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Surface Morphology and Tensile Strength of Natural Rubber Films Filled with Sulphur Free Lignin Derived from Rubberwood

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Lignin derived from rubberwood was added to natural rubber latex as a filler and its influence in affecting the surface morphology and strength of the resulting films was investigated via *scanning electron microscopy, tensile strength measurements and XRD analysis. The SEM results indicated random dispersion of lignin in the unaged lignin filled rubber films, in which most films exhibited rougher and incoherent surfaces in comparison to control rubber films. Upon ageing at 70 °C for seven days, the lignin filled rubber films displayed changes from relatively rougher surfaces to smoother surfaces. Results suggest that the most obvious influence of lignin is the increment in tensile strength. This increment in strength is particularly obvious with lignin filled rubber films at loading of 10 and 12 weight percent. Consequent increase in tensile strength values after ageing is shown by lignin filled rubber films at a 12% loading. The results of crosslink density obtained from stress-strain data infer that the addition of lignin increased chain entanglement in unaged films as indicated by the C_2 values. Further analysis using XRD revealed observable changes in the amorphous rubber peak at $2\theta = 18$.*

Keywords: rubber; lignin; tensile strength; SEM; crosslink density

Lignin is a complex biopolymer found in the structure of wood. Lignin is polymerised mainly from three monomers called monolignols, namely, p-coumaryalcohol, coniferyl alcohol and sinapyl alcohol. Types of lignin are categorised according to their content of monolignols[1]. These monolignols are propylphenol derivatives with a difference in the number of methoxy groups attached to the main ring as shown in *Figure 1*.

In order for lignin to be utilised as an additive or a filler in rubber, one of the common features for lignin incorporation in rubber compounding is the addition of lignin in the form of rubber latex coprecipitate[2,3]. The incorporation of lignin into dry rubber does not lead to the desirable reinforcement.

Sagajllo[4] described that the incorporation of lignin into rubber by means of conventional

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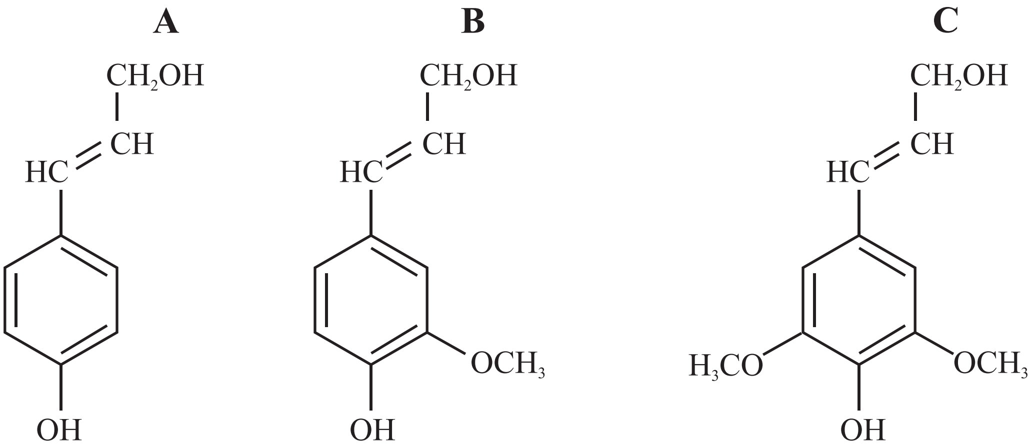

Figure 1.Monomer forming lignin polymer. A: p-coumaryl alcohol (4-hydroxyphenyl), B: Coniferyl alcohol (Guaicyl), C: Sinapyl alcohol (Syringyl)

mill mixing techniques did not produce reinforced rubber whereas reinforcement is observed when the lignin-rubber stock is obtained *via* latex coprecipitation or coagulating the lignin-latex mixture so as to form rubber masterbatch. The main reason for using lignin-latex coprecipitate is the occurrence of lignin binding or aggregation during dry rubber mixing. The binding of lignin particles to one another by hydrogen bonds leads to agglomeration, preventing the dispersion of lignin particles in rubber during dry rubber mixing[5].

Sirianni and Puddington[6] suggested that non-lignin constituents could prevent lignin from dispersing into rubber during milling by acting as an agglomerating agent. This was overcome by laundering or cleaning the lignin through repeated precipitation and rinsing. Nonetheless, in order for lignin to be feasibly utilised in rubber, an approach of preparation by means of latex coprecipitate is described.

In spite of numerous works conducted to show the good use of lignin in rubber, properties of the rubber films acquired from mixing of lignin in rubber latex prior to rubber masterbatch precipitation are rarely described. Thus, the present investigation describes the use of lignin derived from rubber wood as filler in unvulcanised natural rubber latex. Subsequently, rubber films obtained are characterised to indicate the influence of lignin in affecting the surface morphology and tensile strength of the resulting lignin filled rubber film.

In the present study, the strength of rubber films is shown to be increased by the presence of lignin at loadings of 10 and 12 weight percent. Changes in the rubber film surface morphology influenced by the presence of lignin are observed using scanning electron microscopy and it is shown that lignin is randomly dispersed with incoherent film formation at the surfaces of the lignin filled rubber films. In order to substantiate observed improvements in tensile strength of lignin filled rubber films, crosslink density and the elastic constantare determined from the stress-strain data, while changes in the rubber amourphous structure are observed *via* XRD thin film analysis.

MATERIALS AND METHODS

Preparation of Natural Rubber Latex Film

The lignin used in the present study was derived from rubber wood (RRIM Clone Series 2000) by means of alkaline digestion at 150°C and pressure of four bars for 30 minutes. Crude lignin solubilised in the digestion liquor was further precipitated and isolated by centrifugation at 15 000 × g. The precipitated lignin was further processed by crushing in liquid nitrogen to acquire a particle size which is compatible with natural rubber latex. Details of the lignin derivation from rubber wood are described elsewhere[7]. Properties of lignin used in the present study are tabulated in *Table 1*.

