

## ***Increasing the Interaction between Starch and the Rubber Matrix by Coupling Agent Addition***

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*A previous study showed that the modulus of a starch filled natural rubber (NR) compound was low compared to the carbon black filled compound and probably insufficient for many engineering applications. Hence, it was considered interesting to determine whether coupling agents such as bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT)/Si 69, polybutadiene maleic anhydride (PBMAH) and resorcinol formaldehyde (RFH) resin with a methylene donor could improve starch filled vulcanisate properties, particularly by increasing the modulus.*

*In this study, TESPT/Si 69 (5 p.h.r.), PBMAH (5 p.h.r.) and RF/HMT (3 p.h.r./2 p.h.r.) were used as coupling agents in the starch filled compounds. It was observed that the rubber adhesion was increased by adding PBMAH and RFH coupling agents and, as a result, the stiffness and the elasticity increased whilst the water absorption decreased.*

**Keywords:** adhesion; rubber; stiffness; starch; coupling agents

Coupling agents are usually used for polymers containing inorganic fillers to improve reinforcement by increasing the adhesion between fillers and polymer, preferably *via* chemical bonding. There is extensive literature pertaining to the mechanical behaviour of filled polymers, which focuses attention on the influence of coupling agents on the physical and mechanical properties of composites containing inorganic fillers<sup>1–3</sup>. Among these additives, coupling agents have gained most attention because of their special, bi-functional, structures. They have two different functional groups, one that reacts with the polymer and the

other that reacts with the surface of the filler. Some of the most commonly used coupling agents are alkylsilanes and organotitanates that have been developed for use with specific composites.

It has been reported that treatment with resorcinol formaldehyde gave satisfactory results in a starch/SBR composite<sup>4</sup> and in a short coir fibre reinforced natural rubber composite<sup>5–6</sup>. Nakason *et al.*<sup>7,8</sup> observed that Mooney viscosity, apparent shear stress and shear viscosity of a starch filled NR compound improved with addition of maleic

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anhydride and methyl methacrylate grafted natural rubber. He claimed that the chemical reaction between the polar groups in the NR graft copolymer and cassava molecules was responsible for the changes found. However, very little information has been published with respect to starch blends treated with these three coupling agents.

In this work, TESPT/Si 69 (5 p.h.r.), PBMAH (5 p.h.r.) and RFH/HMT (3 p.h.r./2 p.h.r.) were used as coupling agents in the starch filled compounds. The formulation used for the RFH compound was based on the data given by INDSPEC<sup>9</sup>. Aziz<sup>10</sup> found that the optimum tensile strength of unfilled and black filled natural rubber compounds could be obtained with a combination of 1.8 HMT and 3 p.h.r. of resorcinol formaldehyde. A loading of 36 p.h.r. starch was chosen for the coupling agent experiments because it gave optimum properties, particularly tensile strength. Also, a loading of 36 p.h.r. starch gives an equivalent volume loading to carbon black used in common rubber engineering compounds.

## Materials

Natural Rubber (SMR L) and corn starch were supplied by the Malaysian Rubber Board (MRB) and National Starch and Chemical Company. Bis (triethoxysilylpropyl)-tetrasulfide (TESPT/Si 69) is a bi-functional, sulphur containing organosilane for rubber applications in combination with white fillers such as silica, which was supplied by Degussa Corporation. On the other hand, the polybutadiene maleic anhydride (PBMAH) was supplied by the Sartomer Company Incorporation where the MA content is 17%. The resorcinol formaldehyde (RFH) resin and hexamethylene tetramine (HMT) were supplied by the Tun Abdul Razak Research Centre. The formulations for this experiment are shown in *Table 1*.

## Mixing

All the mixing was done in a Francis Shaw A KI Intermix. The mixer has a chamber volume of 5.5 litres with a variable speed drive and circulating water temperature control, automated feeding system and computer control. After going through the internal mixer, each batch was passed once through a two-roll mill set with a 2 mm nip.

## Mixing Conditions

The mixing conditions of the compounds used are shown in *Table 2*.

## Mixing Cycle

The mixing cycle used is shown in *Table 3*. The viscosity and curing characteristics were assessed by a Mooney Viscometer and Oscillating Disc Curemeter at 100°C and 150°C.

## Test Procedure

In this study the dynamic rheology of the uncured compounds was analysed using a rubber processing analyser (RPA 2000) Mosanto, USA, with strain sweep 1 - 150% at 100°C, at a frequency of 1 Hz.

The stress strain properties and tear strength of the compounds were measured by using the Hounsfield 500 L testing machine with a cross-head speed of 500 mm/min in accordance to *BS 903:Part A2* while the hardness of the compounds was measured by the Shore type A Durometer according to *BS ISO 7619-1:2004*.

Hardness is a measure of the small strain elastic modulus of the rubber and is

TABLE 1. EVALUATION OF THE EFFECT OF COUPLING AGENTS ON THE STARCH FILLED NR COMPOUND

Material (p.h.r.)	NR/Starch/ PBMAH	NR/Starch/ TESPT	NR/Starch/ RFH
Rubber (SMR L)	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Starch	36	36	36
Anti ozone wax	2	2	2
6PPD*	1.5	1.5	1.5
TMQ*	1	1	1
TBBS*	0.7	0.7	0.7
TMTD*	0.5	0.5	0.5
Sulphur	1.7	1.7	1.7
PBMAH	5	-	-
TESPT/Si 69	-	5	-
*Resorcinol formaldehyde	-	-	3
*Hexamethylene tetramine	-	-	2

6PPD\*-N-(1,3-Dimethylbutyl)-N-phenyl-p-phenylenediamine)

TMQ\*-2,2,4-Trimethyl-1,2-dihydroquinoline polymerised

TBBS\*-N-tert-butyl-2-benzothiazolsulfenamide

TMTD\*-Tetramethylthiuram disulfide

TABLE 2. MIXING CONDITIONS

Variables	Conditions
Fill factor	0.55
Temperature (°C)	40
Rotor speed (r.p.m.)	45

TABLE 3. MIXING CYCLE FOR THE STARCH - RUBBER COMPOUND

Time (s)	Material
0	Rubber, Stearic acid, Zinc oxide, Wax and 6PPD, TMQ, PBMAH, TESPT/Si 69, RFH
120	Starch
360	TBBS, TMTD and sulphur
420/600	Dump

determined by measuring its resistance to a rigid indenter to which is applied a force. A Durometer of Shore type A was used in this experiment with a test specimen of at least 6 mm in thickness, according to *BS ISO 7619-1:2004*.

Compression set was determined according to *ISO 815:1991*, using a round test piece which was prepared with a diameter of 6.3 mm according to *ISO 815:1991(E)*. While rebound resilience on the other hand was determined by measurement of the energy absorbed by the rubber test piece during impact according to *BS 903-A8:1990*.

The cured test pieces were also subjected to the water absorption test. The test specimens of dimensions  $5.0 \times 5.0 \times 2.0$  mm were weighed on an electronic balance and each test piece was immersed in a glass vessel containing 30 mL of distilled water at 25°C. The test was carried out for 32 days. The weight change was measured periodically. The weight of water uptake was calculated according to the formulation below:

$$\text{Weight change} = \frac{M_i - M_0}{M_i} \times 100 \quad \dots 1$$

where;

$M_i$  = Weight after immersion

$M_0$  = Weight before immersion

In order to measure the surface activity and rubber filler interaction, the bound rubber test was carried out. The solvent used for the bound rubber determination was toluene. For this measurement, 0.23 g of uncured rubber compound was placed individually in 60 mL of the solvent in labelled bottles and allowed to swell. After 72 h at room temperature, the solvent was removed and the samples were dried in an air fume cupboard for 9 h. The samples were then subsequently dried in an oven at 85°C for 24 hours and allowed to stand

for an extra 24 hours at 25°C before they were accurately re-weighed.

The amount of bound rubber (in terms of % of initial rubber content of the compound) is given by:

$$\text{BDR (\%)} = \frac{m_0 - (m_2 - m_3)}{m_0} \times 100 \quad \dots 2$$

where;

$m_0$  = weight of rubber content in sample

$m_2$  = weight of the unextracted sample

$m_3$  = weight of the dried and extracted sample

$m_0 = m_2 \cdot 100/\text{cpd}$

cpd is the total formulation (in p.h.r.)

The morphology was carried by examining the tensile fracture using a scanning electron microscope model Leica Cambridge. The surfaces were examined after the first sputter coating with gold to avoid electrostatic charging and poor image resolution.

## RESULTS AND DISCUSSION

### Effect of Coupling Agents on Properties of the Uncured NR:Starch Compounds

In general, the strength of the rubber:filler interaction can be determined from the properties of the unvulcanised compound, without the complication of sulphur crosslinking. Therefore, any improvement in the compound properties observed when the coupling agent is added are most likely to be solely due to an increase in rubber:filler adhesion, *via* physical interaction or chemical reaction.

