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Effect of Starch Loading on the Properties of Natural Rubber Compounds

MAZLINA MUSTAFA KAMAL*# AND JANE CLARKE**

The effect of starch addition on the processing and properties of a natural rubber compound was investigated. The starch loading used was varied from 36 p.h.r. to 66 p.h.r. loading. The compound is based on a simple engine mount compound filled with 49 p.h.r. carbon black which corresponds to the same volume loading as 36 p.h.r. of starch. The extent of the adhesion between filler and rubber under different deformation conditions was determined using several simple models such as the Einstein[1], Guth-Gold[2] and Sato-Furukawa[2] models. In general, the study shows relatively poor reinforcement of natural rubber by starch, resulting in low stiffness and strength compared with a compound filled to a similar volume fraction with carbon black. The poor reinforcement is due to its different polarity and large particle size. In spite of that, it is observed that good adhesion can be obtained at strains below 50% elongation, agreeing with the Einstein model of perfect adhesion. However, at a higher strain, poor adhesion leads to debonding of starch from the rubber, resulting in lower stiffness and strength.

Keywords: reinforcement; adhesion; debonding

In recent years, there has been a growing interest in renewable resources and recyclable new materials available at a competitive price. The potential benefits of using naturally occurring materials are many. The use of renewable, rather than petrochemical resources, will extend the nonrenewable petrochemical supplies. It is also possible that less energy will be required to produce and process the bio materials, so reducing carbon dioxide released by energy production and hence, reducing global warming. Biodegradability is an additional benefit of many renewable biological sources of polymers.

It is possible that the agricultural industry produces sufficient material that could be used as a renewable resource for polymer and filler feed stock. Agriculture offers a broad range of commodities, including trees, crops, farm and marine animals, that have many uses. Plant based materials have been used traditionally for food and feed and is increasingly being used in pharmaceuticals. The three major

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plant based polymers are protein, oil and carbohydrates (starch and cellulose). With the change in emphasis to more biodegradable packaging material and with the concern that the raw material for industrial polymers should be made of economical renewable resources, starch has dominated commercial development in this area[3]. Hence, it is possible that starch could be used as renewable filler in rubber compounds, with the additional possibility of increasing the biodegradability of rubber goods.

For a filler to reinforce a rubber compound and increase its stiffness and strength, it is necessary that there is a sufficiently strong interaction between the filler and the elastomer and that the surface area of the filler is sufficiently large. The strength of interaction and extent of surface of the filler can be investigated indirectly by studying the viscosity and modulus of the filled compound in relation to the unfilled compound where the relative viscosity can be determined.

The relationship between filler content and viscosity has been modeled by several methods. The simplest model is the Einstein equation, which is valid at low filler concentrations[1,2]. Einstein observed that the viscosity of a liquid increased with the addition of spheres, irrespective of their size, due to a hydrodynamic effect. The Einstein equation assumes that there is perfect wetting of the spheres by the fluid and that adhesion between them, means that no slippage occurs at the interface. It is also assumed that there is no interaction between the particles. Einstein's equation has the form:

$$\eta = \eta_m (1 + 2.5\ \Phi) \qquad \ldots 1$$

Where Φ is the volume fraction of particles and η_m and η are the viscosity of the unfilled matrix and the composite respectively.

For more concentrated dispersions, the interaction between spheres must be accounted for and several developments of the Einstein equation have been proposed[2]. For example, the Guth and Gold equation shown below.

$$\eta = \eta_m (1 + 2.5\Phi + 14.1\Phi^2) \qquad \ldots 2$$

For the case of poor adhesion, where the polymer matrix slips by the filler particles, the Einstein equation becomes[2,4,5]:,

$$\eta = \eta_m (1 + \Phi) \qquad \ldots 3$$

The Einstein and Guth and Gold equations have also been widely used in modelling the tensile modulus of a cured filled compound. The relationships are denoted as follows:

$$E = E_m (1 + 2.5\Phi) \qquad \ldots 4$$

$$E = E_m (1 + 2.5\Phi + 14.1\Phi^2) \qquad \ldots 5$$

Sato and Furukawa have also developed an expression for tensile modulus in the case where adhesion is so poor that the polymer matrix pulls away from the filler surface to give cavities around the filler particles[2,4,5]. The equation is:

$$E + E_m \left[\left(1 + \frac{\Phi^{2/3}}{2 - 2\Phi^{1/3}}\right)(1 - \Psi\zeta) - \frac{\Phi^{2/3}\ \psi\zeta}{(1 - \Phi^{1/3})\Phi}\right] \qquad \ldots 6$$

where

$$\Psi = \left(\frac{\Phi}{3}\right)\frac{1 + \Phi^{1/3} - \Phi^{2/3}}{1 - \Phi^{1/3} + \Phi^{2/3}}$$

ζ is the adhesion parameters,
$\zeta = 1$ for poor adhesion,
$\zeta = 0$ for perfect adhesion,

In this paper, the effect of starch addition on the processing and properties of a

natural rubber compound was investigated with particular reference to the extent of reinforcement provided by the starch.

EXPERIMENTAL

Natural rubber (SMR L) and corn starch (10-15 μm) were supplied by the Malaysian Rubber Board (MRB) and National Starch and Chemical Company respectively. The compound formulations shown in *Table 1* were used to access the effect of starch loading on the properties of a natural rubber compound. The compound was based on a simple engine mount compound filled with 49 parts per hundred rubber (p.h.r.) carbon black. The starch loading used was varied from 36 p.h.r. to 61 p.h.r. loading. The 36 p.h.r. loading of starch corresponds to the same volume loading as 49 p.h.r. of carbon black.