In order to prepare lignin filled rubber film, lignin powder without dispersing agent was added directly into commercial grade unvulcanised high ammonia natural rubber latex which was prior diluted with distilled water to a solid content of 30 percent. The mixture was then stirred in a baffled circular vessel using a 45° pitched blade impeller at a speed of 200 r.p.m. Excessive bubbles were removed prior to film moulding by filtering through a stainless steel filter (250 mesh size).

A glass mould was used to obtain films of approximately 0.5 mm in thickness. Drying was carried out at ambient room temperature until sufficient dryness and followed by oven heating at 70°C overnight. Six different mixtures were prepared by varying the lignin loadings per dry rubber weight. The minimum loading was 2 wt. % and varied in 2% increments until the maximum loading of 12 weight percent. In the present work, flocculation of the rubber latex was observed above 12 wt. % lignin loading.

Ageing

The effect of elevated temperature on the lignin filled rubber film was determined by exposing the samples to heat at a temperature of 70°C for seven days in an air circulating oven.

Scanning Electron Microscopy (SEM)

The SEM analyses of the films were conducted on a FESEM JSM 6701F (JEOL, Japan). The sample was placed onto a specimen stub and coated with platinum evaporative coating under high vacuum and later bombarded with 2ke V at 15 mm working

TABLE 1. PROPERTIES OF LIGNIN

Parameters	Properties
Appearance	Powder
Solubility	Soluble in aqueous alkaline
Particle size	3.6 µm (Particle size analyser)
Sulphur content	Undetectable (CNS Elemental Analyser)

distance. The rubber film samples were analysed for surface morphological changes before and after ageing.

Tensile Strength Measurements and Crosslink Density (η_{phys}) Determination

Dumbbell test pieces were prepared using the type 2 die as described in the *ISO 37* standard[8]. Measurements of tensile strength were carried out on five samples using a Universal Testing Machine QC 505 (Protest, Taiwan) at a crosshead speed of 500 mm/min with a 500N load cell. Median values were used for data analysis.

The degree of physical crosslink density was determined from stress-strain data[9] using the Mooney-Rivlin equation as shown in *Equation 1*, where F is the force to stretch the rubber, A_0 represents the cross sectional area of the original sample, and λ is the extension ratio, while C_1 and C_2 are constants. The value of stress (F/A_0) is denoted by the symbol σ.

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \qquad \ldots 1$$

Using data from stress-strain measurement in the region of $1/\lambda = 0.5$ to 0.7, the curve of $\sigma/(\lambda\text{-}\lambda^{-2})$ against $1/\lambda$is plotted according to *Equation 2*, where the constants C_1 and C_2 can be obtained. $2C_1$ is the x-axis intercept of the curve and $2C_2$ is the slope of the curve. From the plot, the curve fitted linear trend line is generated to determine the crosslink density (η_{phys}).

$$\frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + \frac{2C_2}{\lambda} \qquad \ldots 2$$

The crosslink density (η_{phys}) is calculated using *Equation 3* where R is the gas constant (8.314 $J.Mole^{-1}K^{-1}$) and T is the absolute temperature.

$$\eta_{phys} = \frac{C_1}{RT} \qquad \ldots 3$$

X-Ray Diffraction (XRD) Analyses

XRD analyses were conducted using a D8 Advance X-ray Diffractometer (Bruker, Germany) at CuKα of 1.54A radiation operating at 40 kV and 40 mA. Powder XRD analysis with a scan range of 5° to 70° was conducted for the lignin sample with a phi rotation of 15 rpm/min. Utilising the Bruker Diffrac.eva software, the percentages of crystallinity was measured as a ratio of crystalline area to total area on the diffractogram, while the crystallite size was measured using the Scherrer equation. The peak width is defined using Full Width at Half Minimum (FWHM) method. Thin film analysis using a Göbel mirror attachment was also conducted for the control and lignin filled rubber films with a scan range from 2° to 50° in a step size of 0.004°.

RESULTS AND DISCUSSION

Surface Morphology

With respect to its inherent nature as a thin film, surface morphology and the level of coherency play an important part in affecting the strength of rubber films. Morphology of the rubber film surfaces reflects the dispersibility of lignin in rubber. Surface morphology of the rubber films observed *via* SEM, showed differences between the rubber films as illustrated in *Figures 2* to *4*. The unaged control rubber films without the addition of lignin as shown in *Figure 2* exhibited larger undulation in contrast to the aged control sample.

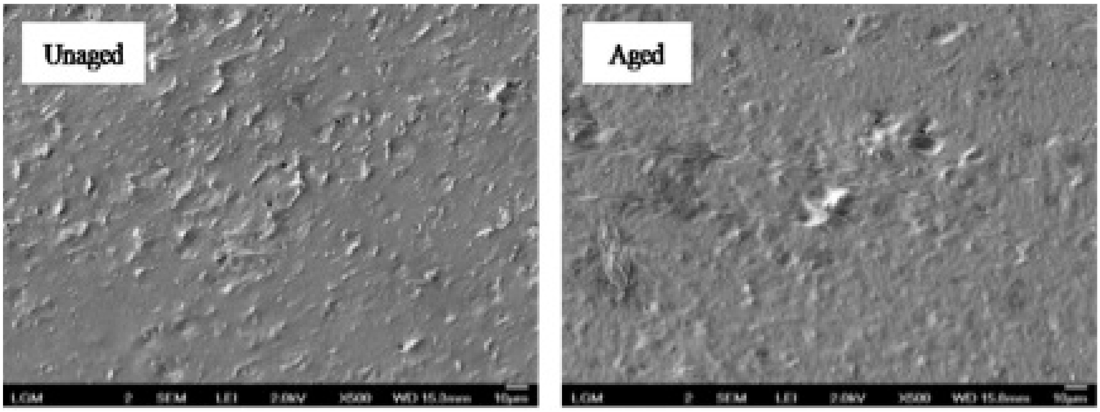

Figure 2. Surface morphology of control (0% lignin loading) before and after ageing.

