

## ***Effect of Low Temperature Curing on Short Isora Fibre Reinforced Natural Rubber Composites***

LOVELY MATHEW<sup>\*,\*\*</sup>, SHINY PALATTY<sup>\*\*\*</sup> AND RANI JOSEPH<sup>\*\*,#</sup>

*'Isora' a natural fibre obtained from Helicteres isora plant is used for reinforcement of rubber composites. The fibre is separated from the bark of the plant by a retting process. Composites were prepared using chopped untreated and alkali treated isora fibre of lengths 10 mm at different fibre loadings in natural rubber (NR) using both low temperature curing accelerators (ZDC/xanthates) and conventional accelerators (CBS/TMTD). The bonding between the fibre and rubber was improved by the use of RF resin. Cure characteristics of the composites heated to various temperatures were studied. The mechanical properties of the composites prepared using a conventional system were compared with those of the composite prepared using xanthates, at different temperatures from 80°C–140°C. Composites with the conventional accelerator system were vulcanised at 150°C. The results showed that the xanthates were effective in low temperature curing of NR and the composite vulcanised at 100°C showed optimum properties. At high temperature, fibre and rubber showed a tendency to degrade and hence a decrease in properties. Alkali treated fibre composites showed enhancement of mechanical properties in both systems. Properties are improved by the use of bonding agent. The tensile fractured surface has been investigated by SEM studies and the failure mechanism has been explained. The swelling behaviour of these composites were also studied in toluene and it was found that low temperature cured composites restrict swelling considerably.*

**Key words:** natural rubber; Isora; fibre; composites; reinforcement; bonding agent; low temperature; zinc; xanthate; ZDC; toluene; mechanical properties; fracture

Rubbers or elastomers constitute an important class of engineering materials without which modern technology would be unthinkable. They have such remarkable and desirable properties that they are used in a multitude of engineering applications such as bearings, springs, and seals in addition to bulk products like tyres, tubes, belts, hoses *etc.* Even though gum natural rubber (NR) vulcanisates show

high tensile strength they are not suitable for many commercial applications. Fillers are almost always generally incorporated for improved processability, reinforcement and cost reduction. The fundamental aspects of rubber-filler interaction have been studied in detail in a number of elastomers<sup>1–4</sup>. Reinforcement of rubbers with short fibres combines the rigidity of the fibre with the

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\*Department of Chemistry, Newman College, Thodupuzha, Kerala, 685585, India

\*\*Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, 682022, India

\*\*\*Department of Chemistry, Bharatha Matha College, Thrikkakkara, Kerala, 682022, India.

#Corresponding author (e-mail: rani@cusat.ac.in)

elasticity of rubber. They present the additional benefit that the fibre is incorporated in the compound as one of the ingredients during mixing and hence they are amenable to the standard rubber processing steps of extrusion, calendaring and various type of moulding. A considerable amount of research has been done in the field of short fibre reinforced elastomer composites. Various synthetic and natural fibres have been studied as reinforcement in rubbers<sup>6-14</sup>. The natural fibre under consideration here is isora, a bast fibre separated from the bark of the *Helicteres isora* plant by a retting process. Isora shrub grows in many parts of South India, especially in Kerala. It resembles jute in appearance but is better in strength, durability and luster<sup>15</sup>. Detailed investigation on the characterisation and properties of isora fibre have been studied and reported<sup>16</sup>. It imparts mechanical properties comparable to those of other natural fibres. Recently we have reported about the possibilities of using isora fibre as a potential reinforcement in NR and polyesters<sup>17-18</sup>. Use of biodegradable matrix and natural fibres as reinforcement has opened new potential applications for these composites as they are eco-friendly materials. Vulcanisation temperature is very important in determining the quality of a rubber product and optimum properties are usually obtained when the curing is done at the lowest possible temperature<sup>19</sup>. Linear rubbers like NR, NBR, *etc.* are degraded when the temperature is raised<sup>20</sup>. The high modulus developed by the incorporation of fillers decreases as cure temperature is raised<sup>21</sup>. Low temperature curing results in products of good quality and fine appearance. The additional advantage is that low temperature curing also reduces energy consumption. Moreover it will be extremely useful in the repair of defective products, since subjecting finished products to high temperatures during the process of repair will adversely affect the quality of the product. A new accelerator consisting of zinc xanthate-ZDC system for low temperature curing of NR with particulate fillers has been

prepared and reported<sup>22</sup>. Although xanthates are known to act as accelerators for low temperature vulcanisation, their use as a curing agent in natural fibre reinforced rubber composites has not been investigated. In this paper, we propose to report the use of the zinc xanthate-ZDC system for the curing of NR-isora composites at different temperatures. The properties of these composites containing untreated and treated fibres vulcanised at low temperature are compared with the composite cured at 150°C by a conventional accelerator system. The swelling behaviour of the composites cured at 100°C and 150°C at varying fibre loadings in toluene was also investigated.

## MATERIALS AND METHODS

Isora fibre is lignocellulosic in nature. The physical properties of isora and some other natural fibres are given in *Table 1*. The NR used in the study is ISNR grade 5 supplied by RRII, Kottayam, Kerala. All the chemicals used in compounding were of commercial grade.

### Fibre Preparation and Alkali Treatment

Fibre was separated from the bark of the *Helicteres isora* plant by a retting process and dried. It was then chopped to an average length of 10 mm and designated as untreated fibre. Untreated short fibres were immersed in a 5% aqueous NaOH solution for 3 h to 4 h, then washed with water and dried in an air oven at 70°C for 24 h.

### Composite Preparation

Xanthate was prepared in the laboratory as per the method reported earlier<sup>22</sup>. The formulations of the test mixes are given in *Table 2*. The mixing was done as per *ASTM D 3184-80* in a two-roll mixing mill (150 × 300 mm) with a nip gap of 1.3 mm. The

TABLE 1. PROPERTIES OF ISORA AND SOME OTHER NATURAL FIBRES

Fibre	Diameter ( $\mu\text{m}$ )	Micro-fibrillar angle (degrees)	Cellulose/Lignin content (%)	Tensile strength (MPa)	Density ( $\text{g}/\text{cm}^3$ )
Isora	10–20	2–25	75/23	500–600	1.35
Coir	100–460	30–49	43/45	130–170	1.15
Sisal	50–200	10–22	67/12	400–600	1.45
Oil palm	50–500	40–46	65/19	200–250	1.45
Jute	12–25	8–10	63/12	430–530	1.45
Banana	80–250	10–15	65/5	500–700	1.35