The mixing was done in a Francis Shaw A KI Intermix and later the viscosity and curing characteristics were assessed by a Mooney Viscometer and Oscillating Disc Curemeter at 100ºC and 150ºC respectively.

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

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

TABLE 1. FORMULATION OF STARCH AND CARBON BLACK FILLED NR COMPOUND

Material (p.h.r.)	Unfilled NR	NR/ Starch	NR/ Starch	NR/ Starch	NR/ CB
Rubber (SMR L)	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Starch	-	36	51	66	-
*Carbon black N660	-	-	-	-	49
Anti ozone wax	2	2	2	2	2
6PPD	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1
TBBS	0.7	0.7	0.7	0.7	0.7
TMTD	0.5	0.5	0.5	0.5	0.5
Sulphur	1.7	1.7	1.7	1.7	1.7

* Carbon Black N660 (Sterling V N660 from Cabot Company)
6 PPD – N-(1,3-Dimethylbutyl)-N-phenyl-p-phenylenediamine)
TMQ - 2,2,4- Trimethyl- 1,2- dihydroquinoline polymerised
TBBS - N – tert –butyl-2 benzothiazolsulphenamide
TMTD – Tetramethylthiuram disulphide

RESULTS AND DISCUSSION

Viscosity

Figure 1 shows that viscosity of the NR compound increased fairly linearly with the addition of starch up to 51 p.h.r. with only a slight increase in viscosity with further starch addition. It is possible that at very high concentrations of filler, there is insufficient rubber matrix present for the compound to flow smoothly and that it breaks up under the shearing action of the rheometer. The resulting melt fracture could result in a low torque being measured and hence, a low viscosity being recorded.

The effect of starch loading on viscosity is clearly an important factor in itself, since it will affect the ease with which the compound is processed. However, viscosity of the filled compound is also important in that it reflects the strength of the starch: filler interaction, which is very important in determining the degree of reinforcement. The magnitude of the increase in viscosity with starch loading can be used to indicate the strength of this interaction. For example, Nakason[6] in his work on starch filled natural rubber (STR 5L), found that the increment in viscosity with starch loading, was very small in comparison to starch filled maleic anhydride grafted natural rubber. The same trend was also observed for starch filled air dried smoked (ADS) natural rubber in comparison with starch filled polymethyl methacrylate (PMMA) - grafted NR7. At the same level of starch added, the compound of NR-PMMA: starch showed a higher Mooney viscosity value. The lesser increment in viscosity with increased starch loading observed for the unmodified NR compounds was attributed to the poor interaction between the starch and the rubber, due to their differences in chemical nature, particularly polarity.

In the current study, the strength of the interaction between starch and natural rubber was investigated more quantitatively by applying the Einstein and Guth-Gold equations to the viscosity data. The experimental data obtained, neither fits the Einstein equation for perfect adhesion, nor the Guth-Gold equation which is valid at higher concentrations (*Figure 2*). The experimental data however, showed quite a good match with the Einstein equation for poor adhesion. The agreement with the equation for poor adhesion shows there is very little interaction between the starch particles and the natural rubber matrix.

Apart from the strength of the interaction with the polymer, there are other characteristics of the filler that can affect both reinforcement and viscosity, including a) particle size and surface area, b) particle shape and c) surface roughness of the particles. Each of these characteristics will be described in the following paragraphs and their relevance to the starch:NR system discussed.

The theories which deal with filled fluid systems indicate that the viscosity for a given particle and matrix should depend only upon the volume fraction of filler and not the particle size. However, experiments generally show an increase in viscosity as the particle size decreases. There are two reasons for this[8]. Firstly, surface area increases with a decrease in particle size, increasing the contact area between filler and matrix. Secondly, as the surface area increases, agglomeration also increases, the matrix trapped in the agglomerates increases and hence the effective filler volume fraction increases. It was reported[9] how specific surface area of fillers affects the properties of silica and carbon black filled rubbers. Both of these reports show that when surface area of the filler increases, there is a higher compound viscosity. In the case of starch, the particle sizes (15 - 20 μm) are significantly larger

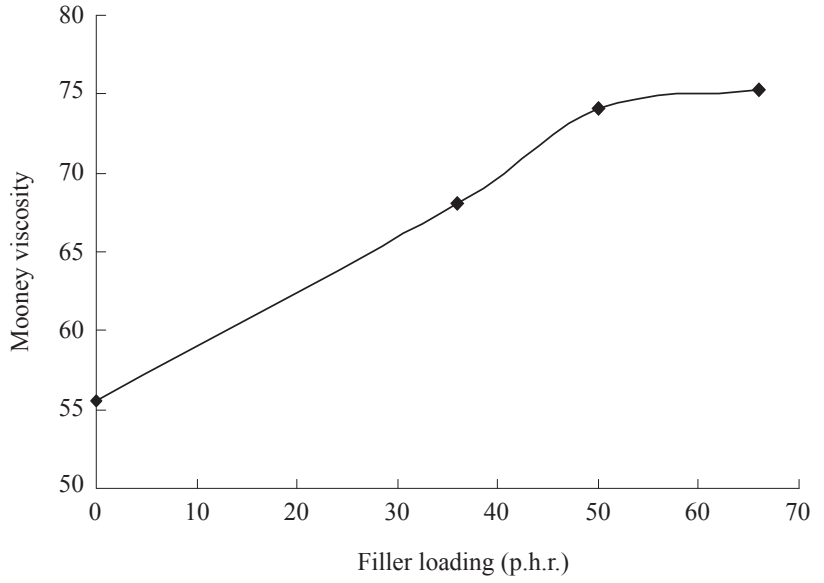

Figure 1. Variation of viscosity with starch loading in the natural rubber compound.