*Figure 1* shows that the stiffness of the unvulcanised compound, based on 100% and 300% modulus, depends on the coupling agent used. With the addition of

Si 69, there was no significant increase and perhaps even a slight reduction in modulus. For the compound containing PBMAH the 100% modulus was similar, but the 300% modulus was significantly greater than for the compound without coupling agent. Addition of RFH significantly increased both 100% and 300% modulus. The results suggest that both PBMAH and RFH increase the strength of the interaction between the rubber and the starch.

Figure 2 shows that at strains lower than 14%, the dynamic modulus increases by almost 45% and 65% with addition of PBMAH and RFH respectively. Therefore, in the presence of these coupling agents, stronger rubber:filler interactions were achieved. The increases in filler adhesion are also confirmed by the decrease in  $\tan \delta$  (tan delta) values with the addition of the coupling agent (Figure 3). The decrease in  $\tan \delta$  indicates that the increase in interaction was big enough to reduce slippage of the molecules over the filler surface and may

indicate that chemical bonding or very strong specific interactions exist between the coupling agent, starch and rubber. Although the elastic modulus ( $G'$ ) decreases with increasing strain amplitude, the coupling agents continue to enhance stiffness up to a strain amplitude of about 50% to 100% elongation. This suggests that the improvement in rubber:starch adhesion brought about by the coupling agents persists to these relatively large strains.

Bound rubber is used as a measure of the reinforcing capabilities of fillers. The amount of bound rubber for a given elastomer depends on a number of factors, such as surface area, structure and surface activity of the filler and the dispersion state<sup>11</sup>. In the current study, with other factors being equal, it is believed that bound rubber will relate to the strength of the rubber:filler interaction.

Bound rubber contents for the compound with and without coupling agents are shown

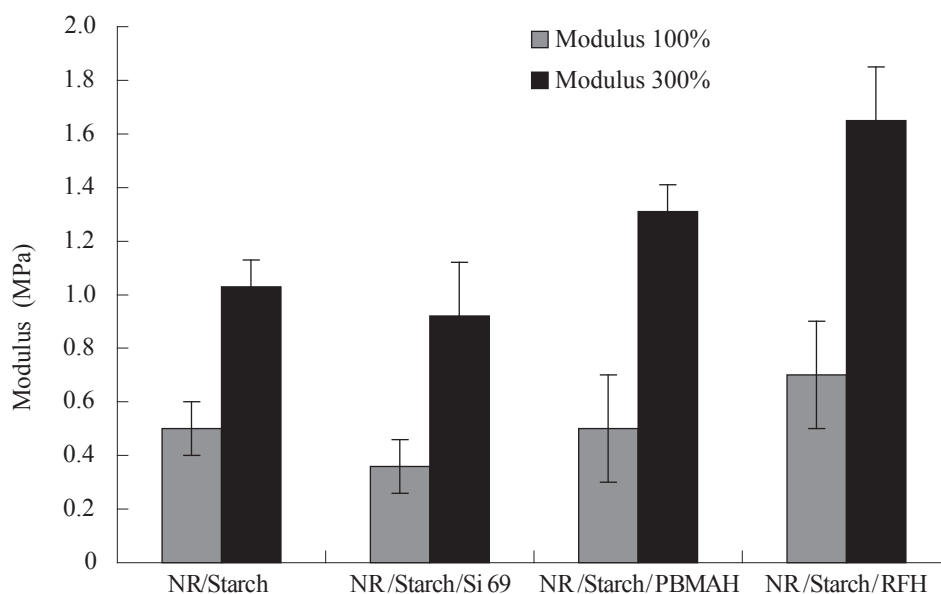


Figure 1. Effect of coupling agent on the modulus of the uncured, starch filled NR compound.

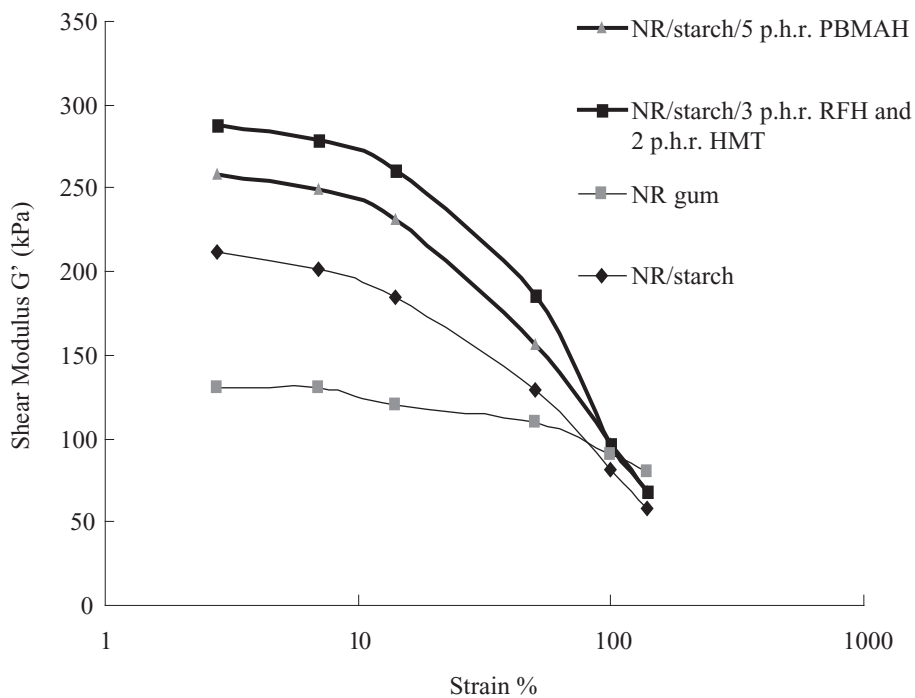


Figure 2. Influence of coupling agent and strain on elastic dynamic modulus (1Hz) of the starch filled, uncured NR compound.

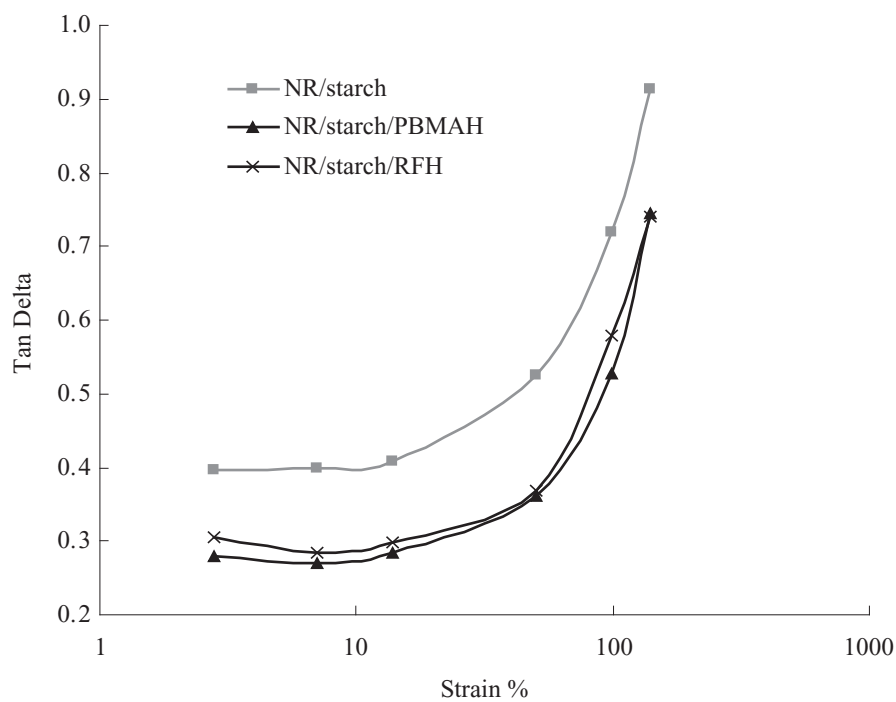


Figure 3. Influence of coupling agent and strain on elastic dynamic modulus (1Hz) of the starch filled, uncured NR compound.

in Figure 4. The low bound rubber content for the starch blend without coupling agent is likely to be due to the weak interaction between the polar starch and the non-polar rubber. The bound rubber content, however, increases with the addition of PBMAH and particularly RFH, implying an increase in rubber:filler interaction. Though some improvements can be obtained with the addition of PBMAH and RFH system, the bound rubber content obtained is still considered low, probably due to the large particle size of starch. With a smaller particle size, a higher surface area would be accessible to rubber segments for rubber:filler interactions to develop and contribute to a higher bound rubber content.

The tensile modulus, dynamic modulus and bound rubber measurements all indicate that the addition of PBMAH and more particularly RFH, significantly increase the interaction between the starch and the rubber. The increase could be due to physical and/or chemical interactions. The adhesion is

probably enhanced by the coupling agents forming chemical and/or hydrogen bonds with the starch and good compatibility between the backbone chain of the coupling agent with the natural rubber phase. The nature of the interactions between the coupling agents, starch and rubber will be discussed in more detail later at the end of this section.