TABLE 2. COMPOUND FORMULATION (p.h.r.)<sup>a</sup>

Ingredients	Mixes with varying fibre loading								
	Gum	X <sub>10</sub>	X <sub>20</sub>	X <sub>30</sub>	X <sub>40</sub>	Y <sub>10</sub>	Y <sub>20</sub>	Y <sub>30</sub>	Y <sub>40</sub>
Fibre (Untreated)	0	10	20	30	40	–	–	–	–
Fibre (Treated)	0	–	–	–	–	10	20	30	40
Ingredients	Mixes with varying fibre loading and bonding agent								
	Gum	X <sub>10b</sub>	X <sub>20b</sub>	X <sub>30b</sub>	X <sub>40b</sub>	Y <sub>10b</sub>	Y <sub>20b</sub>	Y <sub>30b</sub>	Y <sub>40b</sub>
RF resin	0	2.5	5.0	7.5	10.0	2.5	5.0	7.5	10
Hexa	0	1.6	3.2	4.8	6.4	1.6	3.2	4.8	6.4
Silica	0	1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0
Fibre (Untreated)	0	10.0	20.0	30.0	40.0	–	–	–	–
Fibre (Treated)	0	–	–	–	–	10.0	20.0	30.0	40.0

<sup>a</sup>Basic recipe: NR–100; ZnO–5; Stearic acid–2; TDQ–1; CBS–0.6; TMTD–0.1; S–2.5.

For low temperature curing system represented by X (ZDC–1.0, Xantahate–0.75), for conventional curing system represented by X<sub>0</sub> (CBS–0.6; TMTD–0.1). Conventionally cured composites are represented by X<sub>0</sub>30b–30 p.h.r. untreated fibre with bonding agent cured by conventional systems. Y represents treated fibre.

ingredients were added in the order given in *Table 2*. The bonding agents used was RF: Hexa: silica in the ratio 5:1.6:1 per 10 p.h.r. of fibre. The samples were milled for sufficient time to disperse the ingredients and fibres uniformly in the matrix. Blanks cut from the uncured sheet were marked with the mill grain direction and the samples were vulcanised at different temperatures (80°C to 140°C) for the ZDC/xanthate system and at 150°C for CBS/

TMTD system in a hydraulic press for their respective cure times obtained from a Goettfert Elastograph.

### Characterisation of Treated Fibres and Testing of the Composites

The SEM photographs of the fibres and the fractured surfaces were taken using a

JEOL JSM 35 C model Scanning Electron Microscope. The fibre and the fracture surfaces were sputter coated with gold within 24 h of testing by using a fine coat JFC-1100. Dumb bell and crescent shaped tensile and tear specimens with longitudinal fibre orientations were punched from the vulcanised sheets. Stress-strain measurements were carried out at a crosshead speed of 500 mm/min on a Shimadzu Model AG1 universal testing machine. Tensile and tear strengths were measured according to *ASTM D 412-68* and *D 624-54*, respectively. Compression set of the specimens was carried out in accordance with *ASTM D 395-86 (Method B)*. Abrasion resistance of the samples was tested using *DIN 53516* and hardness was measured using the Shore A type durometer according to *ASTM 2240-81*.

### Sorption Experiments

Circular specimens of diameter 20 mm were punched out from the vulcanised sheets. Specimens of known weight were immersed in the solvents (toluene and hexane) in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper. The weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. Thickness and diameter of the specimen after equilibrium swelling were also measured.

### Swelling Data Analysis

The swelling parameters like mol% uptake of solvent, and change in the volume fraction of rubber due to swelling were calculated.

### Calculation of $Q_t$ (Mol% Uptake of the Solvent)

The mol% uptake of the solvent  $Q_t$  for the composite samples was determined using the equation:

$$Q_t = \frac{(W_2 - W_1/M_s)}{W_1} \times 100 \quad \dots 1$$

where  $W_1$  and  $W_2$  are the weights of the specimen before and after swelling, and  $M_s$  is the molar mass of the solvent.

### Calculation of $V_\tau$ (Ratio of the Change in the Volume Fraction of Rubber due to Swelling)

To determine the volume fraction of rubber in the unswollen vulcanisates, the test specimens were weighed both in air and in water. Using the base formulation, the amount of rubber present in the weighed samples and its volume were calculated. From these data the volume fraction of rubber present in the unswollen sample  $V_i$  was calculated. The volume fraction of rubber in the swollen sample  $V_f$  was calculated by the expression:

$$\frac{[(D-FT)/(d_r)]}{+ [AO/d_s]} \div \frac{[(D-FT)/(d_r)]}{+ [AO/d_s]} \quad \dots 2$$

where  $d_r$  and  $d_s$  are the densities of the rubber and solvent,  $D$  is the deswollen weight of the test specimen (dry weight),  $F$  is the weight fraction of the insoluble components,  $T$  is the weight of the specimen and  $AO$  is the weight of the absorbed solvent corrected for swelling increment, respectively.

The ratio of the change in the volume fraction of the rubber due to swelling was calculated as:

$$V_\tau = (V_i - V_f)/V_i \quad \dots 3$$

where  $V_i$  is the volume fraction of rubber in the unswollen sample and  $V_f$  is the volume fraction of rubber in the swollen sample.

## Optical and SEM Studies

The physical nature of the composite samples before and after sorption studies was analysed using an optical microscope.

## RESULTS AND DISCUSSION

### Cure Characteristics

*Table 3* shows the variation of cure characteristics of composites cured at various temperature from 80°C to 140°C for a particular fibre loading (30 p.h.r.). The maximum torque is a measure of crosslink density and stiffness in the rubber. In general for all the mixes the torque initially decreases, then increases and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix while the increase in torque is due to the crosslinking of the rubber. The leveling off is an indication of the completion of curing. It is found that the addition of fibres into the mix generally increases the torque values. It also shows that for a particular fibre loading, the torque increases with increase in temperature and reaches a maximum at 100°C. At higher temperatures the fibre shows a tendency to degrade and hence a decrease in the torque values. These torque values are also increased by alkali treatment as the treated fibre may provide a better surface for reinforcement. Results show that cure time decreases as temperature of curing is increased from 80°C to 140°C. *Figures 1a* and *1b* show the variation of cure time and maximum torque with fibre loading for the composites cured at 100°C. At a particular temperature when the cure time of gum compound is compared with the fibre filled compound, it was found that the curing becomes slower when fibres are added.