From the SEM micrograph in *Figure 3*, lignin is observed as globules or particles at the surface of the rubber films and is randomly distributed. This indicates that lignin is not well dispersed in the rubber film. The lignin filled rubber film at 2 wt. % loading did not show any particles of lignin on its surface. However, the film is rougher than the control rubber sample with more pronounced undulating curves. At loadings of 4 wt. % and higher, particles of lignin are very clearly accompanied by cracks and grooves. The formation of surface cracks suggests the occurrence of phase separation between the hydrophilic lignin filler and the hydrophobic rubber matrix.

The SEM analyses on the rubber films before and after ageing further reveal marked differences between the lignin filled rubber films at various loadings. The lignin particles or globules have completely disappeared from the film surfaces after ageing, as shown in *Figure 4*. The aged lignin filled rubber films also exhibit pronounced undulating voids and rough surfaces. Interestingly however, occurrences of rough surfaces are less pronounced at lignin loadings of 10 and 12 weight percent. The reason for these changes is still unclear in the present investigation.

Tensile Strength

Figure 5 shows the stress-strain curves for the rubber films. In general, typical rubber non-linear curves were obtained for both the control rubber film and lignin filled rubber films. The results suggest that the most obvious influence of lignin is the increment in their tensile strength. The increment in strength is particularly obvious with lignin filled rubber films at loadings of 10 and 12 percent. Reduction in the strength is also observed for the rubber films with 2 wt. % and 6 wt. % lignin loading.

These discrepancies of the strengths observed for the lignin filled rubber film between trends in conventional rubber filler loadings is suggested to occur due to random dispersion and micro phase separation of lignin in the rubber. This is owing to the general notion that the propensity of filler to disperse in a polymer matrix influences the resulting mechanical properties[10]. With imperfect filler dispersion, load transfer from matrix to the filler particle is poor.

The ultimate formation of the filler network is important at a macroscopic length, in which a high filler loading is anticipated to

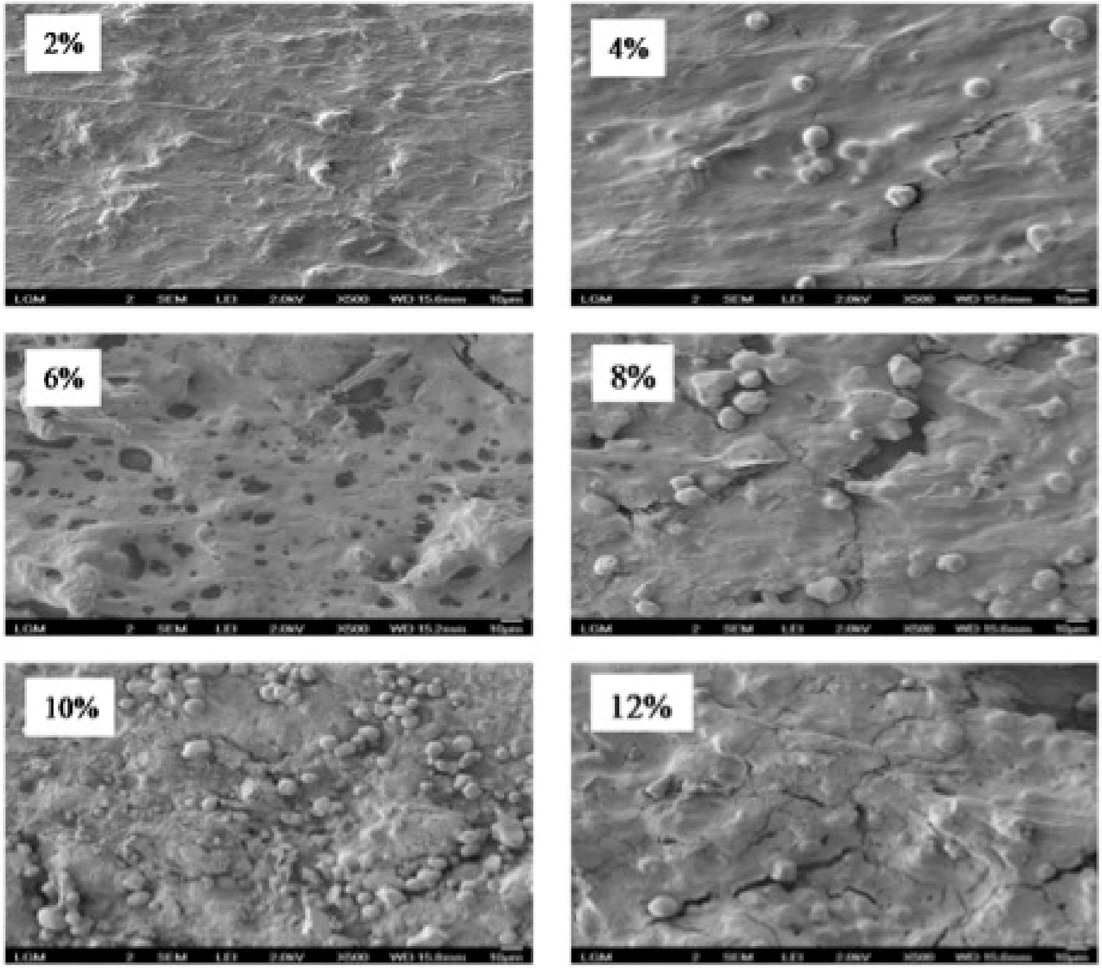

Figure 3. Surface morphology of lignin filled rubber films before ageing.

