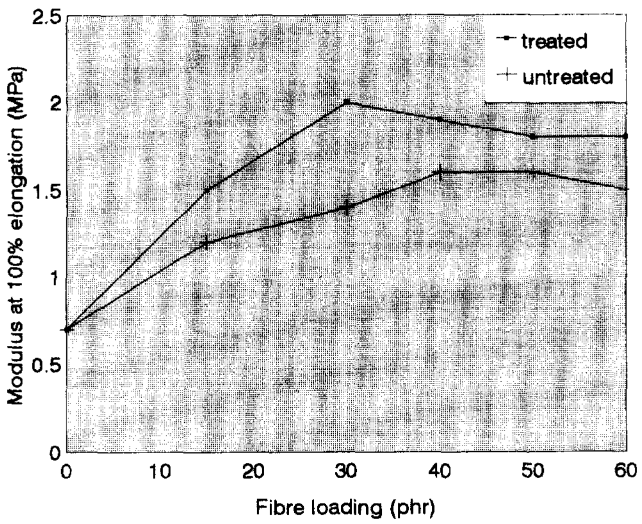

Figure 3 Comparison of the effect of fibre loading on modulus at 100% elongation for treated and untreated fibre

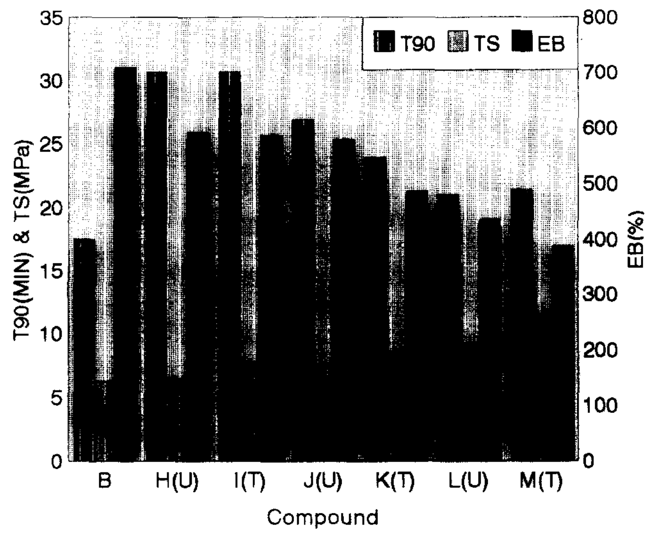

Figure 4 Effect of various bonding agents and fibre treatment on curing time (T_{90}), tensile strength (TS) and elongation at break (EB)

Table 6 Cure characteristics of oil palm natural rubber composites with different bonding systems^a

Cure characteristics	Mix B	 H (U)	 I (T)	 J (U)	 K (T)	 L (U)	 M (T)
Max. torq. (Nm)	10.0	10.4	12.8	12.2	13.4	13.6	14.8
Min. torq. (Nm)	0.4	0.6	0.7	0.6	0.7	0.8	0.9
Cure time, t_{90} (min)	17.5	30.6	30.7	26.9	23.9	21.0	21.4
Scorch time, t_2 (min)	6.1	5.0	4.4	10.1	9.3	5.5	5.3

^{a} Monsanto rheometer at 140°C

up to 30 phr and reduce slightly with further loading (see *Figure 3* for modulus at 100% elongation). Murty *et al.*[16] found that the modulus value increases when the fibre loading is increased for natural rubber–jute, SBR–jute, SBR–glass and natural rubber–glass composites. As for tensile strength, the tensile modulus of composites filled with treated fibre is higher than untreated fibre at similar loading.

Effect of different bonding system

Table 6 shows that the presence of bonding agents in vulcanizate prolong the curing time. *Figure 4* shows the comparison of various bonding agents and control compound on curing time, t_{90}. According to Chakraborty *et al.*[16], the longer curing time is due to better bonding between fibre and matrix when various bonding agents are used.

Generally, the curing time for compounds with treated fibre is not much different compared to compounds with untreated fibre except compounds K and J. The curing

Table 7 Properties of vulcanizate containing different bonding systems[a]

	Mix						
Test	B	H (U)	I (T)	J (U)	K (T)	L (U)	M (T)
Tensile strength (MPa)	6.3	6.5	7.8	6.6	8.6	9.2	11.5
(1) after ageing (48 h)	7.0	7.1	7.8	7.1	9.0	9.7	12.1
(2) after ageing (168 h)	5.6	5.9	6.4	5.2	8.1	9.0	9.6
Elongation at break (%)	710	593	585	579	487	436	388
(1) after ageing (48 h)	655	540	552	588	542	401	405
(2) after ageing (168 h)	622	523	535	512	502	356	334
Modulus at 100% elongation (MPa)	1.2	1.3	1.5	1.5	1.7	2.2	3.1
(1) after ageing (48 h)	1.3	1.4	1.8	1.8	2.2	2.2	3.5
(2) after ageing (168 h)	1.1	1.3	1.9	1.6	2.0	2.1	3.1
Modulus at 300% elongation (MPa)	1.4	2.3	2.6	2.4	2.8	4.0	4.2
(1) after ageing (48 h)	1.6	2.4	2.8	3.0	3.1	4.1	4.6
(2) after ageing (168 h)	1.2	2.5	2.4	2.6	2.8	3.9	4.0
Tear strength (kN m^{-1})	32.8	33.9	37.6	38.3	42.7	43.9	45.9
(1) after ageing (48 h)	33.9	35.8	40.6	43.7	46.9	45.7	49.0
(2) after ageing (168 h)	30.1	32.1	39.0	40.1	39.8	37.9	46.3
Hardness (shore A)	55	57	65	60	63	62	65