Due to the presence of this acidic groups on the fibre, the curing may be retarded. It was confirmed by gradually increasing the fibre loading from 0 p.h.r. to 40 p.h.r. The presence of fibres retards the formation of crosslinks between the polymer chains.

Maximum torque value also increases with the increase in fibre loading as the composites become stiffer and harder at higher loadings. The presence of bonding agent in the composite increases the maximum torque still further. This is due to the strong bonding at the fibre/rubber interface and consequently the composites become stronger, harder and stiffer. It is observed that the curing time is not much affected by the modification of fibre surface. The optimum cure time is found to increase with the addition of bonding agent. According to Chakraborty<sup>23</sup> the longer curing time is due the better bonding between the fibre and the matrix when bonding agent is used. The variation of cure characteristics of the composites as a function of soaking time of isora fibres in 5% NaOH solution is shown in *Table 4*. It is found that the composite containing four-hour soaked fibres has a maximum cure time and torque value due to the better reinforcement of the treated fibre. Increase of soaking time decreases the vulcanisation parameters as the fibre becomes partially degraded on prolonged treatment.

### Effect of Fibre Modification

*Figures 8a* and *8b* show SEM photographs of untreated and alkali treated isora fibre surfaces. The multi-cellular nature of the untreated fibres is shown in *Figure 8a*. The porosity of the fibres and their fibrillar structure is revealed from the fibre topography. The porous surface morphology provides better mechanical interlocking of the matrix in composite fabrication. Fibre shows an uneven surface due to protrusions constituted of hemi-cellulose and pectin. The surface contains a

TABLE 3. EFFECT OF TEMPERATURE ON CURE CHARACTERISTICS

Temperature (Degrees)	Composite X <sub>20</sub> (Untreated fibre without bonding agent)			
	t <sub>10</sub> (min)	t <sub>90</sub> (min)	Min. torque (dNm)	Max. torque (dNm)
80	22.160	51.60	0.114	3.033
100	4.980	19.40	0.078	4.032
120	1.470	7.36	0.023	3.640
140	0.487	1.57	0.020	3.360
Composite Y <sub>20</sub> (Alkali-treated fibre without bonding agent)				
80	26.3	54.46	0.111	3.170
100	5.67	21.8	0.010	4.252
120	1.60	7.26	0.039	4.108
140	0.51	1.64	0.045	3.808
Composite Y <sub>20b</sub> (Alkali-treated fibre without bonding agent)				
80	27.49	59.20	0.163	3.396
100	6.07	25.80	0.035	4.682
120	1.98	8.87	0.045	4.385
140	0.57	2.61	0.084	4.007

TABLE 4. EFFECT OF SOAKING TIME ON CURE CHARACTERISTICS AND MECHANICAL PROPERTIES OF THE COMPOSITES (X<sub>30</sub> AND Y<sub>30</sub>) CURED AT 100°C

Time of soaking (Hour)	(0 h)	(4 h)	(24 h)	(48 h)	(72 h)
Cure time (min)	23.4	26.1	25.9	24.9	22.2
Max. torque (dNm)	4.69	5.39	4.25	3.96	3.85
Modulus (300% elongation) (MPa)	5.8	6.7	6.1	5.6	4.9
Elongation at break (%)	317	300	325	357	380
Tear strength (kN/m)	52.1	56.3	53.4	49.1	42.3

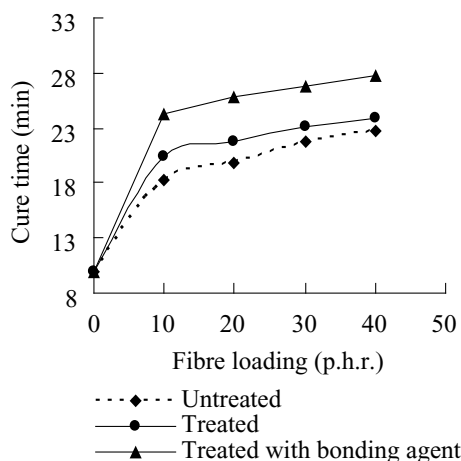


Figure 1a. Effect of fibre loading on cure time of the composites cured at 100°C.

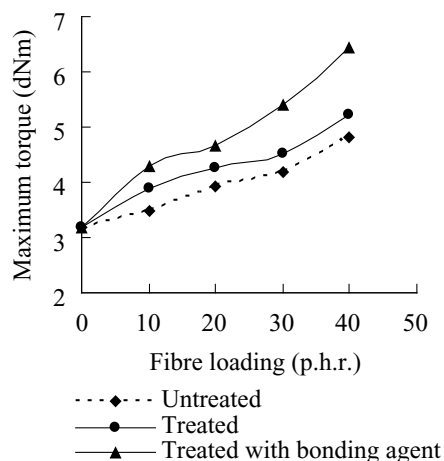


Figure 1b. Effect of fibre loading on maximum torque of the composites cured at 100°C.

waxy cuticle layer which also prevents a better interlocking with the rubber. SEM gives strong evidence for the physical and micro-structural changes occurring on the fibre surface during alkali treatment. On alkali treatment, due to the dissolution of impurities and waxy materials from the surface the pores become more significant and fibres become thinner than the untreated fibre (See Figure 8b). This renders roughness to the fibre thereby enhancing the mechanical interlocking at the interface.

### Mechanical Properties

Variation of mechanical properties and cure characteristics of the composites as a function of soaking time of isora fibre in 5% NaOH solution is shown in Table 4. It is seen that the tensile properties like tensile moduli, tensile strength *etc.* increased with soaking time and reached a maximum for composites containing fibres with soaking time of 4 h followed by a decrease. This is associated with the better interaction between the treated fibre and rubber. However, prolonged treatment up to 72

h decrease the properties marginally. This may be due to the excessive removal of binding material such as lignin, hemicellulose *etc.* Tear strength also shows a similar trend. Figures 2a to 7a show the properties of the composites vulcanised at various temperatures using ZDC/Xanthate systems. Many of the properties were found to reach a maximum for composites vulcanised at 100°C. Same trend is observed in the case of treated fibre composites and composites with bonding agent. Treated fibre composites show enhancement in properties as treated fibre provides better surface for reinforcement. Also composites with bonding agent show still better mechanical properties. The bonding resin form chemical crosslinks with rubber and the cellulosic hydroxyl groups of fibres creating a strong interface between fibre and rubber<sup>24</sup>. Figures 2b to 7b show a comparison of the mechanical properties of the composites cured at 100°C with that vulcanised using conventional systems. Composites with conventional accelerator system were vulcanised at 150°C and at high temperature, fibre shows a tendency to degrade and hence a decrease in properties as evidenced from

figures. *Figures 9 and 10* are the tensile fracture surfaces of composites (30 p.h.r.) cured at 100°C and 150°C, respectively. SEM studies provide additional information regarding fibre rubber interface. In both cases, for untreated fibre composites, due to the weak interfacial adhesion between the fibre and rubber, fibre pull out may take place leaving holes on the surface when stress is applied. *Figures 9b and 10b* show the presence of broken fibres on the fracture surface which is due to the strong adhesion between the fibre and rubber matrix for composites with treated fibres. SEM studies also revealed that for composites without bonding agent, failure occurred at the weak fibre/rubber interface while for composites containing treated fibre and bonding agent failure occurred at the fibre due to strong adhesion between fibres and matrix. Broken fibres can be seen on the fracture surfaces which also revealed the indication of high interfacial adhesion for the composites with treated fibres and bonding agent.

