

Lignin Filled Unvulcanised Natural Rubber Latex: Effects of Lignin on Oil Resistance, Tensile Strength and Morphology of Rubber Films

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ABSTRACT : Relative to its synthetic counterpart, natural rubber has disadvantages such as low resistance to oil and solvents. Hence, the use of a material having polyphenols, such as lignin is anticipated to solve such problem. Lignin derived from rubber wood was added to natural rubber latex as filler with varying loading and its influence in affecting the oil resistance, tensile strength and morphology of the resulting films was investigated via tensile strength measurements, scanning and transmission electron microscopy respectively. The results show that oil resistance of lignin filled rubber latex films is enhanced with the addition of lignin above 2 wt% loading. The tensile strengths are increased by 60% and 73% at loading of 10 wt% and 12 wt% lignin respectively. The increase in tensile strength is accompanied with the increase in chain entanglement as indicated by the C_2 values and better dispersion of lignin in the rubber matrix as shown by morphological analysis using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Keywords -Rubber, lignin, tensile strength, SEM, TEM, crosslink density

I. INTRODUCTION

Lignin is a complex biopolymer found in the structure of wood. It is polymerized from three main monolignols, namely, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. These monolignols are propylphenol derivatives with difference in the number of methoxy groups attached to the main ring as shown in Figure 1. In its native form, lignin is categorized according to its content of monolignols [1]. For example, softwood lignin consists mostly of coniferyl alcohol.

Lignin is considered as a renewable material and finds its uses in a variety of applications such as mud mixture for oil well drilling, concrete composites, polymer additives and rubber fillers. However, little attention has been given on its hydrophilic properties to impart oil resistance in elastomers particularly natural rubber.

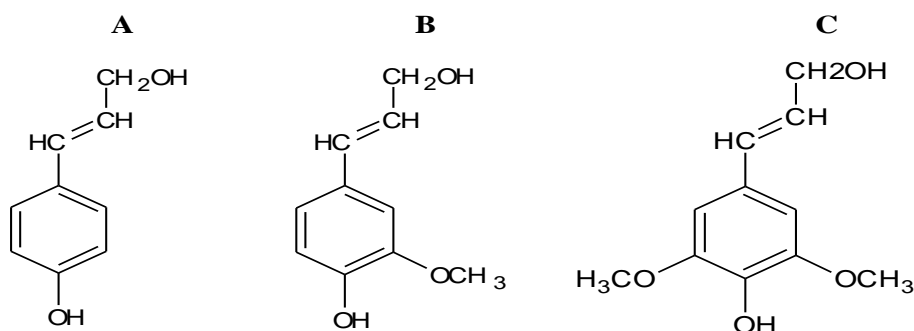


Figure 1: Monomer forming lignin polymer. A: p-coumaryl alcohol (4-hydroxyphenyl), B: Coniferyl alcohol (Guaicyl), C: Sinapyl alcohol (Syringyl)

In the application of lignin as rubber filler, 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]. However, the direct incorporation of lignin into dry rubber does not lead to the desirable reinforcement. This was reported by *Sagajlo*[4], where the incorporation of lignin into rubber by means of conventional mill mixing techniques did not produce reinforced rubber. On the other hand, reinforcement is observed when the lignin-rubber mixture was obtained via latex coprecipitation or coagulating the lignin-latex mixture so as to form rubber master-batch. The main reason for using lignin-latex coprecipitate is because of 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 Paddington[6] suggested that the non-lignin constituents could prevent lignin from dispersing into rubber during milling by acting as agglomerating agent. This was overcome by laundering or cleaning the lignin through repeated precipitation and rinsing. Nonetheless, in order for lignin to be feasibly incorporated in rubber, the technique of preparation by means of latex coprecipitate was described.

In spite of numerous works conducted to show the good use of lignin in rubber, the mechanical properties of the rubber films such as oil resistance and tensile acquired from the mixing of lignin in rubber latex prior to rubber masterbatch precipitation are rarely described. Furthermore, the use of lignin which is a hydrophilic macromolecule as a rubber filler to improve the oil resistance properties in unvulcanised natural rubber latex films has not been described. With adequate strength, such film materials is anticipated to produce a cost efficient oil resistant coating material and upon further co-precipitation, a new modified raw rubber comprising lignin as filler can be attained.