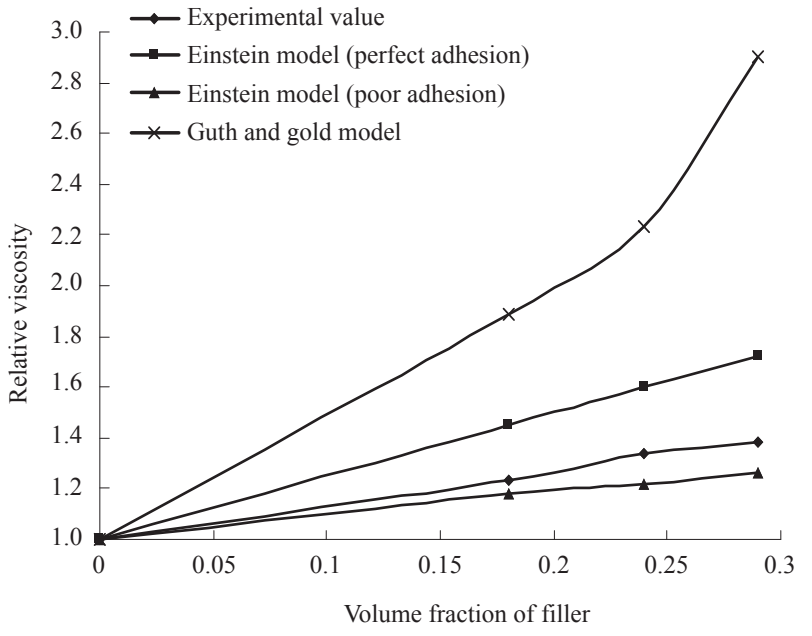

Figure 2. Plot of relative viscosity against volume fraction of starch in the natural rubber compound.

than those of conventional reinforcing fillers (0.049 – 0.060 µm / 49 – 60 nm)[10] and so there is likely to be little increase of viscosity or reinforcement due to either surface area or agglomeration effects, *Figures 3a* and *b*.

The viscosity of a filled compound may also be affected by particle shape. Boonstra[11] observed that the viscosity is highest when acicular filler particles are used, intermediate for platelet particles and lowest for spheroidal particles. In general, anisometric particles, having a significant difference between length and width, are more effective as reinforcement than isometric particles with similar length and width. Starch particles, being roughly spherical or polygonal are essentially isometric and hence, there is no additional increase in viscosity due to the shape factor.

The roughness of the particle surface also affects the viscosity of a filled compound. In his study, Shenoy[12], concluded that lower viscosity was obtained with round edged particles compared to the sharp edged particles of coal suspended in mineral oil. A higher viscosity was obtained with sharp edged particles, primarily by harsh frictional contact and by trapping layers of liquid on its surface and so causing an increase in the effective concentration of filler. It was concluded that, the higher the surface roughness, the greater the resistance to flow deformation and the higher the viscosity of the filled system. However, starch surfaces are rather smooth, rounded and lack porosity, so that there is little or no trapped rubber present to increase the effective filler concentration. Hence, there is no surface roughness effect to increase the viscosity of starch filled rubber beyond the level predicted by Einstein's equation.

In addition to the individual particle characteristics discussed above, interparticulate interaction or agglomeration can affect viscosity, particularly at high concentrations, as shown by the Guth-Gold equation. *Figure 2* also shows that, the viscosity of the starch filled rubber compound fails to follow the Guth-Gold equation, since it does not increase more significantly at higher concentrations. The result indicates that filler-filler interactions are relatively weak. Although this may be surprising, considering the polar nature of starch, the relatively large particle size will minimise the influence of any such interaction.

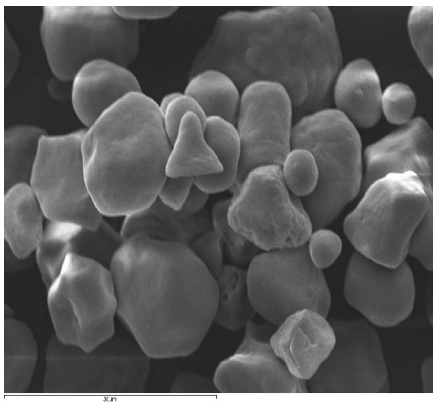

Figure 3a. SEM micrograph of corn starch.

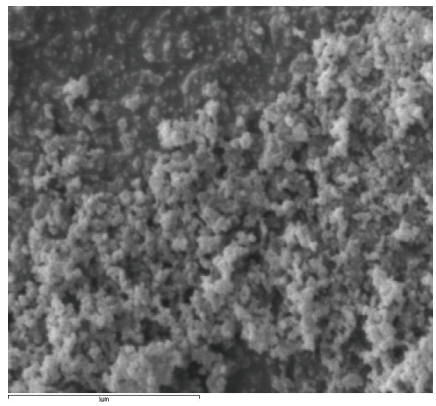

Figure 3b. SEM micrograph of carbon black (N660).