### Solvent Swelling Characteristics

*Effect of curing temperature.* *Figure 11* shows the variation of the mol% uptake in toluene with curing temperature of the composites. The uptake of solvent is lowest for the composite vulcanised at 100°C. The same trend is observed in the case of composites containing treated fibres and with bonding agent. A comparison of the mol% uptake of the solvent for the composites cured at 100°C and 150°C is given in *Figure 12*. It may be observed that the uptake of solvent is high for the composites cured at high temperature (150°C). This shows that the reinforcement is most effective when the composite is cured at 100°C and it is likely that at higher temperature (150°C) the fibre and rubber shows a tendency to degrade consistent with the results of mechanical properties discussed above.

*Effect of fibre loading and bonding agent.* *Figure 13* gives the variation of mol% uptake of the toluene with fibre loading for the composite cured at 100°C. From the results it is clear that as fibre loading increases, equilibrium solvent intake decreases. This is obviously due to the increased hindrance exerted by the fibres at higher loadings. For the composites containing bonding agent there is a sharp decrease in the uptake of solvents. It has already been established that for cellulose fibres and NR bonding agents like HRH system (Hexa-Resorcinol-Hydrated silica) can be used which involves a condensation reaction between resorcinol and Hexa to form methylol groups which in turn reacts with the unsaturation in the rubber chain resulting in a covalent linkage between resin and rubber. On the other hand the methylol groups of the resin interact with the hydroxyl groups of the cellulose by the way of a methylene ether bridge. Thus the bonding resin act as an intermediate in binding rubber and the fibre. Since there is a better bonding between fibre and rubber there is a strong interface developed which enhances the mechanical properties. A highly bonded system would exhibit high resistance to swelling compared to the unbonded systems.

The optical photographs of the unswollen and swollen samples cured at 100°C in toluene are shown in *Figure 15a*. From the figure it is clear that as fibre loading increases, the diameter of the swollen samples decreases. At the same fibre loading (30 p.h.r.) the diameter of the bonded composite is lower than that of the unbonded composite as evident from *Figure 15b*. From this it is evident that in highly bonded composites swelling occurs predominantly in the thickness direction. Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.



TABLE 5. EFFECT OF FIBRE LOADING ON MECHANICAL PROPERTIES OF COMPOSITES CURED AT 100°C

Properties	Gum	X <sub>10b</sub>	X <sub>20b</sub>	X <sub>30b</sub>	X <sub>40b</sub>	Y <sub>10b</sub>	Y <sub>20b</sub>	Y <sub>30b</sub>	Y <sub>40b</sub>
Modulus (300% elongation) (MPa)	2.3	3.5	4.8	5.9	6.2	4.2	5.2	6.6	6.8
Tensile strength (MPa)	27.8	20.0	14.2	15.2	10.5	21.6	14.4	15.9	12.5
Elongation at break (%)	1050	683	577	540	374	549	492	433	268
Tear strength (kN/m)	35.8	42.0	45.3	53.0	49.5	42.8	48.9	58.0	49.0
Compression set (%)	22.5	27.5	28.1	28.9	30.0	25.1	26.4	27.0	29.0
Hardness (Shore A)	45	60	72	77	83	72	76	80	84

TABLE 6. CHANGE IN THE VOLUME FRACTION OF RUBBER ( $V_T$ ) DUE TO SWELLING IN TOLUENE

Composites	$V_T$	
	100°C	150°C
Gum	0.94	1.09
X <sub>10</sub>	0.89	0.93
X <sub>20</sub>	0.83	0.87
X <sub>30</sub>	0.79	0.83
X <sub>40</sub>	0.76	0.80
X <sub>10b</sub>	0.80	0.89
X <sub>20b</sub>	0.73	0.85
X <sub>30b</sub>	0.65	0.73
X <sub>40b</sub>	0.55	0.70
Y <sub>30</sub>	0.69	0.76
Y <sub>30b</sub>	0.55	0.65

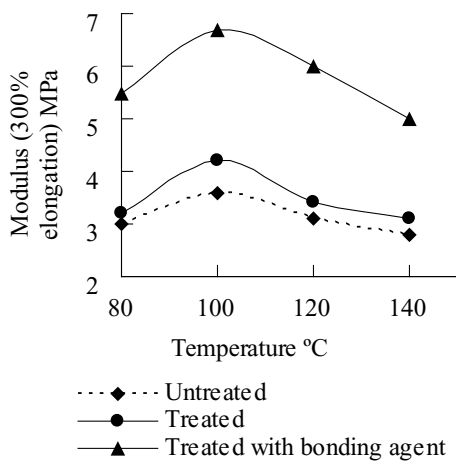


Figure 2a. Effect of temperature on the tensile modulus of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

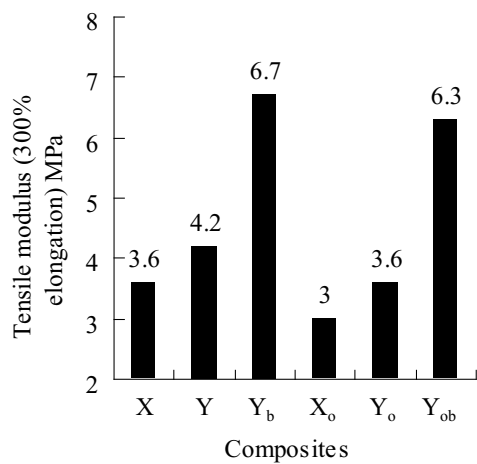


Figure 2b. Comparison of tensile modulus of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