### Effect of Coupling Agents on Properties of the Cured NR:Starch Compounds

The effect of coupling agents on the vulcanised compounds are discussed in the following sections in terms of the effect on stiffness properties, viscoelastic properties and strength properties.

#### Stiffness Properties

Figure 5 shows that tensile modulus is influenced by the addition of coupling

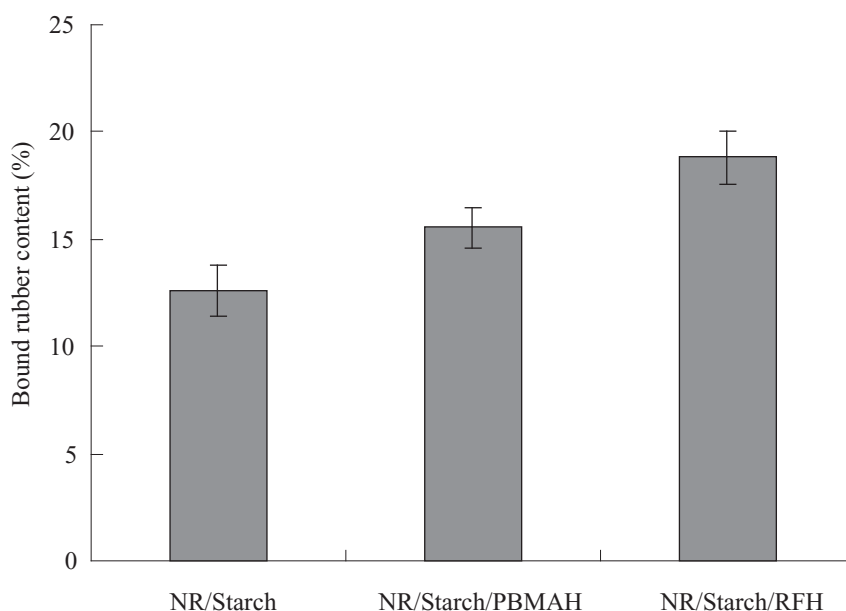


Figure 4. Effect of coupling agent on bound rubber content of starch filled NR.

agent. The order of increasing modulus for various treatments followed the series of Si 69<PBMAH<RFH, reflecting the efficiency with which they increase the adhesion between starch and the rubber. The 100% modulus increased from 1.45 to 1.81 and 2.07 for PBMAH and RFH respectively. The 300% modulus increased from 2.55 to 4.06 and 6.78 MPa respectively. *Figure 6*, shows the effect of PBMAH addition on the 100% modulus of unfilled and starch filled compounds. Addition of PBMAH to the unfilled compound results in a steady decrease in 100% modulus. This indicates that the increase in 100% modulus on addition of PBMAH to the starch filled compound is due to specific interactions between the starch and PBMAH.

Hardness values also increased for the PBMAH and RFH containing compounds (*Figure 7*). The result confirms that the rubber:starch interaction is significantly increased by the addition of PBMAH and RFH. However, *Figures 5 and 7* show that TESPT did not significantly increase the stiffness of the starch filled compound over most of the elongation range and so is not an effective coupling agent. The compound containing silane coupling agent, TESPT was prepared using a single stage mixing sequence which may have not provided adequate time for proper coupling between starch, rubber and the coupling agent to take place. There is also ample evidence in the literature that the coupling action of silane coupling agents is adversely affected by zinc oxide, resulting in poor properties in the rubber compound<sup>12-13</sup>. The ineffectiveness of TESPT as a coupling agent meant that further measurements were not carried out for this compound.

### Viscoelastic Properties

*Figure 8* shows that there is roughly a 20% increase in the elastic dynamic modulus of the

cured compound with the addition of coupling agents PBMAH and RFH. *Figure 9* shows that the loss tangent decreases with the addition of bonding agent, particularly RFH, confirming that the coupling agents increase the level of adhesion between rubber and starch. *Figures 8 and 9* show that the increase in modulus and reduction in  $\tan \delta$  by coupling agents occur over a wide strain range and how effective they are at improving rubber:filler adhesion.

In addition to  $\tan \delta$ , rebound resilience can be used as a measure of viscoelastic properties. Resilience is the ability of an elastomer to return quickly to its original shape after a temporary deflection<sup>14</sup>. It is a measure of stored energy relative to dissipated energy and is therefore expected to be inversely related to  $\tan \delta$ . Good resilience is vital for elastomers used in dynamic applications to reduce heat build-up. *Figure 10* shows the influence of coupling agent on rebound resilience of the starch filled compound. It is observed that the resilience increases with the addition of PBMAH and RFH to the compound, the inverse of the effect on  $\tan \delta$ , as expected. On the other hand, compression set follows a similar trend to  $\tan \delta$  (*Figure 11*). This is also expected since compression set is a measure of unrecovered strain after compression. Hence, all the results indicate that the coupling agents increase starch:rubber adhesion. As the rubber:filler adhesion increases, the elastic modulus increases while at the same time reducing the loss modulus, as discussed previously. In other words, the retractibility of the network upon deformation has been increased by the addition of coupling agents.

### Strength Properties

The effect of coupling agent on the tensile and tear strength of the starch filled vulcanisate is shown in *Table 4*. The addition of coupling



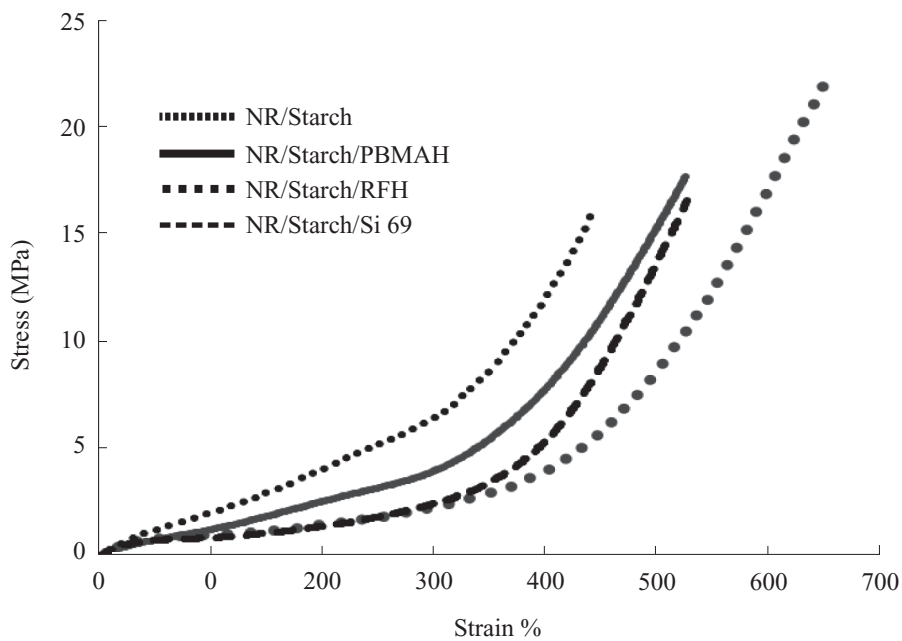


Figure 5. Effect of coupling agent on the tensile properties of the starch filled NR compound.

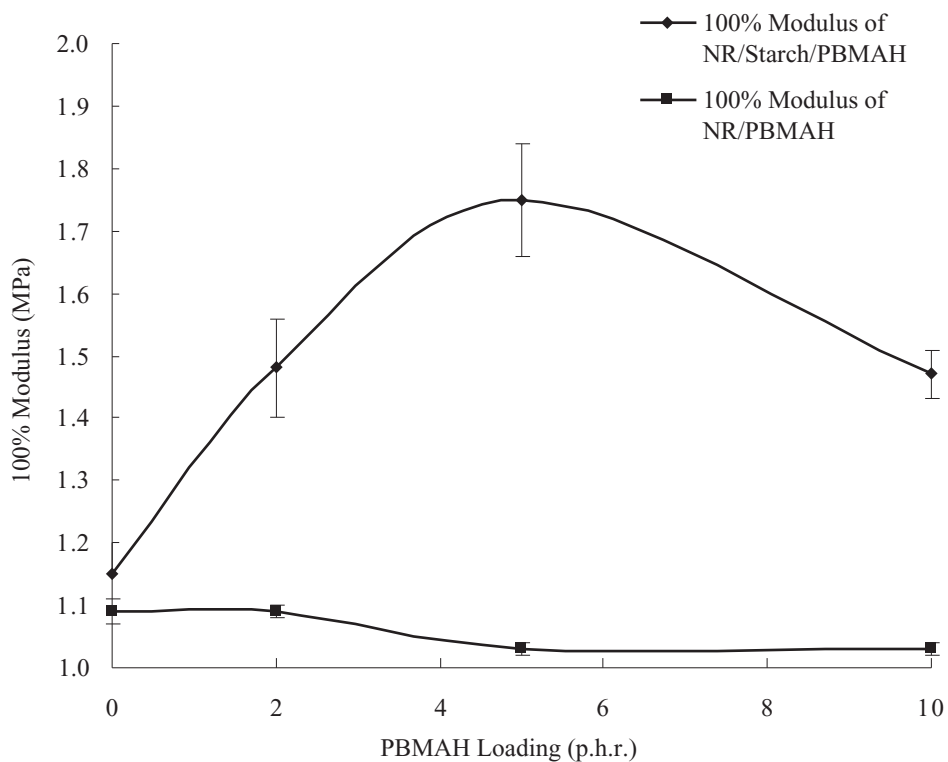


Figure 6. Effect of coupling agent on the 100% modulus of unfilled and starch filled NR compound.