The following conclusions can be drawn from the viscosity results. There is poor adhesion between the starch particles and the rubber. The overall isometric and rounded shape of the grains and their smooth surfaces mean that there are no geometric factors to contribute to an increase in viscosity. The relatively large particle size results in little agglomeration of the starch particles. In a practical sense, the generally low viscosity of the starch filled natural rubber compound will allow easy processing, such as in calendaring and extrusion. However, low adhesion between the starch particles and the rubber suggests that rather weak reinforcement and poor mechanical properties will be expected for the cured compound.

Cure Properties

Figure 4 shows the relationship between MH-ML (maximum torque-minimum torque) and loading of starch. This figure shows that the torque, which is dependent on the number of crosslinks formed per unit volume of rubber, increased with filler content. The torque increased by 5 units for every 15 p.h.r. loading. The marked increment in the torque with increasing starch concentration indicates that the presence of fillers in the rubber matrix has reduced the mobility of the molecular chains of rubber. Because the curemeter torque effectively measures the elastic dynamic modulus at a small strain (at the cure temperature) we can say that the elastic modulus at low strain increases with filler loading.

The variation of relative maximum torque with starch loading is shown in *Figure 5*. The data is compared to the Einstein equation without adhesion and with perfect adhesion. The data for the starch filled NR agrees well with the Einstein equation for perfect adhesion. Hence, the results indicate that the rubber:starch interaction significantly increases dynamic modulus at low strain amplitudes in the cured compounds.

The effect of starch content on curing times/rates of the compound is shown in *Figure 6*. The scorch time and cure time increases with increasing quantities of the starch in the formulation. The increase in scorch and cure time indicate that the starch interferes with the cure process. A similar effect is observed for silica filled natural rubber without silane[13], where the acidity of the filler retards the rate of cure and prolongs the cure time. It was observed that a mild acid solution, with pH 6, was produced when starch was mixed with distilled water. Hence the increase in cure time with increase in starch content could be due to this acidity, as observed in silica filled compounds.

Effect of Starch Loading on Hardness

Apart from curemeter torque, another method of indirectly assessing modulus at low strain is the hardness test. *Figure 7*, shows how the hardness increases with starch loading. It is found that the stiffness increases with the starch concentration and increases from 40 to 50, 56 and 60 Shore A respectively. Results obtained show that the experimental relative modulus data lies between the Einstein perfect adhesion model and the Einstein poor adhesion model.

Effect of Starch Loading on Tensile Strength

Figure 8 shows that the tensile strength decreases gradually with increase in filler loading. Strength of the compound decreases probably because of the weak interaction between the filler and the rubber, which means that stresses cannot be transferred from the matrix to the filler. This will lead to

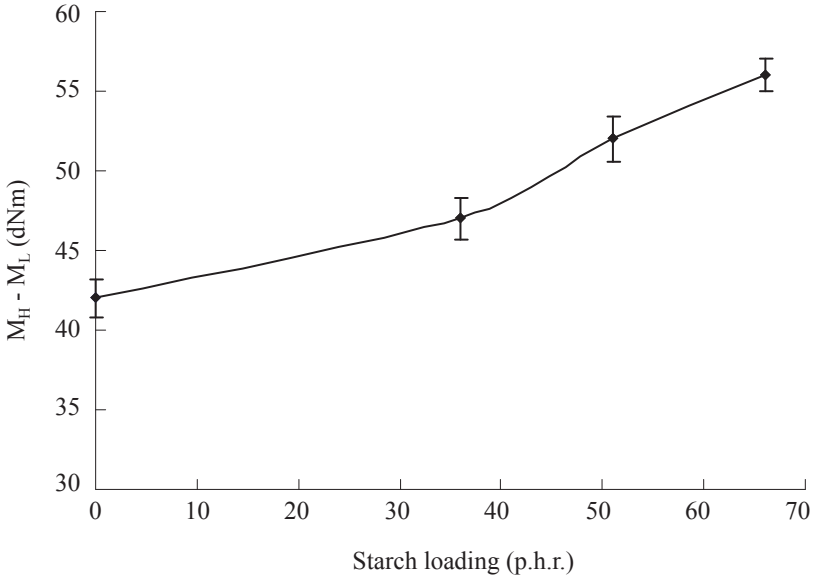

Figure 4. Influence of starch loading on curemeter torque properties of the natural rubber compound.