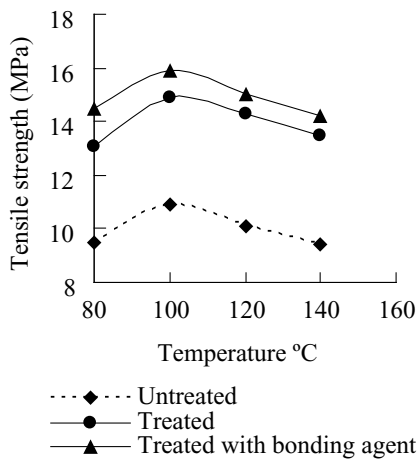


Figure 3a. Effect of temperature on the tensile strength of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

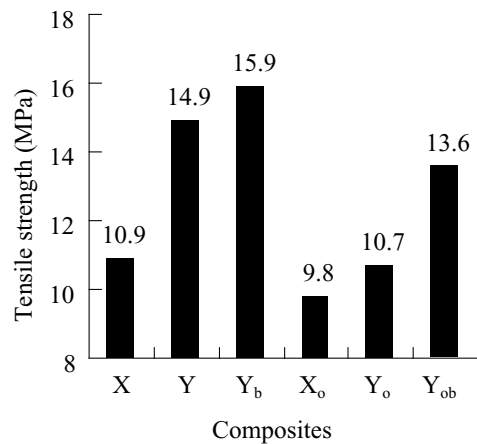


Figure 3b. Comparison of tensile strength of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

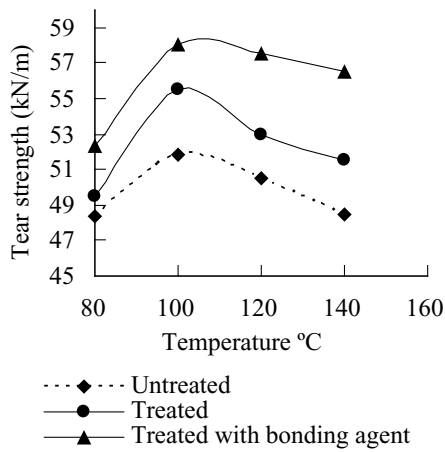


Figure 4a. Effect of temperature on the tear strength of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

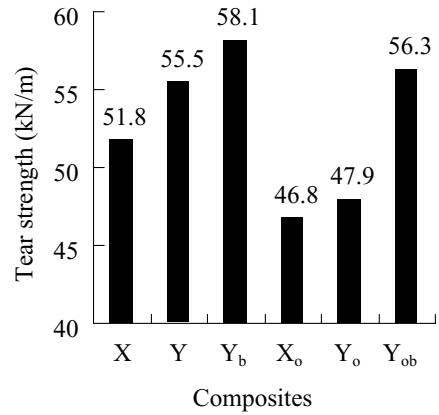


Figure 4b. Comparison of tensile modulus of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

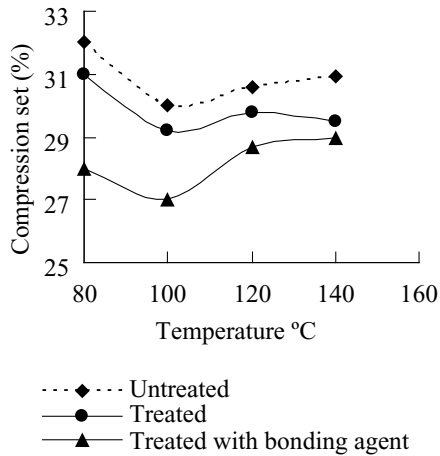


Figure 5a. Effect of temperature on the compression set of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

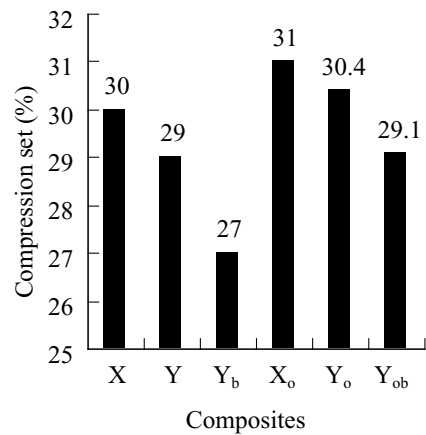


Figure 5b. Comparison of tensile modulus of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

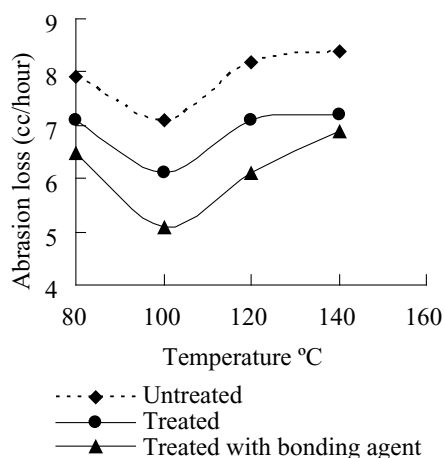


Figure 6a. Effect of temperature on the abrasion loss of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

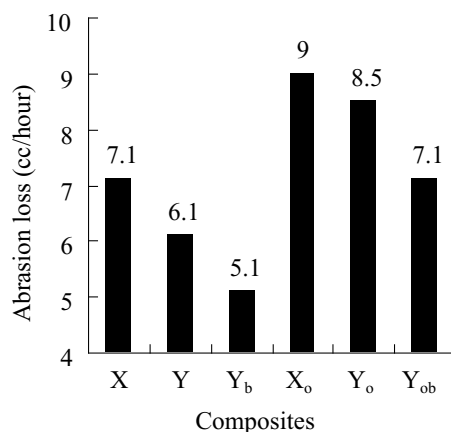


Figure 6b. Comparison of tensile modulus of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

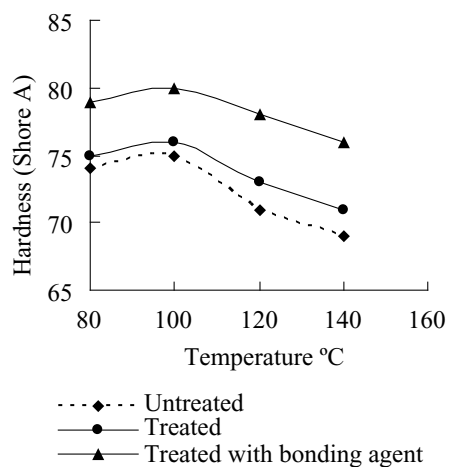


Figure 7a. Effect of temperature on the hardness of the composites ( $X_{30}$ ,  $Y_{30}$ ,  $Y_{30b}$ ).