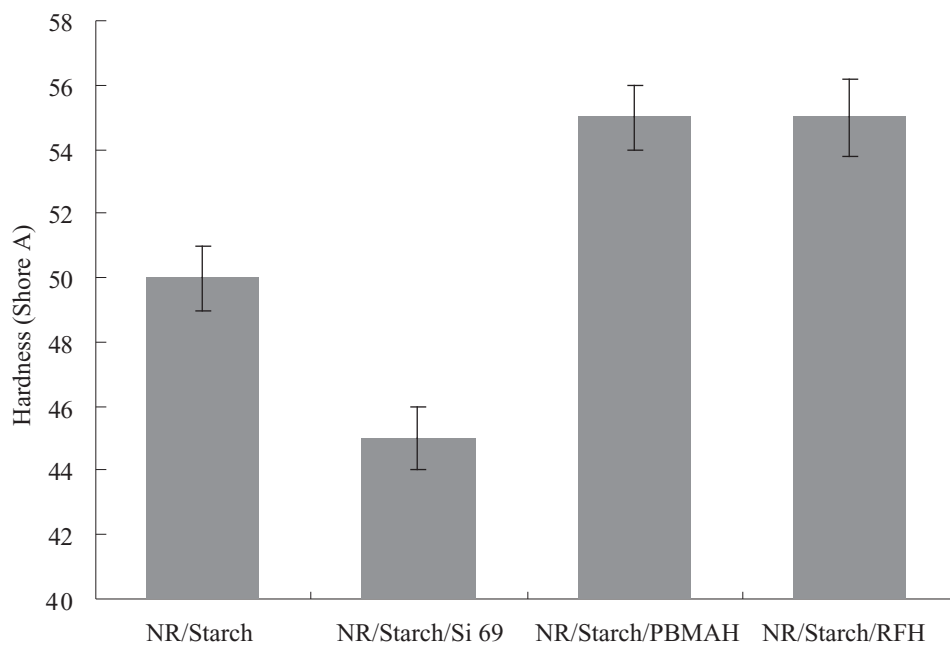


Figure 7. Effect of coupling agent on hardness of the starch filled NR compound.

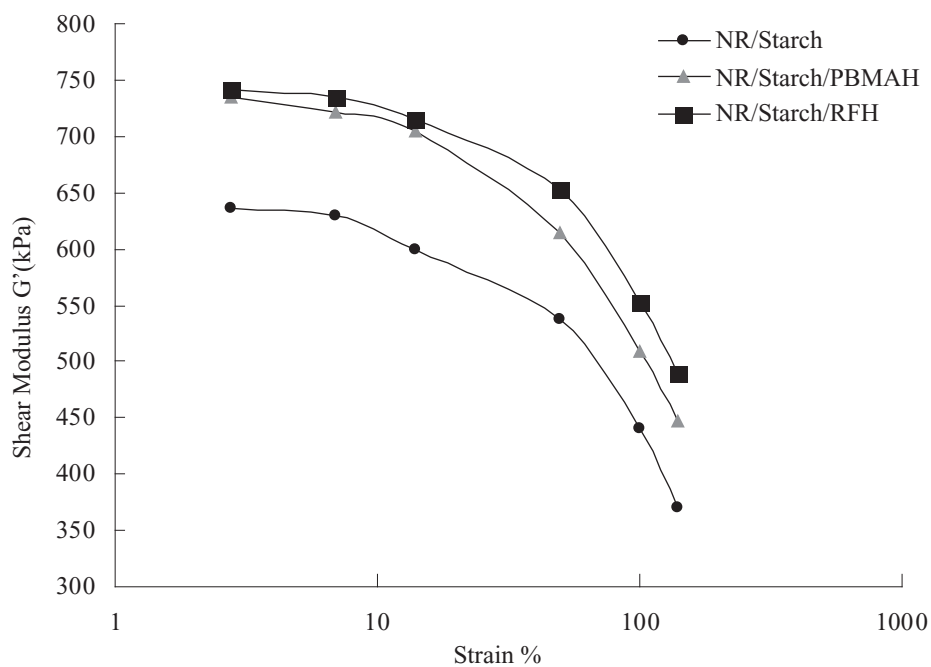


Figure 8. Influence of coupling agent on elastic dynamic modulus (1Hz) of the starch filled NR compound.

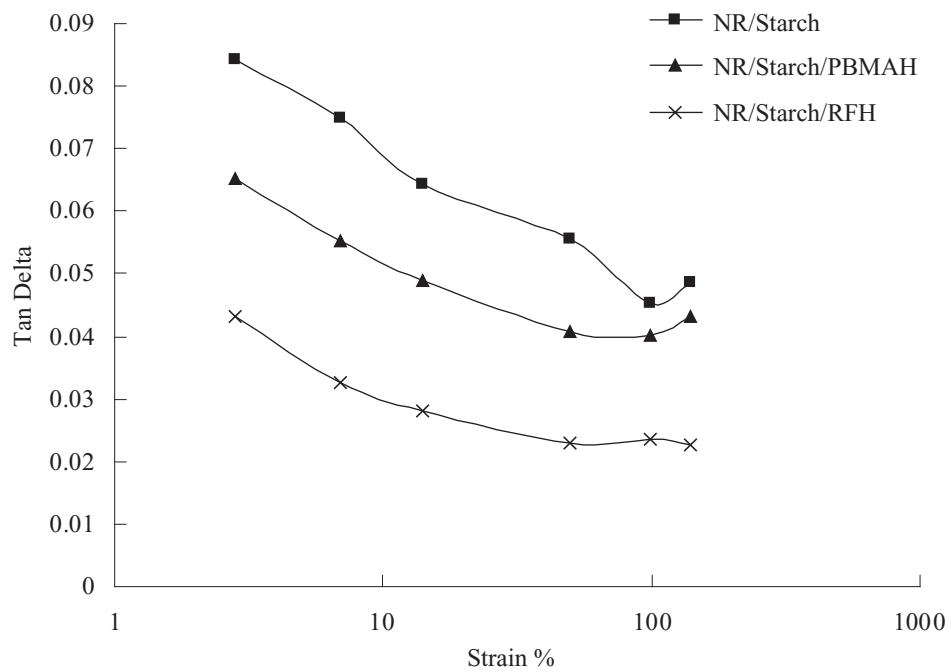


Figure 9. Influence of coupling agent and strain on tan delta (1Hz) of the starch filled NR compound.

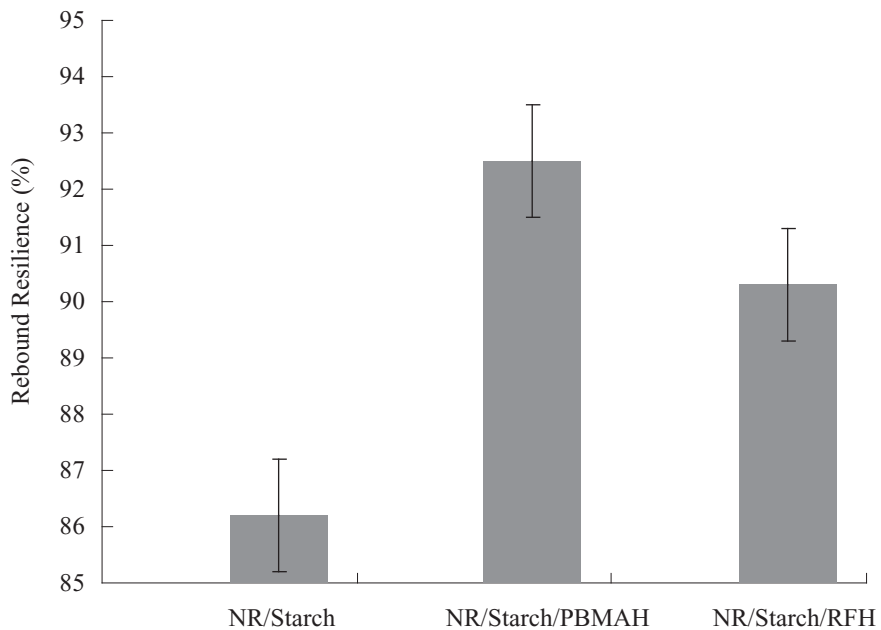


Figure 10. Effect of coupling agent on the rebound resilience of the starch filled NR compound.