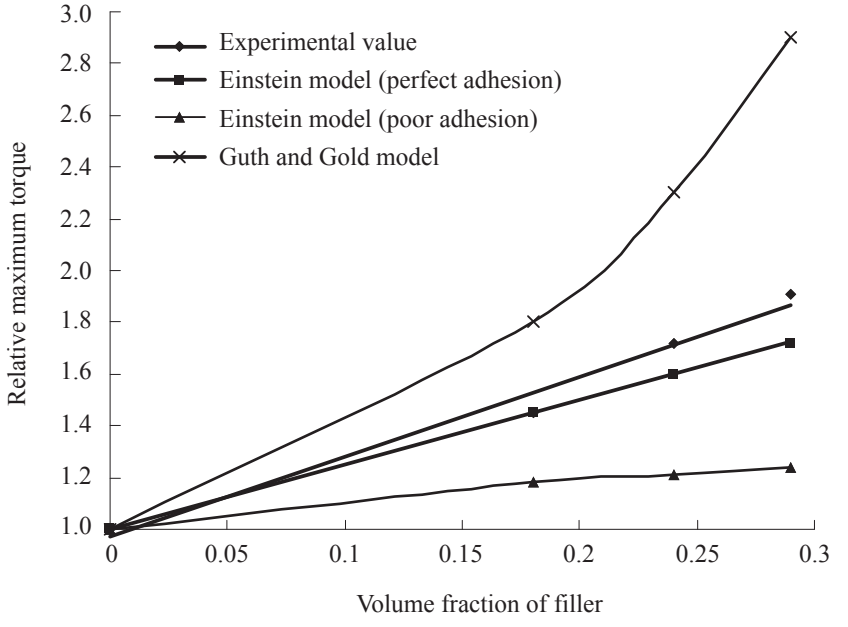

Figure 5. Plot of relative of maximum torque against volume fraction of starch in the natural rubber compound.

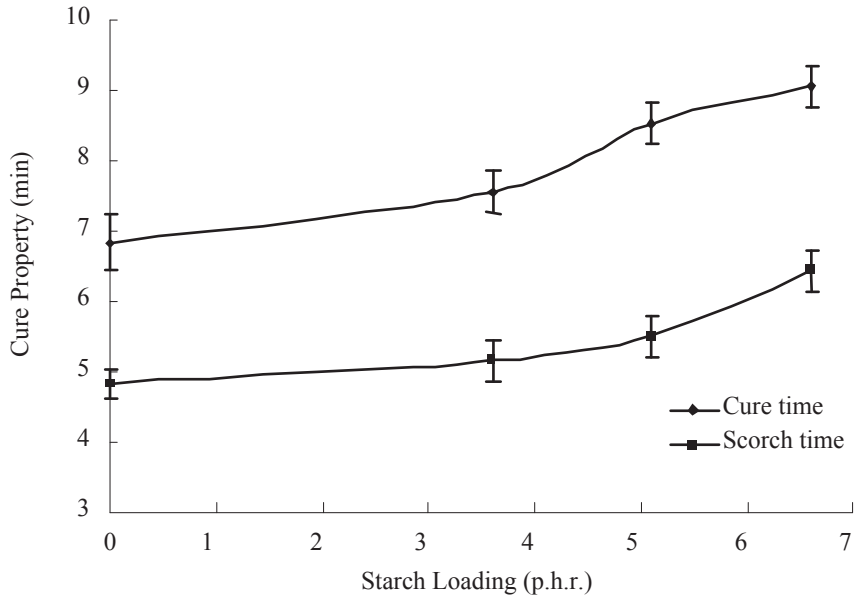

Figure 6. Influence of starch loading on cure properties of the natural rubber compound.

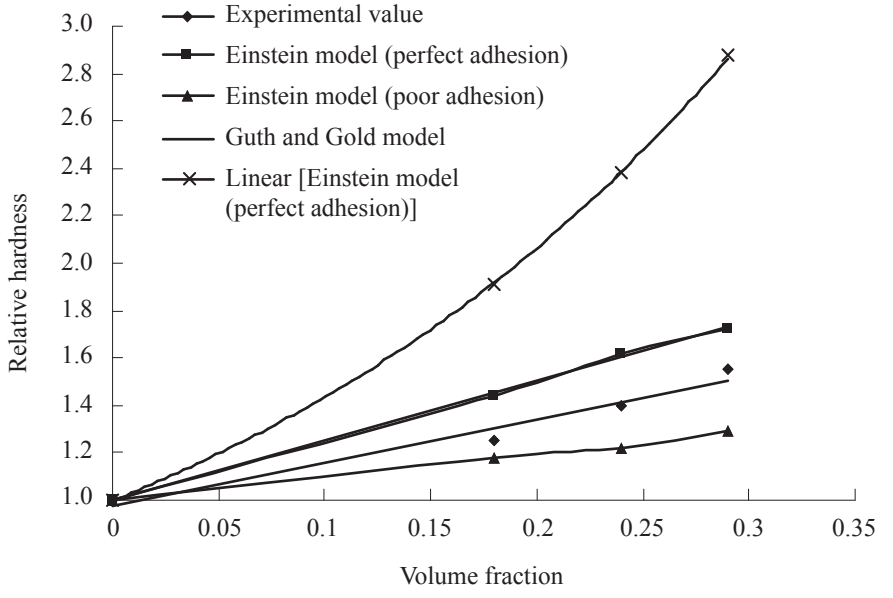

Figure 7. Influence of starch loading on hardness of the natural rubber compound.