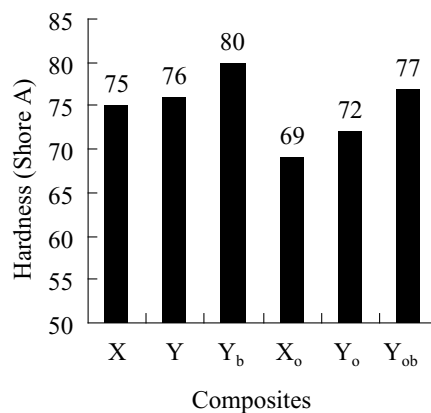


Figure 7b. Comparison of tensile modulus of the composites (30 p.h.r.) cured at 100°C and 150°C ( $X$ : low temperature cured system;  $X_o$ : conventionally cured system).

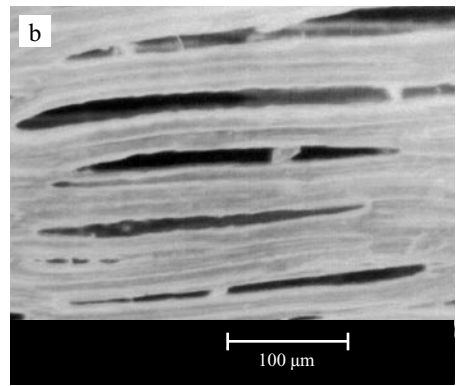
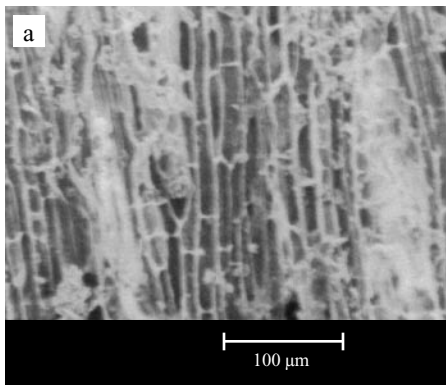


Figure 8. SEM photographs of (a) Untreated isora fibre; (b) Alkali treated isora fibre.

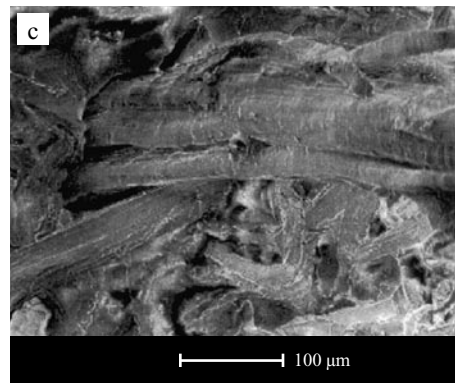
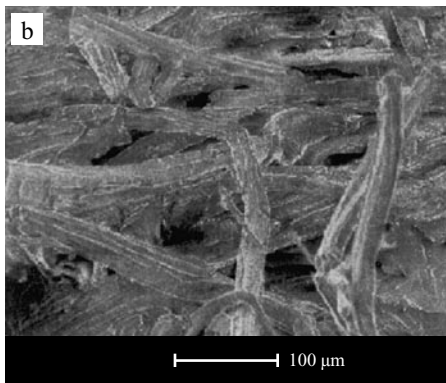
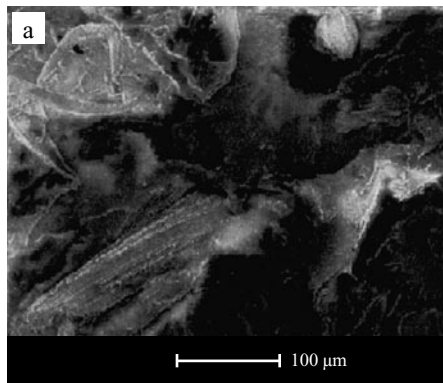


Figure 9. SEM photographs of the tensile fractured surfaces of the composites (30 p.h.r.) cured at 100°C: (a) Untreated; (b) Treated; (c) Treated with bonding agent.

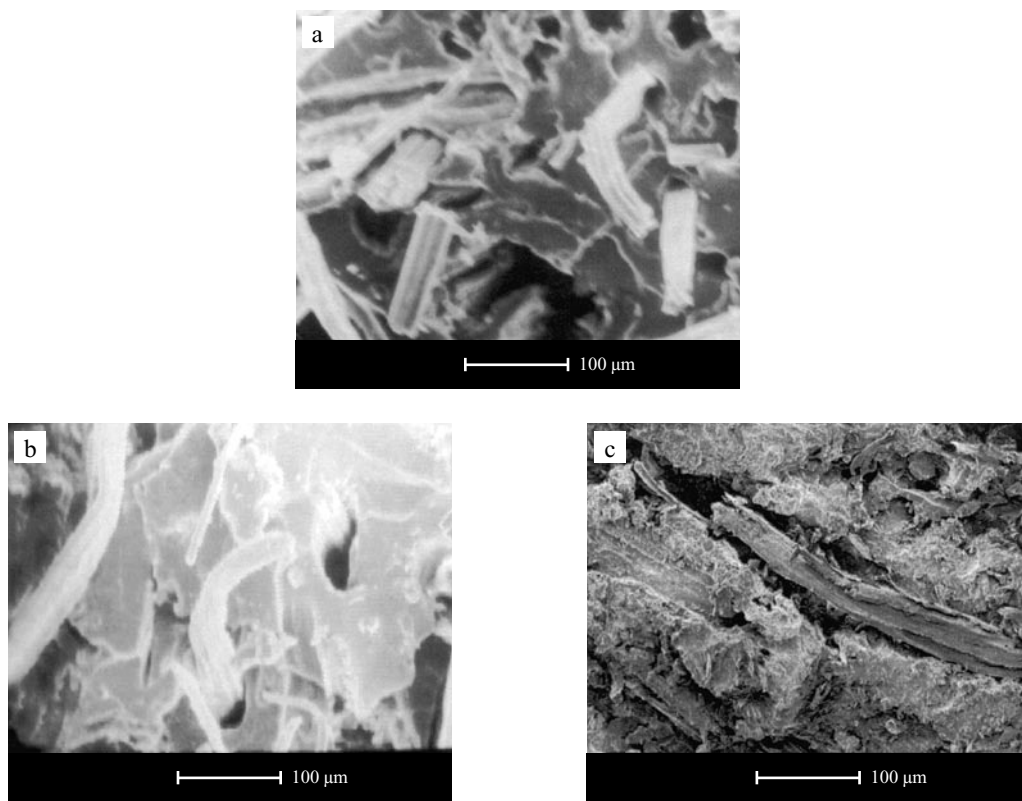


Figure 10. SEM photographs of the tensile fractured surfaces of the composites (30 p.h.r.) cured at 150°C: (a) Untreated; (b) Treated; (c) Treated with bonding agent.