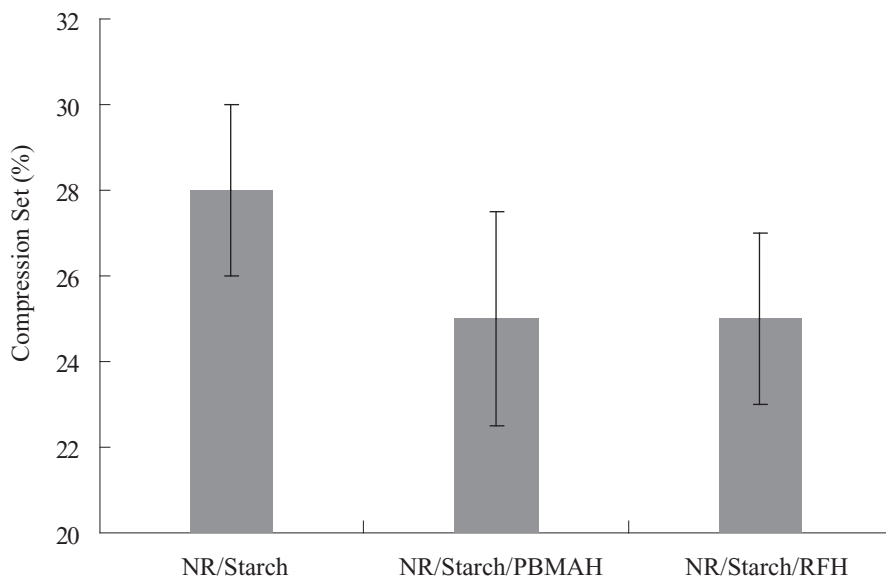


Figure 11. Effect of coupling agent on the compression set of the starch filled NR compound.

TABLE 4. STRENGTH OF THE STARCH FILLED NR COMPOUNDS WITH AND WITHOUT COUPLING AGENTS.

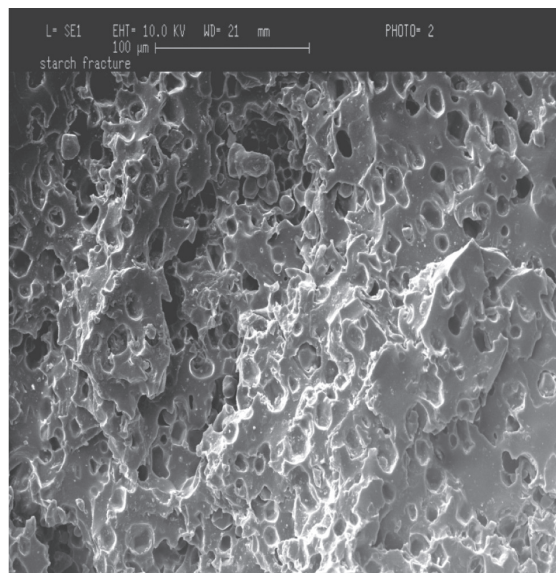
Mix	NR:Starch	NR:Starch: PBMAH	NR:Starch: RFH	NR:Starch: TESPT
Tensile Strength (MPa)	22.2 (2.32)	17.8 (1.31)	16.9 (1.88)	16.8 (1.03)
Tear Strength (N/mm)	15.40 (1.38)	17.30 (1.27)	16.45 (1.02)	4.91 (2.38)

Values in brackets are standard deviation.

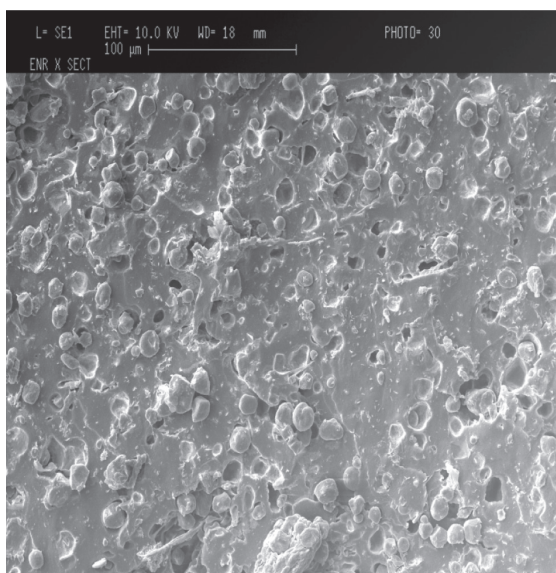
agent reduces tensile strength by about 20%, despite the fact that there is an increase in starch:rubber interaction. The reason for the reduction in tensile strength could be that the adhesion of the filler to the matrix restricts the mobility of the macromolecular chains, increasing local stress. Since the starch particles are relatively large, the increase in stress is likely to result in fracture initiation at fairly low elongations.

Figures 12 to 14 show SEM images of tensile fracture surfaces of the starch filled compounds with and without coupling agents. It can be seen that there were much fewer voids for the compounds with coupling agents, indicating better adhesion of the grains to the rubber matrix. However, the shape of the grains was still clearly visible, indicating that fracture occurred very near the grain surface, even if debonding did not occur. As

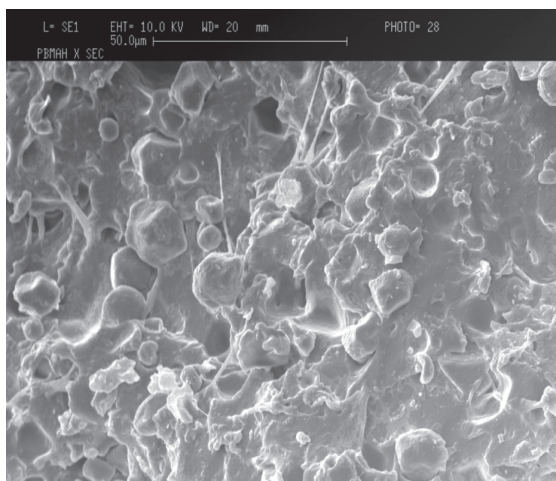
*Figure 12. SEM micrograph of tensile fracture surface of the NR/Starch compound.*



*Figure 13. SEM micrograph of tensile fracture surface of the NR/Starch/PBMAH compound.*



*Figure 14. SEM micrograph of tensile fracture surface of the NR/Starch/RFH compound.*



suggested earlier this is probably due to the large particle size of the starch which results in stress concentration in the rubber close to its surface, particularly if there is good adhesion between the starch and rubber.

By contrast, *Table 4* shows that the tear strength of the starch filled compounds increases slightly with the incorporation of PBMAH and RFH. Therefore, it seems that the propagation of a crack is restricted by the improved adhesion between the rubber and the starch. However, the large particle size of the starch is likely to be responsible for the generally low tear strength, since this property is particularly sensitive to particle size.

#### **Nature of the NR: Coupling Agent: Starch Interaction**

From the results discussed above there is evidence that PBMAH and RFH have significantly increased the interaction between the starch and the rubber. In this section the nature of the possible interaction, whether physical or chemical will be discussed.

#### **Polybutadiene Maleic Anhydride (PBMAH)**

The reaction between the PBMAH and natural rubber is expected to be through crosslinking with the normal sulphur cure system during vulcanisation. The solubility parameters of natural rubber and polybutadiene rubber are 16.7 and 17 MPa<sup>1/2</sup>, thus they are highly compatible<sup>15</sup>. The unsaturation of the butadiene is similarly reactive to the unsaturation in natural rubber, facilitating the formation of sulphur crosslinks between them.

The reaction between PBMAH and starch is likely to be similar to that suggested by Wang as he observed in the PEMA and starch.

Hence the mechanism is also applicable to the hydroxyl group in starch PBMAH which may interact with starch by hydrogen bonds between the hydroxyl groups on starch and carboxylic acid groups of hydrolysed anhydride groups on the PBMAH, as shown in *Figure 15*<sup>16</sup>. It is also possible that a chemical reaction between the hydroxyl group of starch and the anhydride group on the PBMAH will form an ester linkage between them, as shown in *Figure 16*<sup>17</sup>.

To determine whether chemical bonding between the starch and PBMAH had occurred, the compounds were studied with FTIR. The FTIR spectra of starch and PBMAH are shown in *Figures 17* and *18*. The main peaks appearing in the IR spectrum of starch are shown in *Table 5*.

*Figure 18* for the spectrum of PBMAH shows a very strong absorption at 1789 cm<sup>-1</sup> and a weak peak at 1865 cm<sup>-1</sup> which corresponds to succinoyl anhydride.