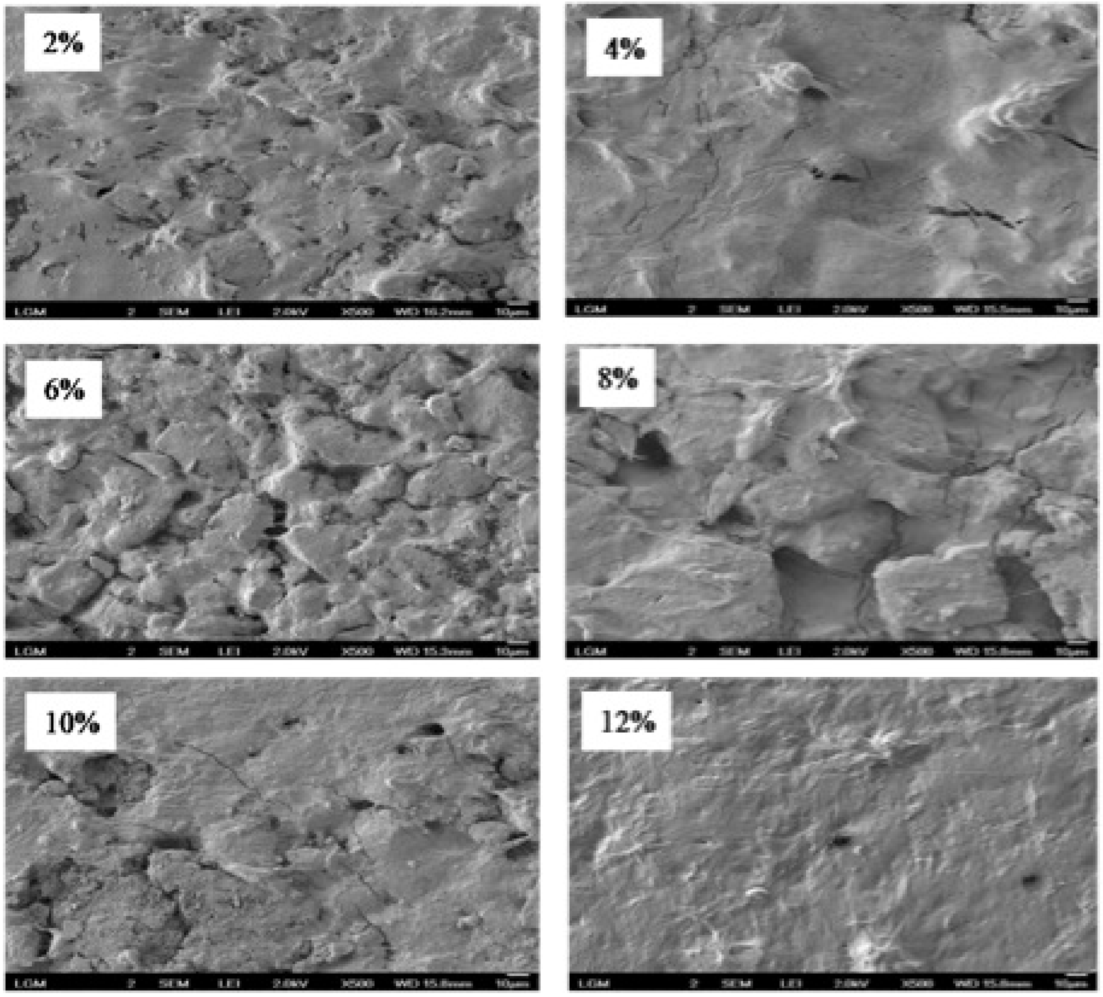

Figure 4. Surface morphology of lignin filled rubber films after ageing.

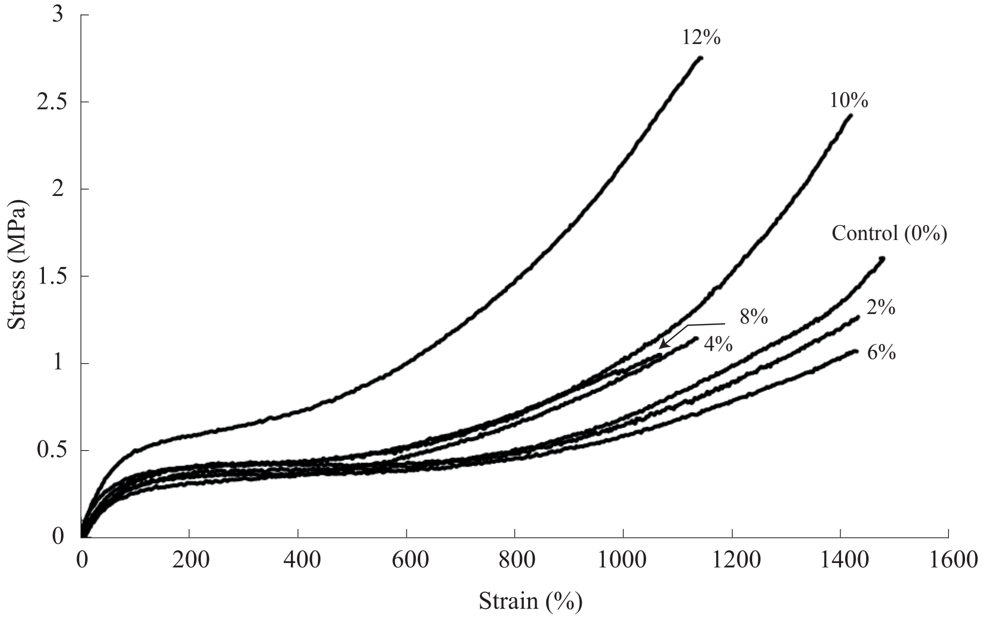

Figure 5. Stress-strain curve relationship for lignin filled rubber films with varying lignin weight percent loading per dry rubber content.

have a greater tendency to form overlapped filler aggregates which contribute to reinforcement[11]. Thus, it is anticipated that when the hydrophilic lignin fails to form a continuous network within the rubber matrix, the load transfer during uniaxial tensile loading is poor. As a consequence, reduced strength is observed when lignin is added in less than 10 wt. % loading which may prove to be the critical loading for lignin in rubber films.

Lignin also seemed to influence the rubber films strength when aged at 70°C for seven days. It provided protection against rubber deterioration by heat as demonstrated by comparison of the maximum tensile strength values of the rubber films before and after ageing, as illustrated in *Figure 6*. The higher lignin filled rubber films considerably retained their tensile strength when compared to the control rubber film. All samples with 10 wt. % and 20 wt. % lignin give a higher tensile strength than the control. It is most plausible that the propylphenol structure of lignin with hydroxyl and methoxyl groups confer a certain level of protection against heat ageing. However, the role of such structures in promoting the increment in tensile strength after ageing was not determined.