Thus the present investigation describes the use of lignin derived from rubber wood as filler in unvulcanised natural rubber latex. Subsequently, the films obtained were characterized to investigate the effect of lignin on the oil resistance, tensile strength and morphology.

II. EXPERIMENTAL

1. Preparation of lignin filled natural rubber latex films

The lignin used in the present study was derived from rubber wood (RRIM Clone Series 2000) by means of alkaline digestion. Details of the lignin derivation from rubber wood are described elsewhere [7]. The properties of the lignin used in the present study are tabulated in Table 1.

Table 1: The Physical Properties Of Lignin

Parameters	Properties
Appearance	Powder
Bulk density (g/cm ³)	1.05
Particle size (µm) (Particle size analyser)	3.6
Sulphur concentration (CNS Elemental Analyser)	Undetectable

In order to prepare the lignin filled rubber films, lignin powder was added directly into commercial grade unvulcanised high ammonia natural rubber latex which was first diluted with distilled water to a solid content of 30%. The mixture was then stirred in a baffled circular vessel using a 45° pitched blade impeller at a speed of 200 rpm. 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. Different mixtures were prepared by varying the lignin loadings based on dry rubber weight (wt%).

2. Determination of changes in mass after oil immersion

For mass change, circular test pieces with diameter of 22 mm were immersed in IRM 903 oil at room temperature for 22 hours in accordance to ASTM D471 standard [8]. In order to obtain percentages of mass change, the mass differences of the samples after and before drying were calculated using *Equation 1*. Whereby, M_1 is the mass of samples before swelling and M_2 is the mass of the samples after oil immersion.

$$\text{Change in mass, } \Delta M, \% = \frac{(M_2 - M_1)}{M_1} \times 100 \quad \text{Equation 1}$$

The oil immersion was conducted to evaluate the comparative ability of the lignin filled rubber film to resist oil swelling and maintains its intactness. The ASTM IRM 903 oil was used as it has a flash point and aniline point of 163°C and 70°C respectively, and is considered comparable to typical hydraulic oils [9].

3. Tensile strength measurements and estimation of crosslink density (η_{phys})

Measurements of tensile strength were carried out on five samples using a Universal Testing Machine QC 505 (Protest, Taiwan) according to ASTM D412 standard [10] with a crosshead speed of 500 mm/min and a 500N load cell. Median values were used for data analysis.

The degree of crosslink density was determined from the stress-strain data [11] using the Mooney-Rivlin equation (Equation 2), where F is the force to stretch the rubber, A_0 is 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 using the symbol σ .

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \quad \text{Equation 2}$$

Using data from stress-strain measurement in the region of $1/\lambda = 0.5$ to 0.7 , the curve of $\sigma/(\lambda - \lambda^{-2})$ against $1/\lambda$ was plotted following Equation 3, where the constants C_1 and C_2 can be obtained. $2C_1$ represents the x-axis intercept of the curve whereas $2C_2$ represents the slope of the curve. From the plot, the curve fitted linear trend line is generated to determine the crosslink density (η_{phys}).

$$\frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + \frac{2C_2}{\lambda} \quad \text{Equation 3}$$

Using the value of y-axis intercept, the crosslink density (η_{phys}) is calculated (Equation 4) with R , the gas constant ($8.314 \text{ J.Mole}^{-1}\text{K}^{-1}$) and T , the absolute temperature (273.15K).

$$\eta_{phys} = \frac{C_1}{RT} \quad \text{Equation 4}$$

4. Scanning Electron Microscopy (SEM)

The SEM analyses of the films surface was 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. The images were derived 2keV accelerating voltage at 15 mm working distance.

5. Visualisation of rubber network via Transmission Electron Microscopy (TEM)

A technique to visualize rubber network involving the analysis of stained embedded swollen samples in a polystyrene matrix using TEM was prepared as described by Cook et al. [12], where rubber film samples were swollen and embedded in polystyrene matrix prior to sectioning. Ultra-thin sections (ca. 100-150 nm) of the samples were obtained using an RMC MT-7000 ultramicrotome using 45° freshly cleaved glass knives set at a shallow-clearance angle. The sections were stained with osmium tetroxide vapour for one hour before examining them using a Philips EM 300 Transmission Electron Microscope operating at 100 kV.