[a] Ageing test is carried out at 70°C in a cell type ageing oven

time for compound K is 23.9 min while for compound J it is 26.9 min. Adding bonding agent also resulted in a small reduction of scorch time except compounds K and J which showed an increase in their scorch times. As in curing time, the scorch time for compounds filled with treated fibre show little difference compared with untreated fibre except compounds K and J.

Maximum torque and minimum torque values also increase with the presence of various bonding agents in the composites (see *Table 6*). This is due to strong bonding at the fibre/matrix interface and, consequently, the composite becomes stronger, harder and stiffer. It can be seen that compounds with treated fibre show higher torque value compared to untreated fibre due to better adhesion achieved between fibre and rubber matrix. Other researchers[16,17] also obtained similar results.

Table 7 shows that vulcanizates with various type of bonding agent have higher mechanical properties compared to the control compound. It can be seen that tensile strength increases when different types of bonding agent are used in the composites. *Figures 2d* and *e* show the SEM fracture surface of compounds K and M (both contain treated fibre and bonding agent). It is clear from SEM for compounds K and M that stronger adhesion occurred at the fibre/matrix interface where the fibre is strongly bonded to the rubber matrix. The surfaces of both compound show that failure occurred at the fibre due to strong adhesion between fibre and matrix. However, the surface of the control compound (*Figure 2a*) shows many holes left after the fibres are pulled out from the matrix when stress is applied. The failure occurred at the weak fibre/matrix interface.

Enhancement in tensile strength (TS) for vulcanizates with treated fibre are higher than vulcanizates with untreated fibre (see *Figure 4*). Treated fibres provide a better surface for strong adhesion between fibre and matrix. The presence of bonding agents lead to stronger adhesion at the fibre/matrix interface. The stress transfer became more efficient and consequently enhanced the tensile strength. According to Miwa *et al.*[13] the strong adhesion between fibre and matrix resulted in higher shear strength at the interface and stronger force must be used to overcome the shear strength at the interface which resulted in higher tensile strength.

Figure 4 also shows that elongation at break (EB) for vulcanizates with bonding agent have a lower value than the control compound. Again for vulcanizate with bonding agent, the treated fibres show lower elongation at break than the untreated fibres.

Table 7 shows that other mechanical properties, i.e. tear strength, modulus at 100% elongation and modulus at 300% elongation follow a similar trend to tensile strength. The presence of bonding agents is also observed to enhance the composites hardness.

It is clear from *Table 7* that different bonding agents give different cure characteristics and mechanical properties. This is due to the different compatibility between various bonding agents, fibre and matrix. The final vulcanizate properties depend on the bonding system, fibre and matrix used. From *Table 7*, it can be concluded that the RF : Sil : Hexa (5 : 2 : 5) bonding system gives the strongest bonding between fibre and matrix. Consequently, better mechanical properties are obtained compared to other bonding systems. The effectiveness of bonding systems used follows the order:

RF : Sil : Hexa (5 : 2 : 5) > RF : Sil (5 : 2) > PF (10 phr)

Ageing resistance

Ageing resistance of all mixes were carried out at 70°C for 48 and 168 h. Results are shown in *Tables 5* and *7*. It can be seen that retention of composites strength (tensile strength, tensile modulus, tear strength and hardness) after ageing was found to be independent of fibre loading but dependent on adhesion between matrix and fibre. Chakraborty *et al.*[10] reported a similar result. After 48 h ageing, the composites strength increased compared to before ageing. This is due to the fibres not deteriorating with ageing, and carrying a maximum load when bonded properly to the matrix[18]. However, after 168 h ageing, the composites strength starts to deteriorate, due to weaker adhesion at the matrix/fibre interface, and becomes dependent on the matrix.

CONCLUSIONS

Mechanical properties of oil palm fibre reinforced natural rubber composites are enhanced with modification on fibre surface and use of various bonding agents. The presence of bonding agents in composites prolonged the curing time. However, the scorch and curing time are found to be independent of fibre loading. Maximum and minimum torque values increase with the presence of various bonding agents and increasing fibre loading. The treated fibres show higher torque values compared to untreated fibres. SEM studies show that for control compound (untreated fibre and without bonding agent) the failure occurred at the weak fibre/matrix interface, while for compounds containing treated fibre and bonding agent failure occurred at the fibre due to strong adhesion at the fibre/matrix interface.

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