Crosslink Density (η_{phys})

In the present investigation, stress-strain measurement was adopted as the technique to determine crosslink density instead of swelling measurements. Although swelling measurements are popular for the

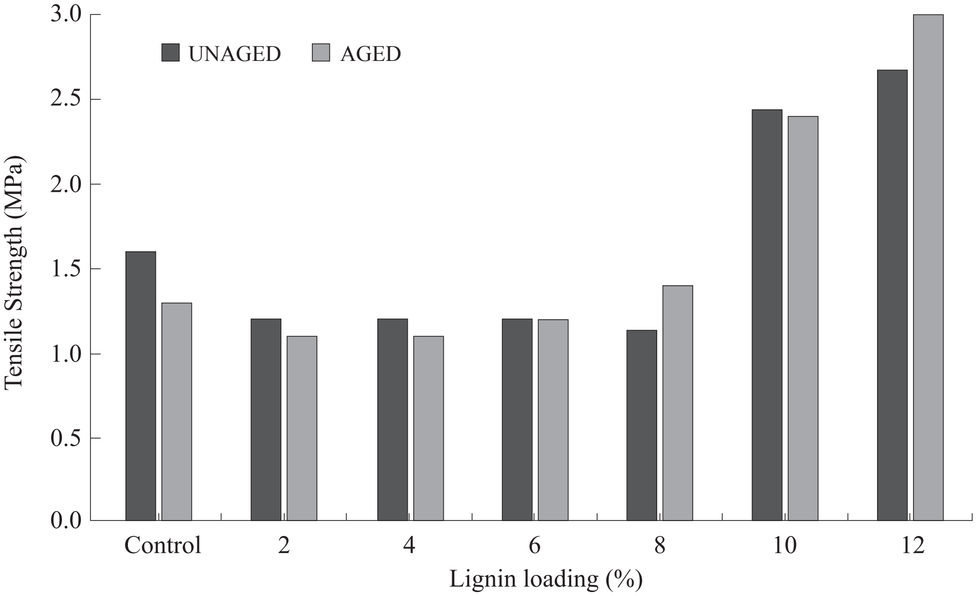

Figure 6. The influence of lignin loading on the rubber films tensile strength before and after ageing.

determination of crosslink density, in the context of the present study, ambiguity may arise owing to the insolubility of lignin in the rubber swelling solvent and its solvent-polymer interaction parameter of the lignin filled rubber film is unknown. In most studies on crosslink density, the interaction between solvent-polymer is assumed to be constant, but the assumption is generally proven incorrect from experimental and theoretical works[12]. Therefore, in the present study data, from stress-strain measurements for the unaged and aged rubber films are used to construct plots of $\sigma/(\lambda\text{-}\lambda^{-2})$ against $1/\lambda$, as shown in *Figures 7* and *8* in order to obtain crosslink densities.

The crosslink density (η_{phys}) is expressed in terms of moles of effective network chains per cubic centimetre of rubber sample. The results of crosslink densities with increasing lignin loadings are shown in *Table 2*. The values obtained for the control sample at 0 wt. % lignin loading, is relatively close to the reported crosslink density value of 4.91×10^{-5} mol/cm^3 for unvulcanised raw rubber sheet[13]. In contrast to the control samples, it is observed that the crosslink densities are fairly reduced with the addition of lignin in both the aged and unaged films. The results of elastic constant, C_2, indicative of the extent of chain entanglements, increase with increasing lignin loading in unaged films. However, the results of crosslink densities and elastic constant do not reflect the increment in tensile strength of films at lignin loadings of 10 wt. % and 12 wt. % after ageing.

Nonetheless, these results infer that the addition of sulphur free lignin does not promote crosslinking in the rubber, which is in agreement with the earlier work by Tibenham and Grace[14] suggesting that primary bond formation is not likely to occur between lignin

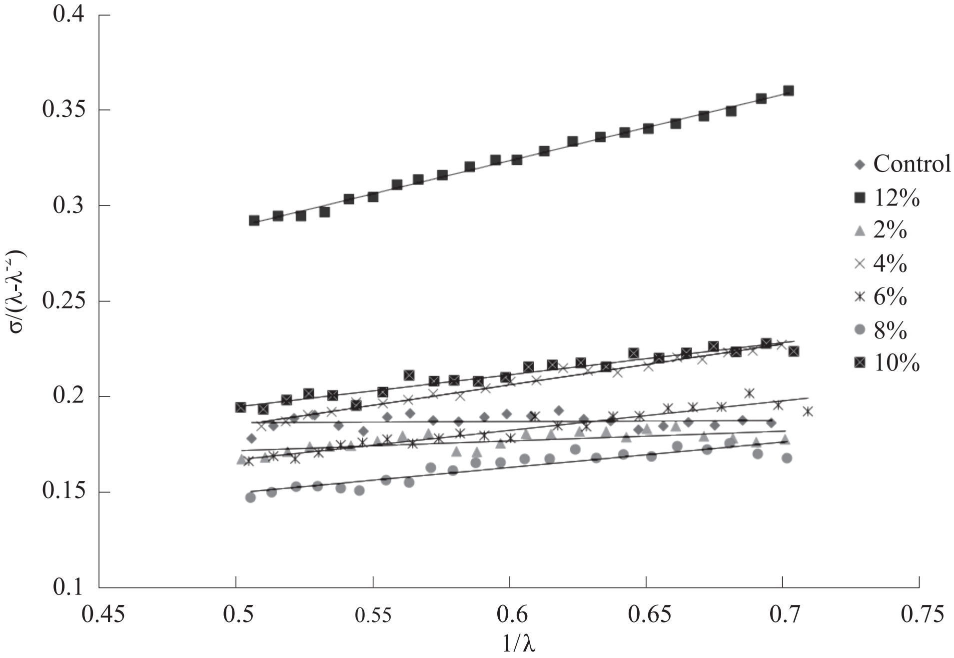

Figure 7. Plot of $\sigma/(\lambda\text{-}\lambda^{-2})$ *against* $1/\lambda$ *for unaged lignin filled rubber films.*