III. RESULTS AND DISCUSSION

1. Effect of lignin on rubber films mass changes in oil immersion – Oil resistance

The result of oil resistance of rubber films with increasing lignin loading is shown in Figure 2. With the addition of lignin, the rubber films exhibited better resistance to oil swelling in contrast to the control film. For example, at 10 wt% loading, the mass change is 170%. The reported value for mass change in oil immersion of vulcanised rubber film was 102.6% [13]. Thus, the result suggests that the lignin filled rubber film even at its unvulcanised state is able to maintain its intactness after immersion in oil. The ability of lignin filled rubber films to resist oil is associated to the hydrophilic lignin structure having substituted phenol with hydroxy and methoxy group which is less soluble in oil. The presence of such hydrophilic component in the rubber matrix complicates the oil penetration process when concentration gradient as the driving force for oil diffusion as a function of time is no longer constant.

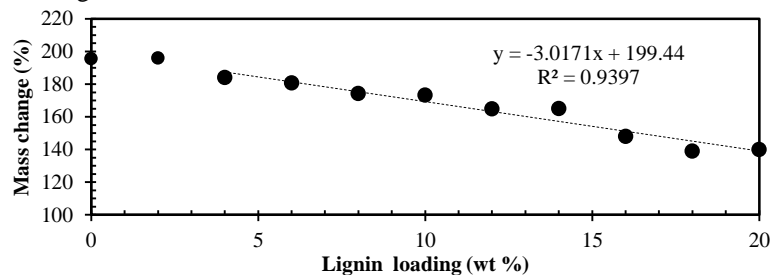


Figure 2: Oil resistance of rubber films showing the percentage of mass change against increasing lignin loadings.

2. Effect of lignin on the tensile strength

The results of tensile strength are shown in Figure 3. Three regions are observed, namely, *Region I*, where the tensile strength was independent of lignin loading up to 8 wt%. *Region II*, where a sharp increase in the tensile strength occurred as a function of rubber wood lignin loading. In this region, the tensile strength is increased by 60 and 73% at lignin loading of 10 wt% and 12 wt% respectively. At these concentrations, rubber wood lignin contributed to the reinforcement of rubber film as seen in the increase in the tensile strength. The final region can be seen in the *Region III*, where irregularities in the tensile properties were observed in lignin loading above 12 wt % which can be attributed to rubber latex flocculation.

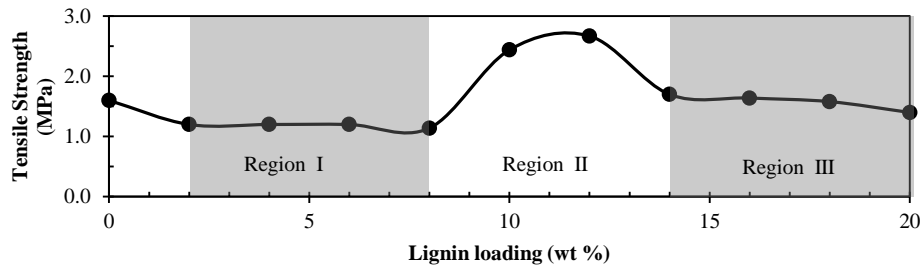


Figure 3: Tensile strength of lignin filled rubber films with increasing lignin loadings.

3. Effect of lignin on the crosslink density (η_{phys})

Stress-strain measurement was used as the technique to determine crosslink density instead of swelling measurements. Although swelling measurements are the most popular for the determination of crosslink density, it was not used in the context of the present study due to ambiguity which may arise owing to the insolubility of lignin in the rubber swelling solvent. Furthermore, the solvent-polymer interaction parameter (χ) 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 [14]. Data from stress-strain measurements for rubber films was used to construct plots of $\sigma/(\lambda-\lambda^{-2})$ against $1/\lambda$ to obtain the values elastic constants and estimation of crosslink density. The results of the crosslink density and elastic constant, C_2 , are shown in Figure 4.