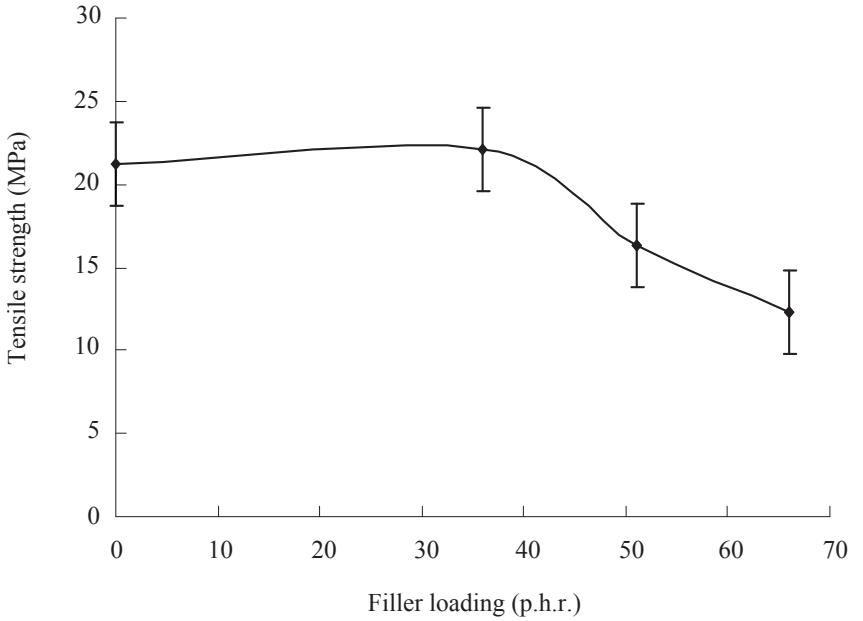

Figure 8. Variation of tensile strength as a function of starch loading in the natural rubber compound.

slippage occurring at the interface between the rubber matrix and the filler. Slippage of the rubber chains around the surface of the starch particles may help to equalise stresses, delaying crack initiation and hence, increasing strength. However, as the extension increases, further debonding may occur. Evidence for debonding is indicated by the micrographs of the tensile fracture surfaces shown in *Figures 9* and *10*. The micrographs show some loose starch particles and rounded holes, the size and shape of starch particles, indicating that dewetting of starch from the matrix had occurred. The debonding and void formation means that the stress the sample is exposed to is effectively only being supported by the rubber matrix. As the filler loading increases, there is a smaller cross section of the rubber available to support the load and hence, failure of the sample is likely to occur at a lower stress and strain.

However, *Figure 8* shows that the tensile strength of the compound containing 36 p.h.r. starch is fairly similar to that of the compound containing the same loading of carbon black, even though there is a great difference in stiffness. It is likely that the relatively high strength observed, despite the considerable debonding that is likely to occur, is due to strain crystallisation in the rubber.

Effect of Starch Loading on Tensile Modulus

Figure 11 shows stress-strain curves for unfilled, starch filled and carbon black (N660) filled compounds. The curves for the starch filled compounds are between those of the unfilled and carbon black filled compounds. The stress – strain curves of the unfilled and starch filled compounds show a steep increase in stress up to about 10% elongation but then

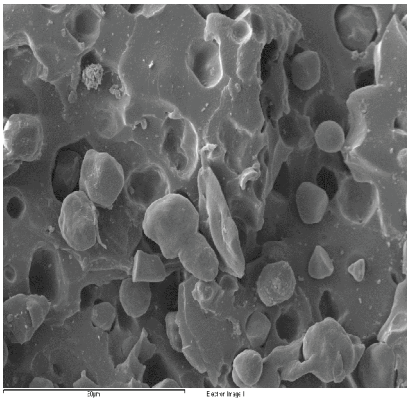

Figure 9. SEM micrograph of tensile fracture surface (36 p.h.r. starch).

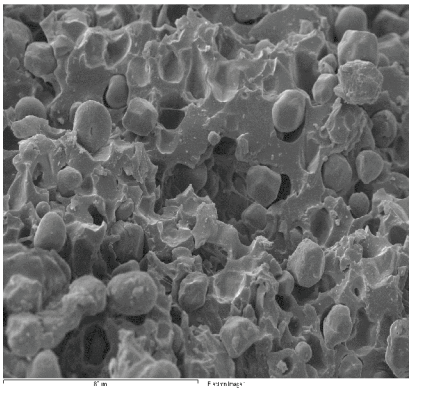

Figure 10. SEM micrograph of tensile fracture surface (51 p.h.r. starch).

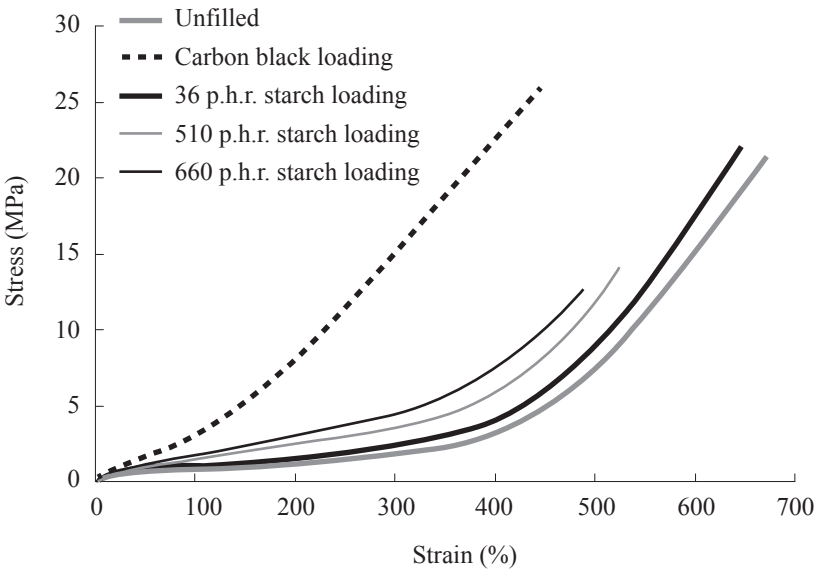

Figure 11. Effect of starch loading and carbon black filler on the tensile stress – strain curve of the natural rubber compound.

only a gradual increase in stress with increase in strain, until much higher elongations are reached (300 to 400% elongation) and the stress then rises more steeply. The steep upward curve in stress at high elongations is likely to be due to strain crystallisation and the fact that the finite extension of chains between crosslinks is being approached. *Figure 11* shows that this steep upward trend in stress starts at lower elongations as the starch content increases. The apparent shift in the curve to lower elongations is presumably due to the hydrodynamic effect of the filler, which results in strain amplification in the rubber matrix.