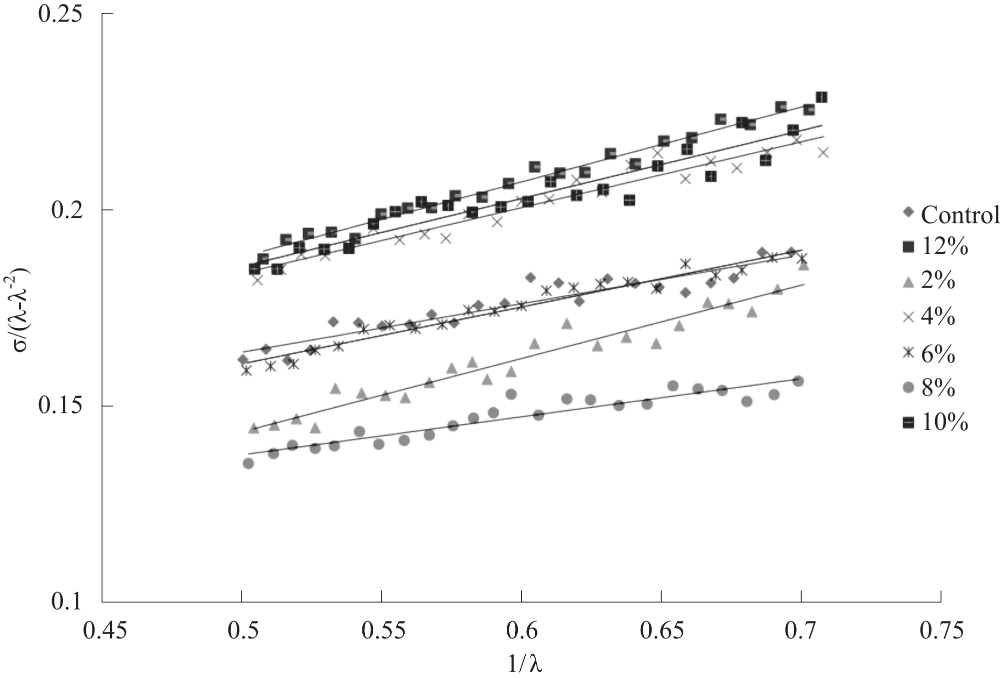

Figure 8. Plot of $\sigma/(\lambda\text{-}\lambda^{-2})$ *against* $1/\lambda$ *for aged lignin filled rubber films.*

TABLE 2. RESULTS OF CROSSLINK DENSITY DETERMINATION

Loading (%)	**Elastic constant, C_2**		**Crosslink density (× 10^{-5}mol/cm^3)**	
	Unaged	**Aged**	**Unaged**	**Aged**
0	0.005	0.123	4.03	2.22
2	0.051	0.187	3.19	1.08
4	0.213	0.167	1.72	2.18
6	0.155	0.145	1.96	1.94
8	0.133	0.097	1.83	1.96
10	0.168	0.173	2.42	2.16
12	0.346	0.191	2.53	2.03
X-Y Correlation Coefficients	0.82	0.23	-0.55	0.27

and rubber[14]. In contrast, the work by Gregorová *et al*[15]. using sulphur free lignin[15] in a natural rubber dry compound showed that lignin is capable of introducing crosslinking in vulcanised rubber during ageing. It is plausible that in order for lignin to influence the crosslinking during heat ageing, the presence of an existing sulphur network is most likely to be a prerequisite.

XRD Analysis

The lignin powder XRD analysis as shown in *Figure 9* indicates that the rubber wood lignin comprised amorphous and crystalline components. The percentage of crystallinity was approximately 65% with crystallite size of 75 nm. The lignin used in the present investigation is predominantly crystalline and proved to be different from the previous work by Sirianni *et al.* which described the reinforcement of rubber by highly amorphous lignin[16]. Such difference in crystallinity percentages may be attributed to dissimilarities in the processing technique to acquire the lignin or it is most probable that the lignin used in the present investigation was not in a pure form.

The XRD diffractograms obtained for the control rubber film and lignin filled rubber films are shown in *Figures 10* to *13*. The analyses were conducted to further characterise the variable influence of lignin on the strength of the rubber films, *i.e.* addition of lignin imparted a detrimental influence as exemplified by rubber films at 6 wt. % loading and imparted considerable improvement in tensile strength in rubber films with lignin loading of 10 and 12 weight percent. Qualitatively, the XRD analyses show a broad peak at $2\theta = 18°$ which is attributed to amorphous rubber. A slight shift in 2θ is observed around the amorphous region when lignin is present in the rubber. However, this occurrence is not observed at lignin loading of 12 weight percent. There is also a new peak at $2\theta = 31.5°$ observed at lignin loading of 12 wt. % which resembles the lignin powder XRD results. However, at relatively low counts such a peak cannot be used to associate the presence of crystalline components in the rubber film.

In the present study, it is shown that lignin favourably reinforces rubber films and the reinforcement is accompanied by the increase in physical entanglement as shown by increase