*Figure 19* reveals that NR/Starch and NR/Starch/PBMAH compounds have a similar spectra. There is no indication of the presence of a new peak at about 1702 to 1735 cm<sup>-1</sup> due to the ester group that would be formed if there was a reaction between the anhydride on the PBMAH and the hydroxyl on the starch. One possible explanation is that the relatively low concentration of starch in the NR means that any changes would be too small to detect. For this reason, a further investigation was carried out by heating the starch and PBMAH, in the absence of NR, at 150°C, in order to verify if any reaction has taken place between them. *Figure 20* shows the spectrum of the heated mixture of starch and PBMAH, together with a spectrum of starch for comparison. The spectrum provides evidence of esterification by the presence of the ester carbonyl stretching at 1718 cm<sup>-1</sup> (C = O) (shown as "A" on the spectrum). In different studies, Bikiaris *et al.*<sup>18</sup>

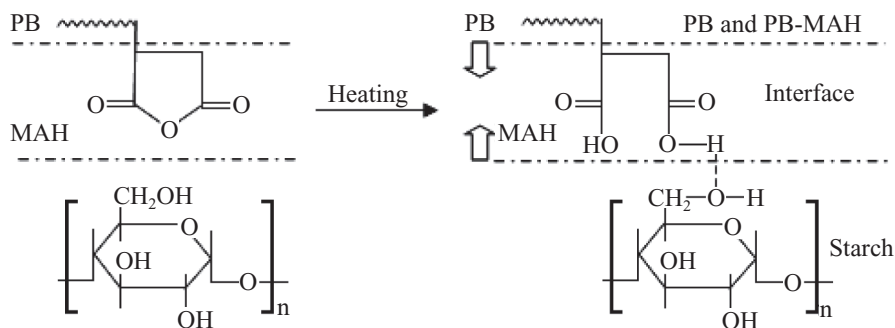


Figure 15. Possible interaction between PBMAH and starch by physical hydrogen bonding<sup>16</sup>.

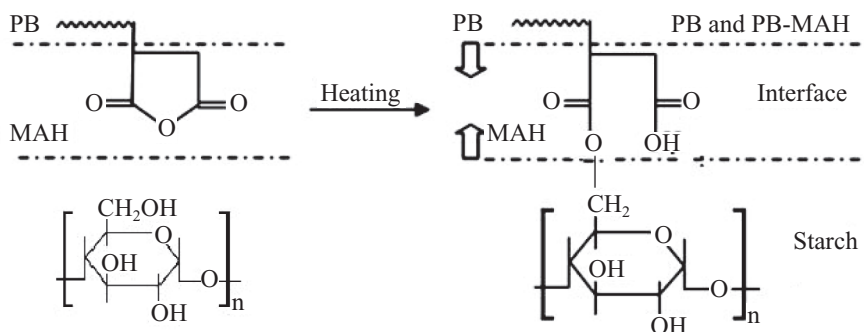


Figure 16. Possible interaction between PBMAH and starch by chemical bonding<sup>17</sup>.

studied an LDPE/plasticised-starch blend compatibilised with PE-g-MA (Polyethylene grafted maleic anhydride) copolymers. They attributed a band at  $1735\text{ cm}^{-1}$  and  $1702\text{ cm}^{-1}$  to an ester carbonyl stretching vibration. Wu *et al.*<sup>19</sup> obtained a similar result for a Polycaprolactone/g-MAH/starch blend that exhibited a new-formed peak at  $1739\text{ cm}^{-1}$ . The appearance of this new absorption peak was attributed to the formation of an ester carbonyl functional group *via* reaction between an  $\text{-OH}$  group of the starch and an anhydride carbonyl group of the PCL-g-MAH.

Hence it can be concluded that there probably is a chemical interaction between

starch and PBMAH when heated during vulcanisation. It is therefore likely that the coupling between starch and rubber with PBMAH involves both physical interactions and chemical reactions.

The great improvement in unvulcanised modulus and bound rubber content resulting from the addition of RFH to the starch filled rubber compound may be due to several possible causes. Conventionally, two-component systems such as RFH, comprising a methylene donor and methylene acceptor, are widely used to enhance the bonding between brass coated steel cords and rubber in the tyre industry. HMT is the methylene donor

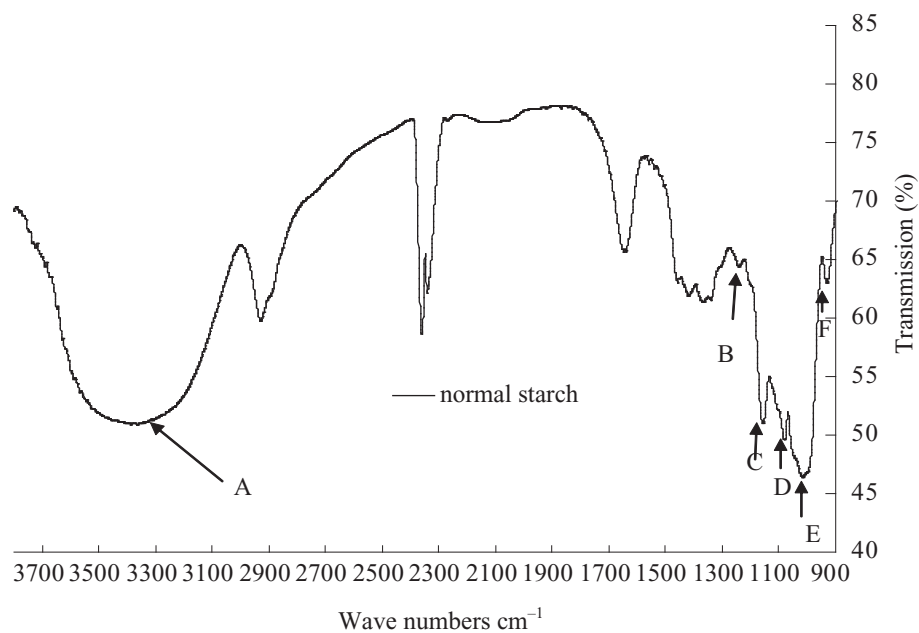


Figure 17. IR spectrum of starch (see Table 6.2 for peaks).

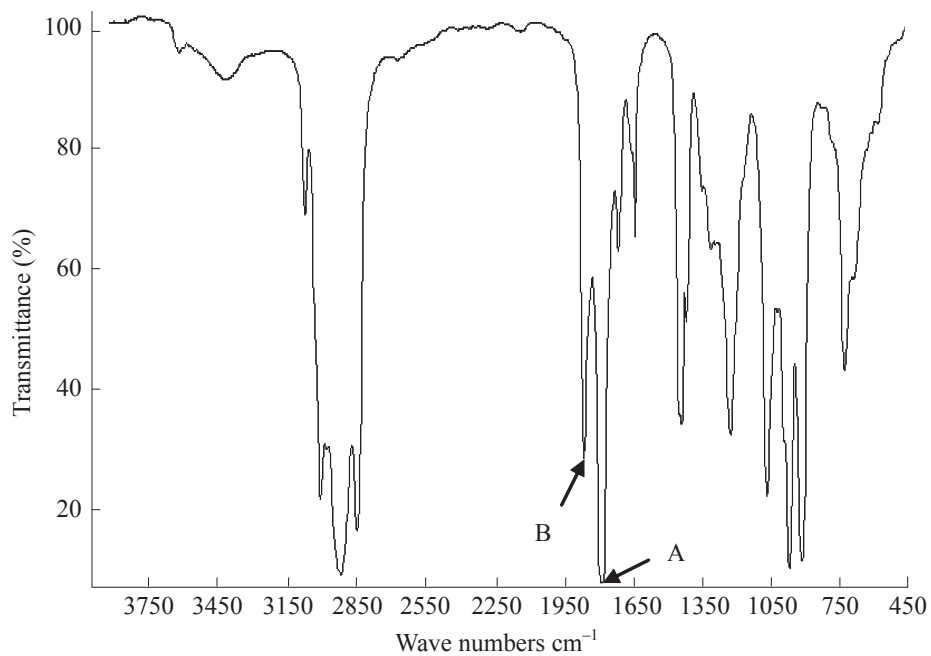


Figure 18. IR spectrum of polybutadiene maleic anhydride (PBMAH).



TABLE 5. MAIN PEAKS IN THE IR SPECTRUM OF STARCH (FIGURE 17)

Peak	Wave Number $\text{cm}^{-1}$	Identification
A	3389	O-H bond stretching
B	1352	O-C-H, C-C-H, C-O-H bending
C	1150	C-O-C, C-C and OH bond stretching
D	1080	C-O-C, Glycosidic bridge bending
E	1022	C-O-H deformation
F	930	C-H bending

and resorcinol is the methylene acceptor, which react to form a highly crosslinked polymer network. The mechanism for the interaction between RFH and rubber is similar to that of the reaction of phenolic compounds with rubber as shown in *Figure 21*. According to A.L. Miller *et al.*<sup>20</sup>, Van der Meer postulated that a methylene quinone intermediate reacts with active hydrogens such as the allylic hydrogen of the isoprene unit in natural rubber.