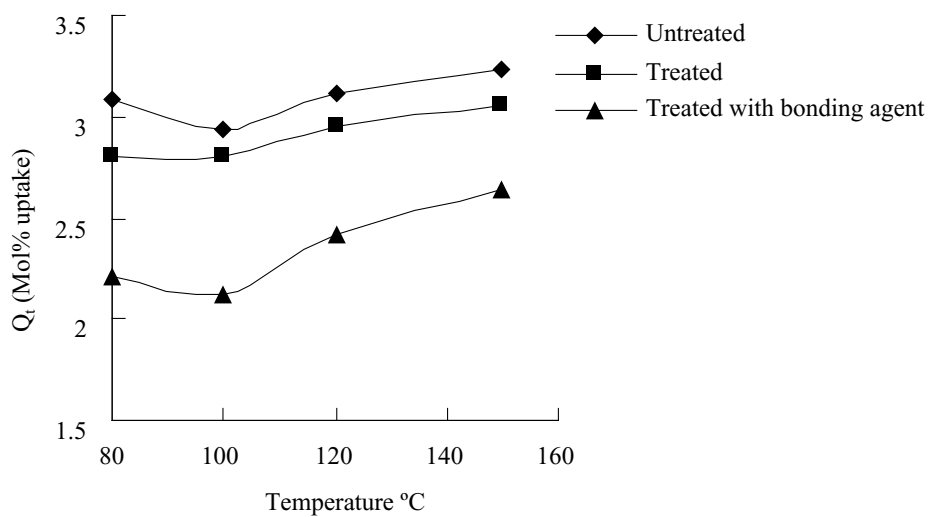


Figure 11. Variation of mol% uptake of solvent with curing temperature of the composites in toluene.

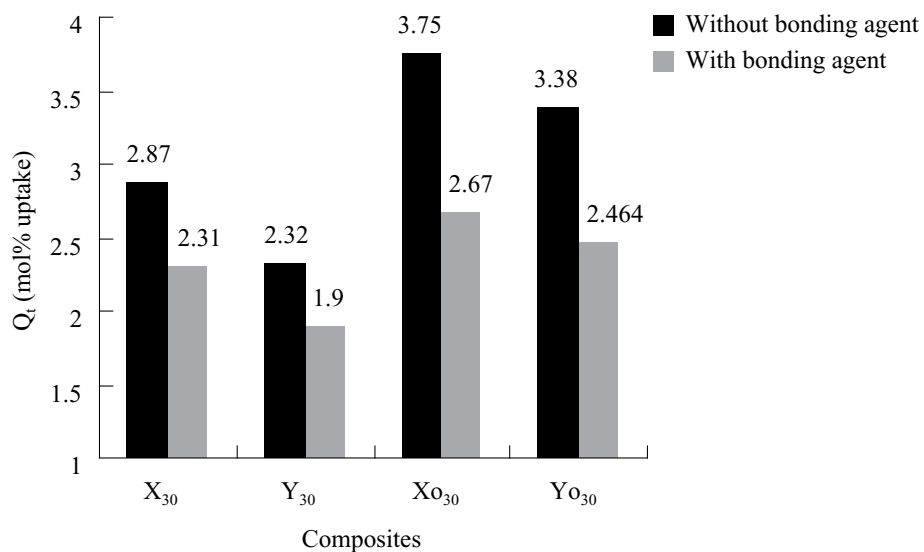


Figure 12. A comparison of the mol% uptake of the solvent for the composites (30 p.h.r.) cured at 100°C and 150°C (Mixes defined in Table 2).

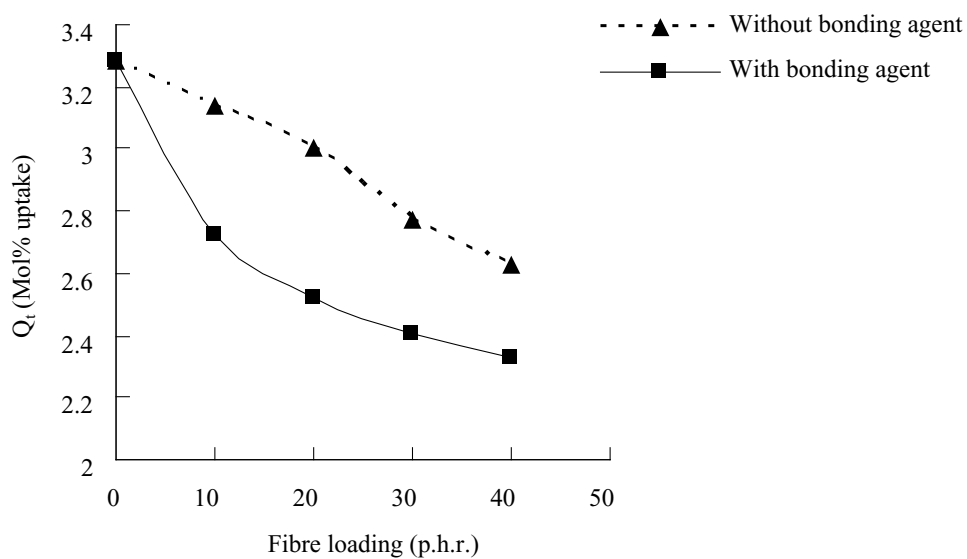


Figure 13. Effect of fibre loading on equilibrium sorption of NR/isora composites with and without bonding agent cured at 100°C in toluene.