The crosslink density is expressed in terms of moles of effective network chains per cubic centimetre of rubber sample. The values obtained for the control sample at 0% lignin loading, is relatively close to the reported crosslink density value of $4.91 \times 10^{-5} \text{ mol/cm}^3$ for unvulcanised raw rubber sheet [15]. In contrast to the control samples, it is observed that the crosslink densities are reduced with the addition of lignin. On the other hand, the result of the elastic constant, C_2 , which is indicative of the extent of chain entanglements is increased with increasing lignin loading. The highest values are observed in *Region II* which corresponded to the increase in tensile strength.

These results also infer that the addition of lignin does not promote any chemical crosslinking in the rubber as it does not contain sulphur or other crosslinker, which is in agreement with the earlier work by *Tibenham and Grace*, suggesting that primary bond formation is not likely to occur between lignin and rubber [16]. However, the increase in tensile strength and improvement in mass change after oil immersion could be due to the formation of secondary bonding between lignin and rubber dispersion forces. This type of bonding can caused chain entanglement as shown in the improvement in physical properties.

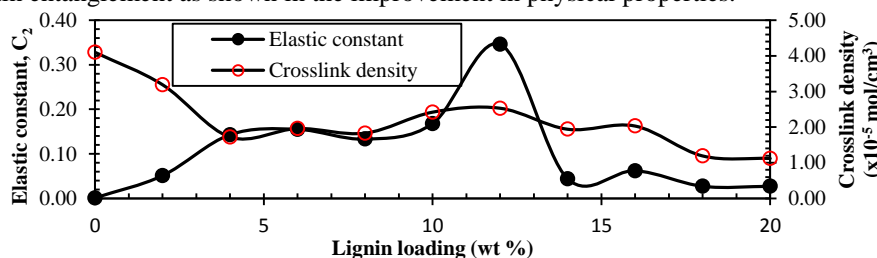


Figure 4: Effect of lignin loadings on the crosslink density and elastic constant (C_2) of unvulcanised natural rubber latex films.

4. Morphology of lignin filled rubber film

With respect to its inherent nature as thin film, morphology and the level of coherency (between lignin and rubber) play an important part in affecting the tensile strength of rubber latex films. The morphology of the

rubber films reflects the dispensability of lignin in the rubber. Surface and bulk morphology of the rubber films observed via SEM and TEM are illustrated in Figure 5 and 6.

The surface of rubber latex films in the absence of lignin can be an undulating surface, reminiscent of latex particle coalescence during drying and film formation. Similarly, the TEM micrograph shows coarse rubber network with large areas of polystyrene. The network does not seem to have been stained so well with osmium tetroxide. Osmium tetroxide reacts with carbon-carbon double bonds and therefore shows the rubber phase as dark region compared to the brighter polystyrene phase.

From the SEM and TEM micrographs, the morphological changes in the lignin filled rubber can be summarised into 3 regions as follows:

Region I: At 8 wt% loading, lignin is observed in the SEM micrograph as globules or particles at the surfaces of the rubber films and was randomly distributed. This indicates the inhomogeneous dispersion of lignin in the rubber film due to phase separation. The formation of surface voids could be due to weak interactions between hydrophilic lignin filler and the hydrophobic rubber matrix. The TEM micrograph (Figure 6a) showed several residual latex particles within the coarse mesh of rubber. There are also many large areas of featureless polystyrene.

Region II: The SEM micrograph showed the presence of large cracks with lower concentration of globules (or particles) at the surface, while the TEM micrograph indicated the appearance of physical crosslinking of rubber with denser particles. Several residual latex particles are also observed within the coarse mesh of rubber.

Region III: SEM micrograph showed surfaces which appeared darker with lump or protrusion. This was probably due to flocculation of the rubber particles leading to incoherent film formation. From the TEM, many large areas of featureless polystyrene and materials which is in explicable at the moment.