Figure 11 shows that although there is a general increase in stress with increase in starch content, even the most highly filled starch compound is a lot less stiff than the carbon black filled compound. The high stiffness of the carbon black filled compound is due to the strong interaction between carbon black and the rubber and the large surface area of the filler available for interaction with the rubber. The fact that the starch filled compounds are much less stiff indicates that there is probably a weak interaction between the starch and the rubber.

As with the viscosity results, it is possible to compare values of relative modulus with values derived from models in order to investigate the strength of the starch:rubber interaction. There are examples in the literature of applying these models to filled polymer systems to indicate the strength of the polymer filler interaction. Maiti *et al.*[5] found that polyolefin (i-PP) filled with untreated $CaCO_3$ fitted the Einstein Model without adhesion, due to there being no chemical and little physical interaction between the polymer matrix and filler. Bliznakov *et al*.[2] in their study of kaolin filled polypropylene also observed poor adhesion, where the polymer matrix slips by the filler particles. Tavman[4], in his study of aluminium particle filled high density polyethylene (HDPE), found that the Einstein equation for perfect adhesion was valid up to 12% elongation, but not at higher elongations. He concluded that, in the case of poor adhesion, the interfacial bond may break when a load is applied beyond a particular level. Bilikiaris *et al*.[14] proposed that the numerator of ϕ in the Einstein equation could have a value of 1 where there was poor adhesion and increase to higher than 2.5 when there was very strong adhesion. In his work he found that a value of 4.5 for the numerator of ϕ fitted the data and he attributed this to very strong adhesion between SiO_2 and PP grafted with maleic anhydride and to the high specific surface area of the filler, which is not taken into account by the Einstein model.

However, for rubber compounds, as well as the effect of the elastomer:filler interaction, the modulus of the compound is strongly influenced by the chemically crosslinked network. The crosslinking becomes increasingly important as the strain increases and chain segments are significantly extended. For this reason, where we are interested in the effect of rubber:filler interaction, it is better to look at the modulus behaviour at relatively low elongations.

The extent of adhesion between starch and rubber was evaluated at 10%, 30%, 50% and 100% elongation by comparing to the Einstein perfect and poor adhesion models. The results obtained show that the experimental relative modulus data lies between the Einstein perfect adhesion model and the Einstein poor adhesion model (*Figures 13, 14* and *15*). However, as elongation increases the experimental data moves closer to the line for the poor adhesion model, indicating that the extent of adhesion decreases as the elongation increases.

Figure 15 shows that the experimental data for 100% modulus almost fits the Einstein equation for poor adhesion but shows higher levels of stress than the Sato model for poor

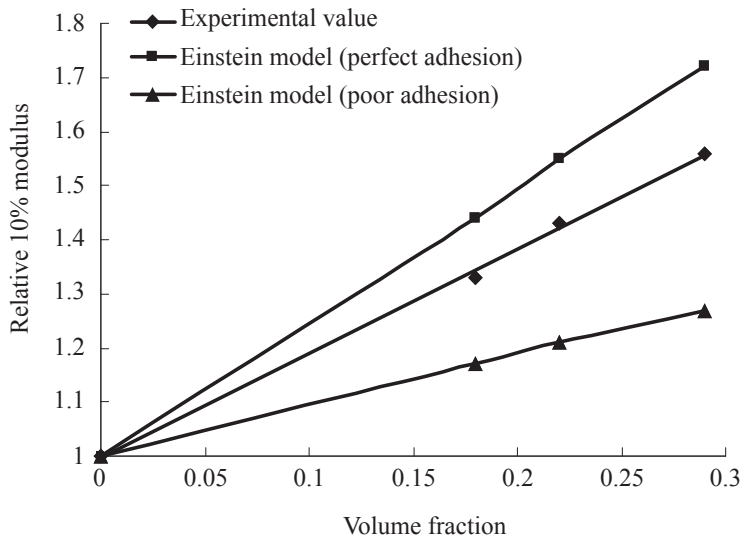

Figure 12. Plot of relative modulus against volume fraction of starch in the natural rubber compound at 10% elongation.

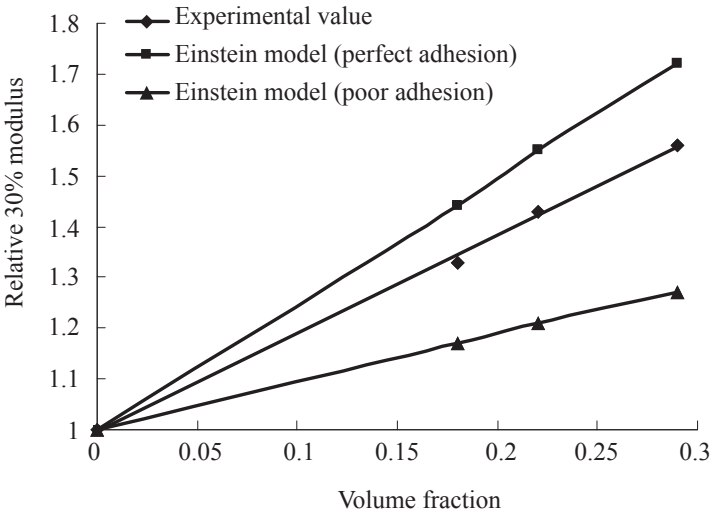

Figure 13. Plot of relative modulus against volume fraction of starch in the natural rubber compound at 30% elongation.