*Correlation with adhesion.* Table 6 gives the change in volume fraction of the rubber due to swelling ( $V\tau$ ) for mixes containing different loading of fibres for both systems. It is evident that the composites containing bonding agent have substantially lower values ( $V\tau$ ) than those without bonding agent. It was reported that the adhesion between rubber and fibres can be evaluated by restricted equilibrium swelling measurements<sup>25</sup>. With the increase in extent of adhesion between rubber and fibre, the factor  $V\tau$  decreases. A high resistance to swelling indicates a highly bonded system. Composites cured at 100°C have a still lower  $V\tau$  values than those cured at 150°C. Figures 14a and 14b give the sorption curves obtained by plotting  $Q_t$  (the mol% uptake of the solvent) versus square root of time in toluene for a 30 p.h.r. loaded fibre composites cured at 100°C and 150°C, respectively. The uptake of the solvent is less in the case of composite cured at 100°C which shows the better reinforcement at lower temperature. At the same fibre loading, the amount of solvent sorbed by a composite at equilibrium is less for the composite containing bonding agent compared to that of composite without bonding agent. Another interesting observation is that the initial rates of diffusion is fast for the composite without bonding agent which is more pronounced in the case of composite cured at 150°C (See Figures 14a and 14b). This is because of the fact that in unbonded fibre rubber composites the solvent can penetrate into the polymer along the thickness direction and also through the weak interfaces parallel and perpendicular to the fibre orientation. The initial driving force for swelling is higher in unbonded composites as a result of large number of voids at the interfaces. But in the case of composites with bonding agent the interface is strong and the liquid can penetrate into the polymer only through the space between the fibre ends. As a result, the diffusion rate is slow in well-bonded composites. The same observations have also been reported in the case of sisal rubber composites<sup>26</sup>.

The effect of chemical treatment of fibres on equilibrium swelling of the composites can also be evident from the Figures 11 and 12. It is observed that in composites containing treated fibres, the solvent uptake is reduced further which is due to the enhanced interfacial bonding between the treated fibre and rubber. This prevents the transport of solvent to some extent through the interface. Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the equilibrium uptake of composites containing treated and untreated isora fibres it can be seen that the former composites are better than the latter in resisting the uptake of solvents for both systems as evident from Figure 12.

## CONCLUSIONS

Mechanical properties and solvent swelling characteristics of short isora fibre reinforced natural rubber composites was investigated with special reference to the curing system, curing temperature, effects of fibre loading, chemical treatment of fibres and bonding agent. The following conclusions can be drawn from this study.

Xanthates are effective in low temperature curing of natural rubber and composite vulcanised at 100°C showed optimum properties. At high temperature fibre shows a tendency to degrade and this results in a decrease in properties. Treated fibre composites with bonding agent showed enhancement in mechanical properties in both systems.

SEM showed strong evidence of the physical and micro-structural changes that occurred to the fibre surface on chemical modification. SEM photographs of the fractured ends of treated fibre composites indicated a strong fibre matrix adhesion. Restricted swelling studies could be used to evaluate the extent of interfacial adhesion between rubber and



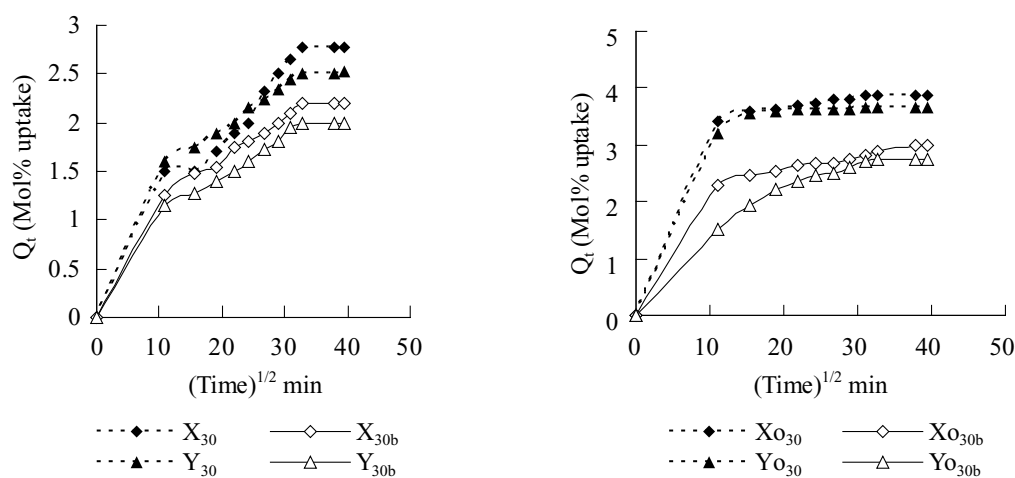


Figure 14. The equilibrium sorption curves of the mixes cured at (a) 100°C; (b) 150°C in toluene at 25°C (Mixes defined in Table 2).

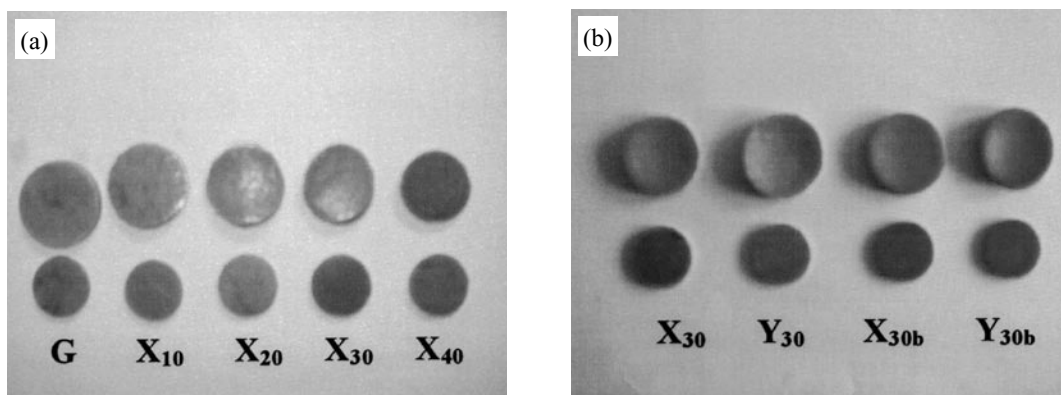


Figure 15. Optical photographs of the samples cured at 100°C before and after swelling in toluene: (a) With varying fibre loadings; (b) Samples containing untreated and treated fibres with and without bonding agent (Mixes defined in Table 2).

natural fibres. Composites cured at 100°C showed lower equilibrium swelling compared to that cured at 150°C in toluene. For composites containing a bonding agent, the value of  $V_{\tau}$  was substantially lower than that of the composite without a bonding agent. This value was lower still for the composite containing bonding agent cured at lower temperature. Increased fibre loading brought about greater restriction to swelling in both systems and the use of bonding agent reduced the swelling considerably. Alkali treated fibre composites with bonding agent absorbed less solvent compared to composites containing untreated fibre without bonding agent indicating that alkali treatment and presence of bonding agent improved the adhesion between rubber and fibre.

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