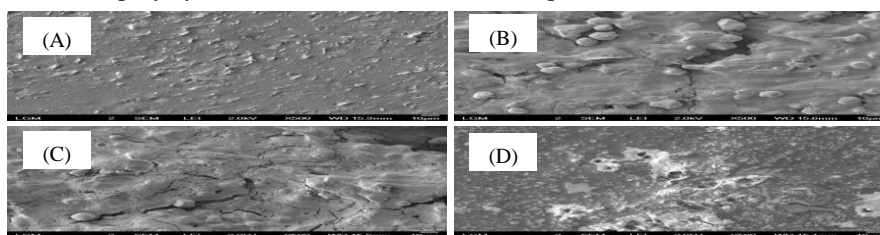


Figure 5: SEM micrographs of rubber latex films with various lignin loadings. A: Control, 0 wt% loading; B: 8 wt% loading; C: 12 wt% loading; D: 16 wt% loading.

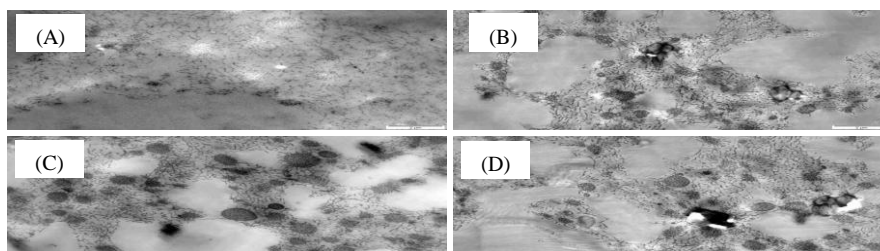


Figure 6: TEM micrographs of rubber latex films with various lignin loadings. A: Control, 0 wt% loading; B: 8 wt% loading; C: 12 wt% loading; D: 16 wt% loading.

It is suggested that the tensile strength of the lignin filled rubber latex films to some extent is dependent on the level of lignin dispersion in the rubber matrix. This is owing to the ability of lignin to disperse in the rubber matrix which causes physical crosslinking resulting in the improvement in tensile properties. The level of filler dispersion is known to affect polymer mechanical properties [17] and with inhomogeneous filler dispersion, load transfer from matrix to the filler particle is poor.

The tensile properties observed for the lignin filled rubber film differs from the anticipated trends in conventional non-reinforcing rubber filler such clay slurry in rubber latex [18], where only two regions exists. The first region is the decrease in strength followed by a plateau region. On the other hand, the trend in tensile properties of the lignin filled rubber latex films showed three distinct regions, namely, *Region I* where there was a decrease in tensile strength, followed by a sharp increase in *Region II* and finally *Region III* where tensile strength is reduced. This is associated to random dispersion and micro-phase separation of lignin in the rubber.

In *Region II*, at lignin loadings above 8% until 12 wt%, rubber wood lignin showed network formation in the rubber matrix which contributed to the reinforcement of rubber film. The formation of the filler network is important at macroscopic length, in which a high filler loading is anticipated to have a greater tendency to form overlapped filler aggregates which contribute to reinforcement [19]. 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 in *Region I*. Reduced tensile strength is observed as in *Region III*, which is higher than 12 wt% loading, can be attributed to flocculation of the rubber particles leading to incoherent film formation having flaws during uniaxial tensile testing.

In the present study, it is shown that lignin is capable of reinforcing rubber films and the reinforcement is accompanied by the increase in physical entanglement as shown an increase in the C_2 values. It is suggested that the reinforcement of lignin resembles the reinforcement of phenolic resin in rubber latex. In the reinforcement of latex using resin, Piccini concluded that a simple combination of resin with hydrocarbon would not occur as the tendency is greater for the resin to combine with itself and reinforcement is contributed to the finely divided state of the resin [20].

IV. CONCLUSION

In the present investigation it is shown that the incorporation of rubber wood lignin markedly improves the oil resistance of rubber latex films. The tensile strength of the lignin filled rubber latex films is shown to increase at lignin loading between 10 wt% to 12 wt%. The increment in tensile strength is accompanied with the increase in the chain entanglement as indicated by the C_2 values and better dispersion of lignin in the rubber matrix as shown using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Therefore, for the purpose of utilising lignin as filler in rubber latex film to attain improvement in oil resistance and enhancement in strength, the minimum loading of 10 wt% lignin per dry rubber is proposed.