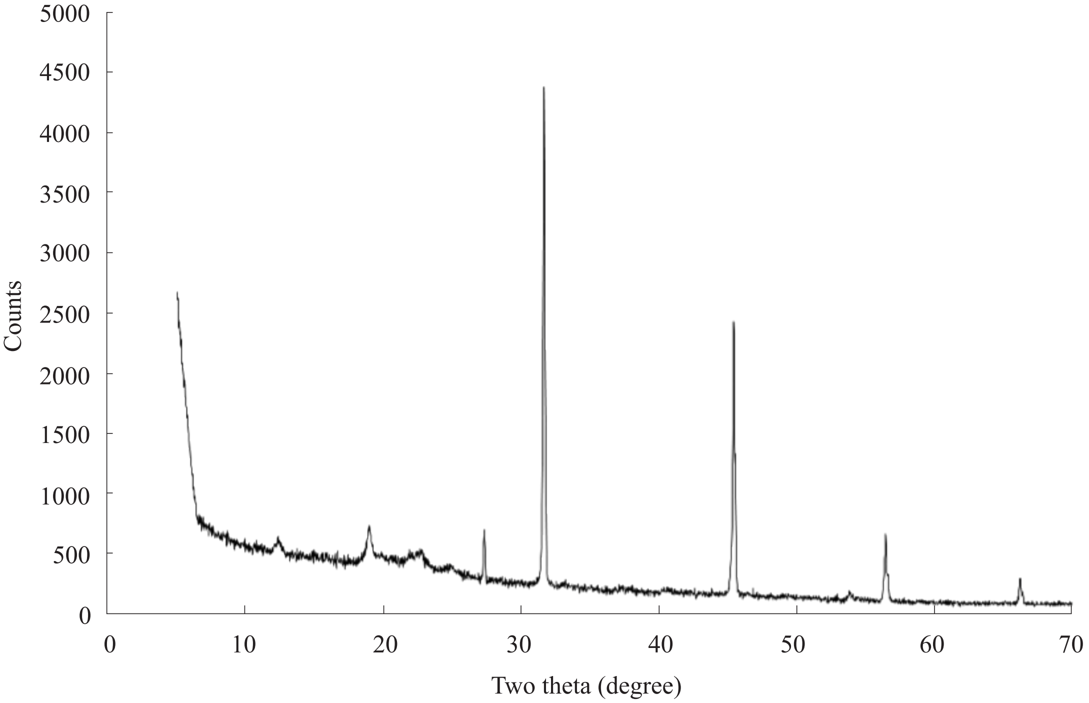

Figure 9. Powder X-ray diffractogram of lignin derived from rubberwood.

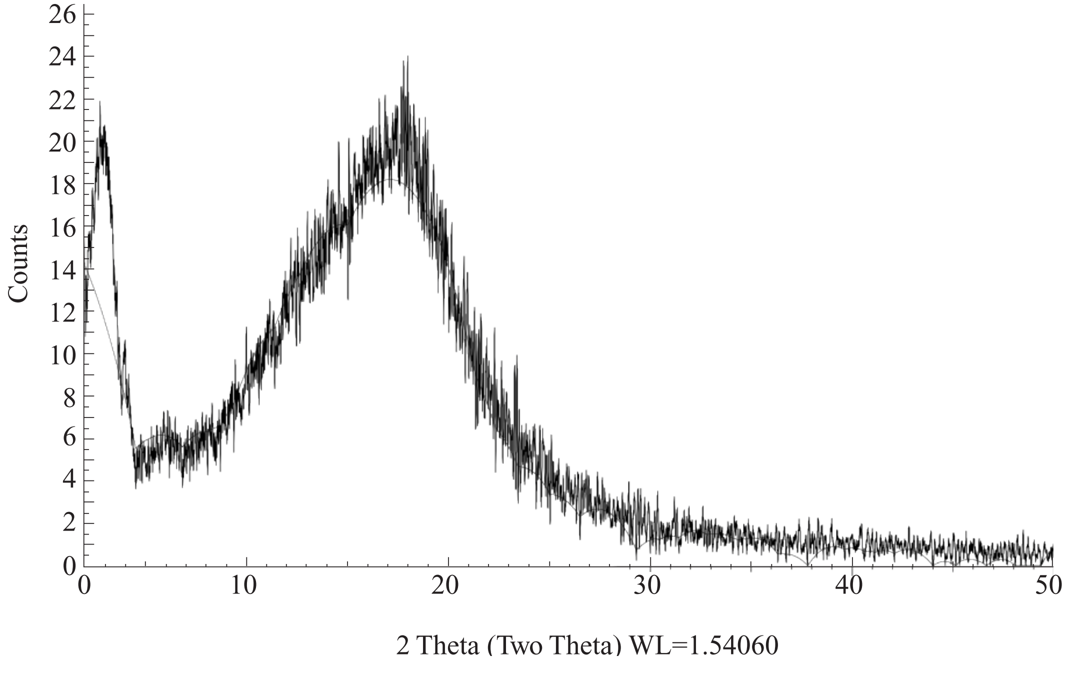

Figure 10. X-ray diffractogram of control rubber film.

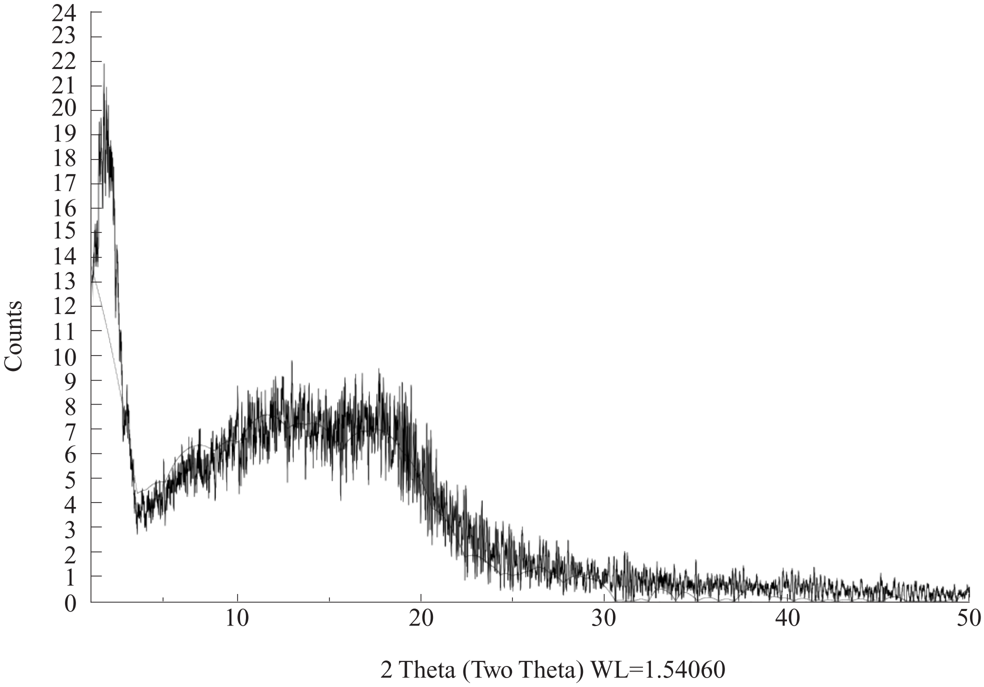

Figure 11. X-ray diffractogram of lignin filled rubber film at 6 wt. % loading.