On the other hand in the same article<sup>20</sup>, Greth proposed that the resin reacts with the double bond in the isoprene unit of natural rubber to form chromans as shown in *Figure 22*. The crosslinking reactions have been shown to be so effective that no other curing system is needed to produce vulcanisates from many natural and synthetic rubber compounds<sup>20</sup>. In addition to crosslinking *via* the resin link, the inclusion of HMT also acts as a secondary accelerator for the sulphur cure system, accelerating vulcanisation and forming more crosslinks. Aziz<sup>10</sup> observed that less swelling in toluene was obtained for vulcanised rubber which contained resorcinol, HMT, sulphur, TBBS and TMTD than that containing sulphur, TBBS and TMTD alone.

The mechanism for the reaction between RFH and starch is likely to be similar to that suggested by Van der Meer in A.L. Miller's<sup>20</sup> report. He postulated that the methylene quinone intermediate produced in the resin cure system could also react with active

hydrogens such as allylic hydrogens in the glucose hydroxyl unit of cellulosic rayon. Hence the mechanism is also applicable to the hydroxyl group in starch. De *et al.*<sup>21</sup> proposed it is possible to form an ether linkage in which the RFH resin interacts with the primary hydroxyl group of cellulose as shown in *Figure 23* which could also be applicable to starch.

In order to ascertain whether any chemical reaction had taken place between the starch and the RFH, an IR spectroscopy study was carried out in which starch was heated in the presence of RFH at 150°C. There were no new peaks in the spectrum that would have indicated the formation of an ether link. However, this result is not conclusive because an ether group would appear in the region between 1000  $\text{cm}^{-1}$  – 1300  $\text{cm}^{-1}$  which already has many peaks due to the ether links in starch (*Figure 17*). In fact, scarcely any information on any chemical reaction in this system can be obtained from infrared characterisation. The only direct evidence of chemical reaction is the in-situ formation of a dark red resin during heating or vulcanisation, which is believed to be due to the reaction of resorcinol and hexamethylene tetramine. Hence, there is the potential for reaction between the RFH and starch and/or rubber. However, it is also possible that there are only physical interactions between the starch and the RFH resin. Several types of physical interaction between RFH and rayon or nylon have been

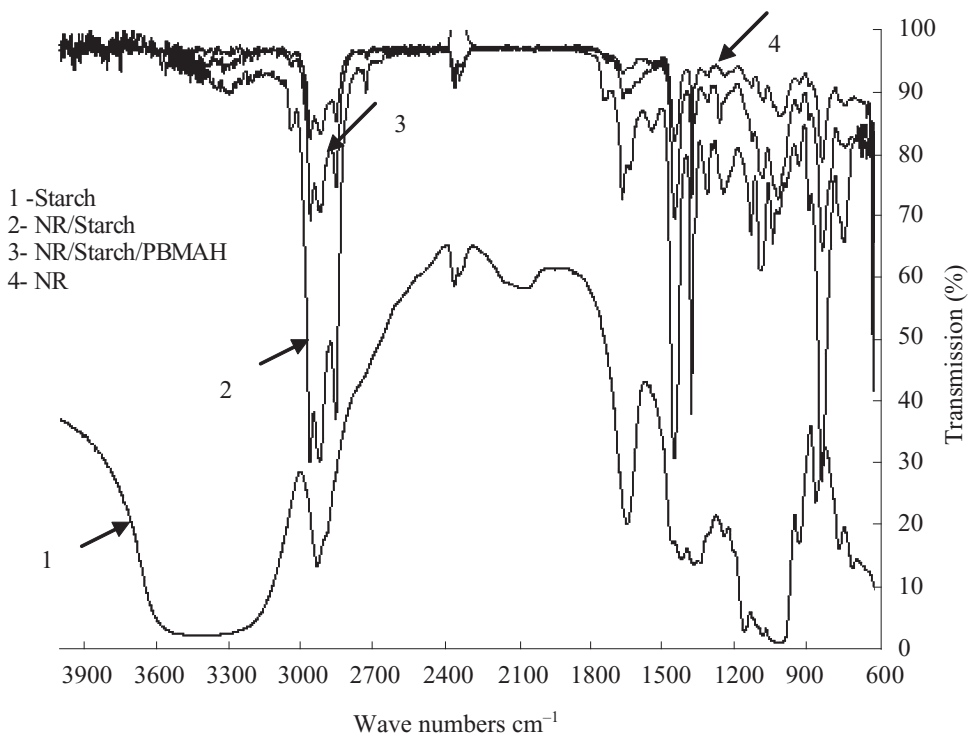


Figure 19. FTIR spectra of NR, starch and compound.

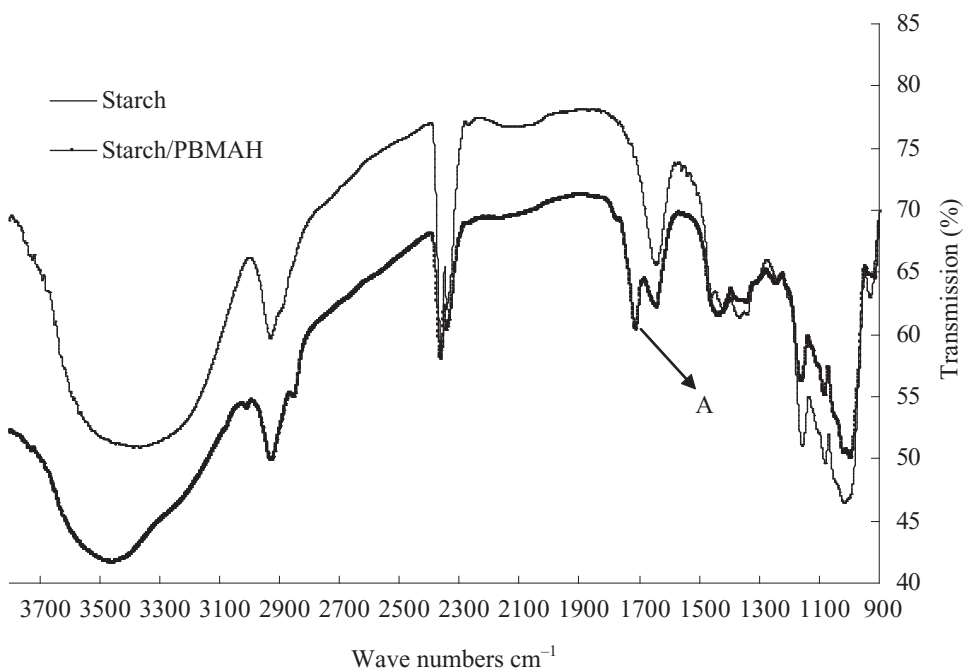


Figure 20. IR spectra of Starch and Starch/PBMAH heated to 150°C.

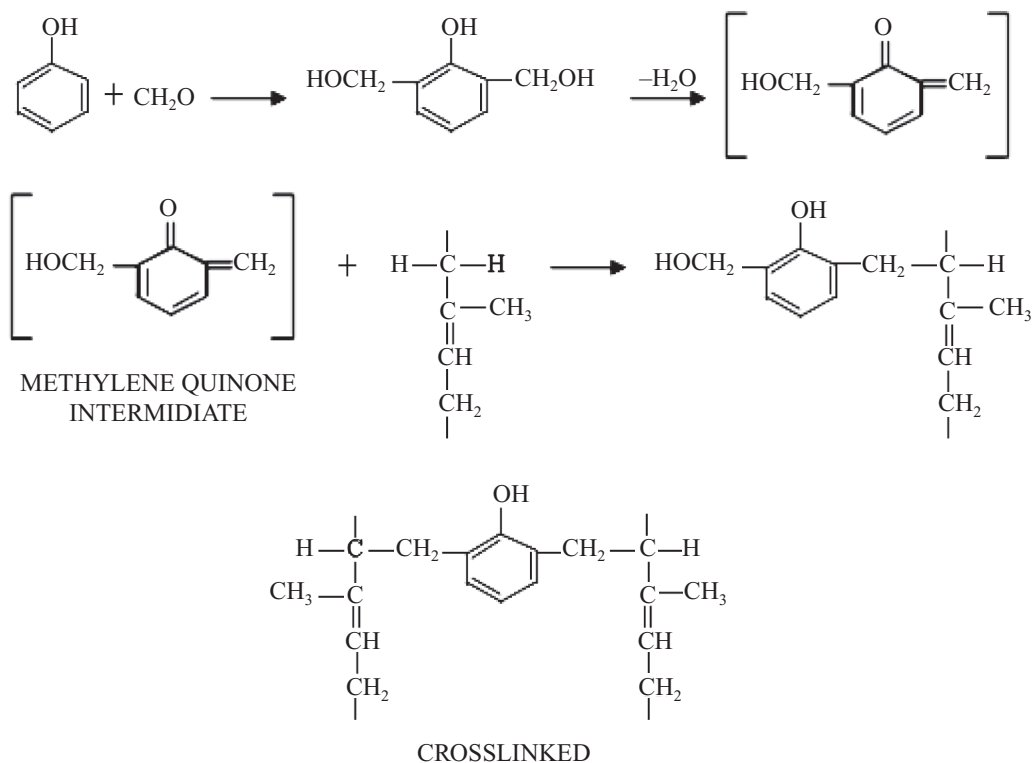


Figure 21. Reactions for phenolic-formaldehyde compounds with the isoprene unit in natural rubbers<sup>20</sup>.