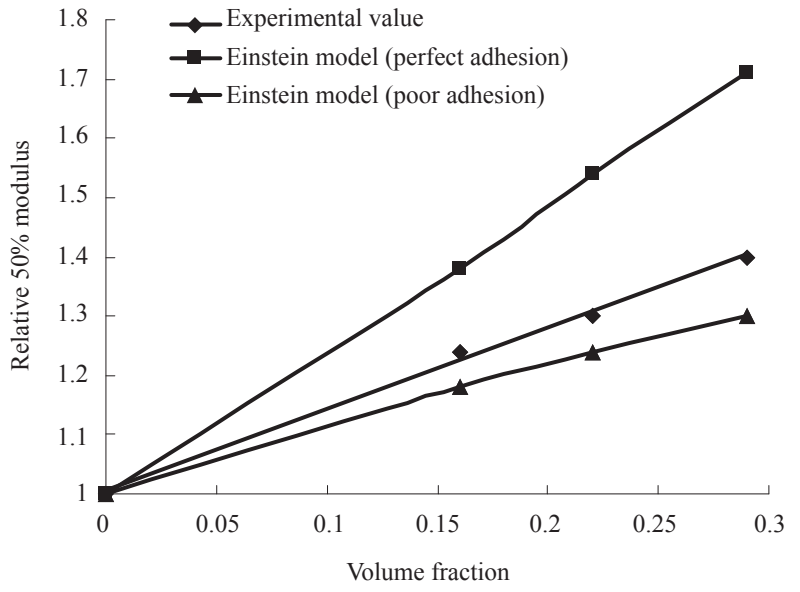

Figure 14. Plot of relative modulus against volume fraction of starch in the natural rubber compound at 50% elongation.

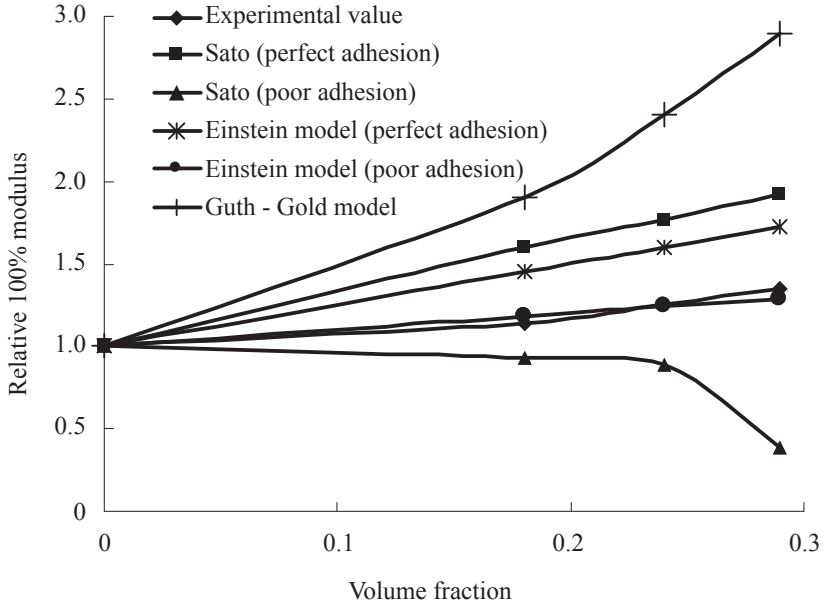

Figure 15. Plot of relative 100% modulus against volume fraction of starch in the natural rubber compound.

adhesion. The result suggests that there is a little adhesion between the starch and rubber, but probably enough to avoid the debonding and void formation suggested by the Sato model, at least at this level of elongation.

It appears from the results that decreases in modulus resulting from an incremental increase in elongation are therefore, generally related to the number of linkages broken in that interval of elongation. This result seems to support the idea of Medalia[15] who considers that there is a progressive increase in bond breakage with increasing levels of strain. Hence, the results obtained, reveal that the extent of adhesion is generally dependent on the strain as was observed in the viscoelasticity results earlier.

CONCLUSIONS

In general, the study shows relatively poor reinforcement of natural rubber by starch, resulting in low stiffness and strength compared to compounds filled to a similar volume fraction with carbon black. The poor reinforcement is due to difference in polarity as starch is hydrophilic and natural rubber is hydrophobic as well as large particle size of starch which is also round and smooth in shape.

The extent of adhesion between starch and rubber depends on the strain applied. Good adhesion between the starch and the rubber is obtained at strain amplitudes, below about 50% elongation (agreeing with the Einstein model of perfect adhesion). At strains higher than 50%, poor adhesion leads to debonding of starch from the rubber and consequently lower stiffness and strength is observed than carbon black filled compounds. Hence, it is expected that greater reinforcement could be obtained by increasing the adhesion of starch to the rubber and reducing its particle size.

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