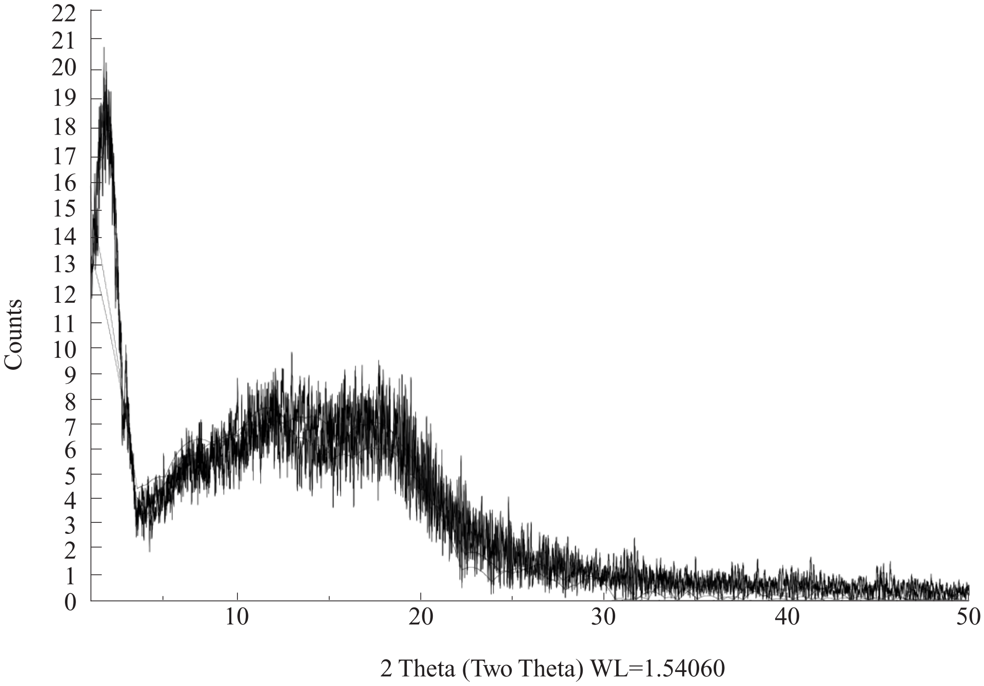

Figure 12. X-ray diffractogram of lignin filled rubber film at 10 wt. % loading.

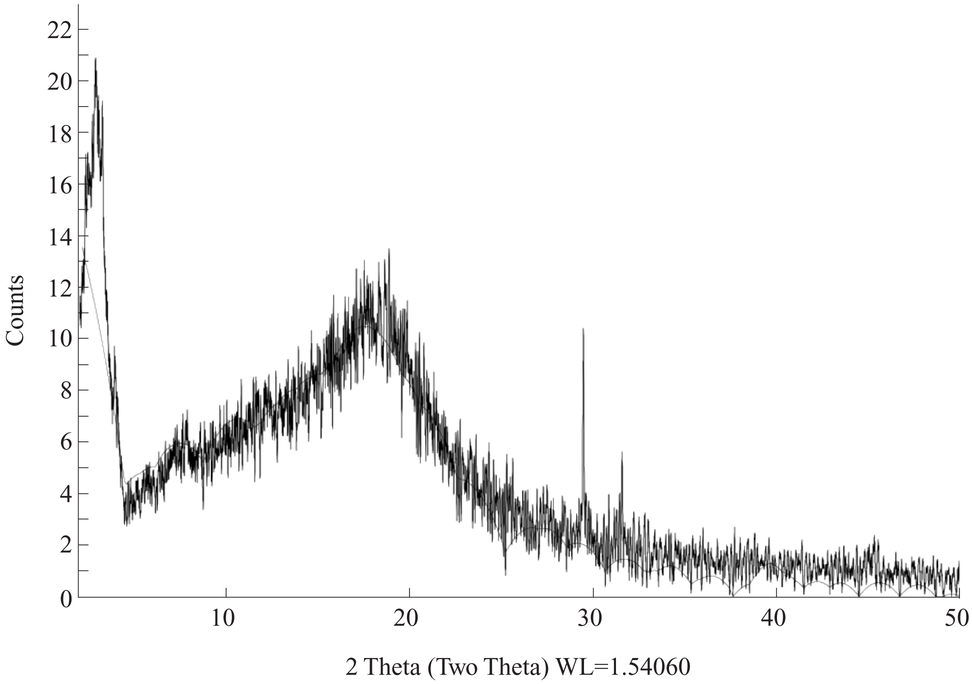

Figure 13. X-ray diffractogram of lignin filled rubber film at 12 wt. % loading.

in the C_2 values, while the XRD analyses reveal certain changes in the rubber amorphous structure. Despite appreciable reinforcement imparted by lignin in rubber particularly in the lignin filled films at 10 wt. % and 12 wt. % loadings, due to various influencing factors, the exact nature governing lignin reinforcement cannot be fully ascertained in the present study. It may be suggested that the reinforcement of lignin resembles the reinforcement of phenolic resin in rubber latex. In the reinforcement of latex using resins, Piccini[17] concluded that a simple combination of a resin with a hydrocarbon would not occur as the tendency is greater for the resin to combine with itself during post condensation and reinforcement is contributed to the finely divided state of the resin[17].

CONCLUSIONS

In the present investigation it is shown that the presence of lignin derived from rubber wood influences the surface morphology and strength of rubber films. The SEM results indicate poor dispersibility of lignin in the rubber film, in which most films exhibited rougher and incoherent surfaces relative to the control rubber film. The tensile strength of the lignin filled rubber films is shown to increase at lignin loadings higher than 10 and 12 weight percent. In unaged samples, the C_2 values increases with increasing lignin loading and the XRD analyses reveal certain changes in the rubber amorphous peak. However, due to various influencing factors, the exact nature governing lignin reinforcement cannot be fully ascertained in the present study. Nonetheless, for the purpose of utilising lignin as filler in rubber films to attain favourable improvement in strength, the minimum loading of lignin is proposed at 10 percent per dry weight rubber.

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