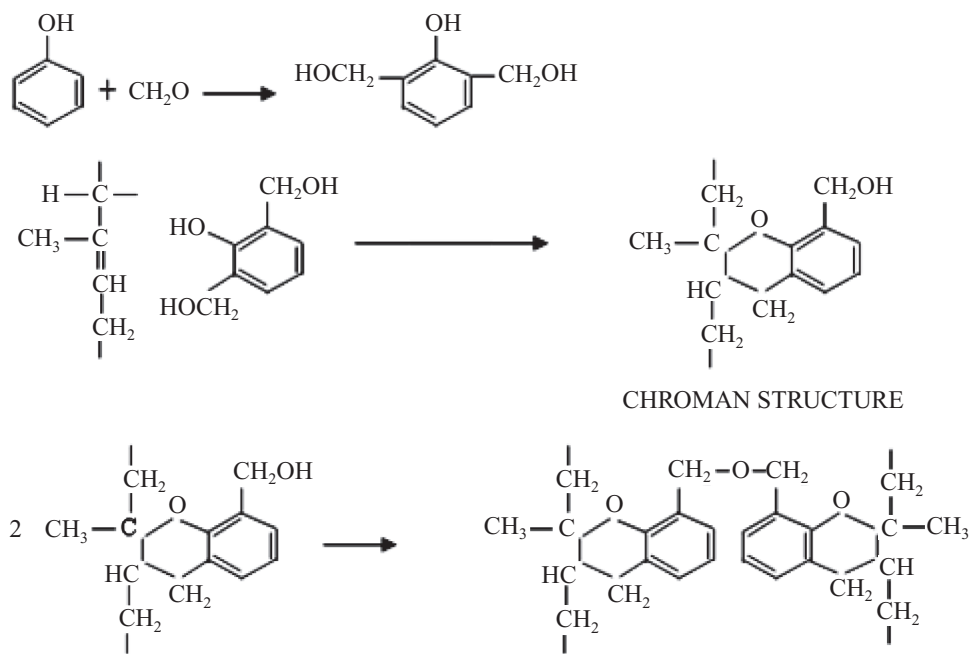


Figure 22. Reactions for phenolic formaldehyde compounds with natural rubber, which show evidence of a chroman structure<sup>20</sup>.

suggested, such as hydrogen bonding between the hydroxyl groups in the RFH resin and electronegative groups in fibres, dipole-dipole interaction and molecular entanglement<sup>22</sup>.

### Water Absorption

It is evident from *Figure 24* that water absorption by the starch filled compound is lower when the coupling agents PBMAH and RFL are used. After 32 days the compounds containing PBMAH and RFH showed about a 50% reduction in water absorption compared to the compound without coupling agent. Water absorption in the starch filled NR is mainly caused by the presence of hydrophilic starch, but it could be made worse by the weak interface between the starch and the rubber matrix.

The PBMAH and RFH could reduce water uptake in different ways. Partial substitution of the OH groups during the reaction between starch and coupling agent reduces the number of hydrogen bonding sites available for water adsorption. Even if there is only hydrogen

bonding between starch and PBMAH or RFH, the adsorption of these molecules could make the starch more hydrophobic. For example, it is known that polysaccharides are more hydrophobic if they have a greater number of internal hydrogen bonds, as their hydrophobicity increases there is less direct interaction with water<sup>23</sup>. Chang and Chang<sup>24</sup> studied how acetylation of wood could be used to reduce water adsorption. They reported that the acetyl group, which is bigger than the hydroxyl groups, occupied more space in the cell wall and thus reduced adsorption sites for water. In a similar way, the maleic anhydride groups or phenolic OH groups could sterically hinder adsorption of water. Another way in which coupling agents could reduce water absorption is by increasing the adhesion between starch and the rubber, preventing debonding and consequent easy access of water to the interior of the material.

### CONCLUSIONS

- Rubber-starch adhesion is increased by adding PBMAH and RFH coupling agents.

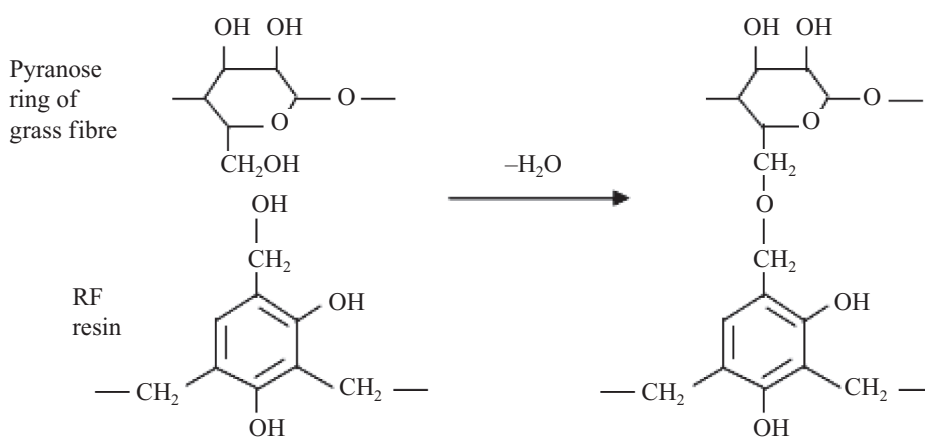


Figure 23. Postulated reactions for grass fibre with RFH<sup>23</sup>.

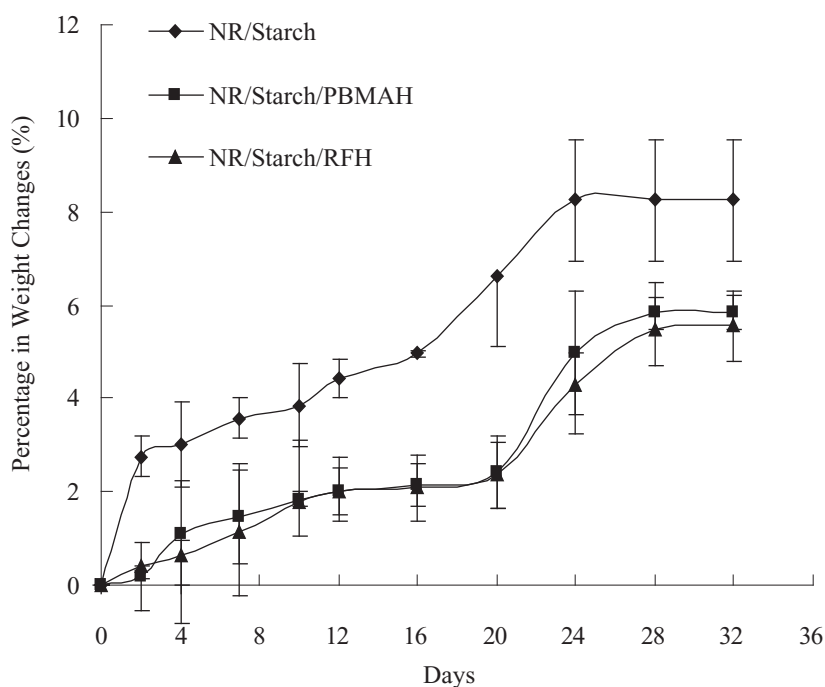


Figure 24. Effect of coupling agents on water absorption by the starch filled NR compound.

As a result of the increase in adhesion, addition of these coupling agents results in:

- Increase in stiffness
  - Increase in elasticity
  - Reduction in water absorption
- Coupling between starch and PBMAH involves an ester linkage between starch hydroxyls and maleic anhydride groups on the PBMAH. Hydrogen bonding is also likely to contribute to the interaction between starch and PBMAH.
  - The nature of the coupling between NR/RFH/Starch is not known but is likely to involve:
    - Hydrogen bonding or polar interactions between hydroxyls on starch and hydroxyls on the resorcinol resin.

b. RFH as secondary vulcanisation agent.

- There was no significant improvement in the vulcanisate properties of the starch filled compound by adding TESPT/Si 69 coupling agent. This poor coupling effect may be due to the conditions during mixing and curing that were not right for the reaction.

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