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REFERENCES

- [1]. G. Henriksson, Lignin. *Pulp and Paper Chemistry and Technology* Vol 1: Wood Chemistry and Wood Biotechnology (Ek, M., Gellerstedt, G. and Henriksson, G., eds.) p. 121-145. (Berlin: De Gruyter, 2009).
- [2]. J. J. Keilen, and A. Pollak, Lignin for reinforcing rubber. *Industrial Engineering and Chemistry*, 39(4), 194, 480-483.
- [3]. M.S. Dimitri, Process for making lignin reinforced polymers. *United States Patent*, 1976, US Patent No. 3991022.
 - a. Sagajilo, Lignin as compounding ingredient. *Rubber Chemistry and Technology*, 30(2), 1957, 639-651
- [4]. E.G. Lyubeshkina, Lignins as Components of Polymeric Composite Materials. *Russian Chemical Reviews*, 52 (7), 1983, 675-691.
- [5]. A.F. Sirianni, and I.E. Puddington, Laundered amorphous lignin. *United States Patent*, 1976, No. 3817974.
- [6]. M. Asrul, M. Othman, M. Zakaria, and M.S. Fauzi, Process for producing reinforced natural rubber latex and the reinforced latex produced. *Malaysian Patent Application*, 2011, No. PI 2011003945.
- [7]. ASTM Standard, Standard Test Method for Rubber Property - Effect of Liquids, ASTM D 471-06, (PA, *ASTM International*, 2006).
- [8]. J. Hanley, N. Murphy, H. Ali, and S. Jerrams, , The Effect of Oil Swelling on the Fatigue Life of Elastomers subjected to Cyclic Bubble Inflation, *11th International Seminars on Elastomers*, 23 -27 Sept, 2007, Freiburg, Germany.
- [9]. ASTM Standard, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers – Tension, ASTM D 412-98, (PA, *ASTM International*, 1998).
- [10]. N. Sombatsompop, Practical use of the Mooney-Rivlin equation for the determination of degree of crosslinking of swollen NR vulcanisates. *Journal of the Science Society of Thailand*, 24, 1998, 199-204.
- [11]. S. Cook, P.E.F. Cudby, R.T. Davies, and M.D. Morris, The Micro structure of Natural Rubber Films. *Rubber Chemistry and Technology*, 70, 1997, 549-55.
- [12]. K. Vivayanganathan and M.Y. Amir Hashim, Natural rubber and carboxylated nitrile-butadiene rubber latex blends and evaluation of coagulant dipped film properties, *Bulletin of Plastic and Rubber Institute of Malaysia*, No. 1, 2006, pp. 4-10.
- [13]. J. L. Valentín, J. Carretero-González, I. Mora-Barrantes, W. Chasse and K.Saalwächter, Uncertainties in the Determination of Cross-Link Density by Equilibrium Swelling Experiments in Natural Rubber. *Macromolecules*, 41, 2008, 4717-4729.
- [14]. W. Kuhn, E. Peregi, Z. Fei, U. Giese, R. Schuster And S. Zhao, Network Dynamics of Crosslinked Polymers - Crosslinking, Filler and Aging Characterized by NMR Parameters. *Macro 2006 - 41st International Symposium on Macromolecules Proceedings* 16-21 July, 2006, Rio de Janeiro, Brazil.
- [15]. F. J. Tibenham and N. S. Grace, Compounding Natural Rubber with Lignin and Humic Acid. *Industrial Engineering and Chemistry*, 46(4), 1954, 824-828.
- [16]. D.W. Schaefer and R. S. Justice, How Nano Are Nanocomposites?. *Macromolecules*, 40(24), 2007, 8501-8517.
- [17]. R.F. Mausser, Other Vanderbilt Compounding Material, in the *Vanderbilt Latex Handbook*, pp. 129-130. (Norwalk CT: R.T. Vanderbilt Co, 1987)
- [18]. J. Liu, S. Wu, L.Zhang, W. Wang. and D. Cao, Molecular dynamics simulation for insight into microscopic mechanism of polymer reinforcement. *Physical Chemistry Chemical Physics*, 13, 2010, 518-529.
- [19]. Piccini, The direct reinforcement of rubber in latex. II Synthetic resins formed in situ by the addition to latex of the starting materials of their resinification. *Rubber Chemistry and Technology*, 26, 1953, 207-219.