5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Effect of Filler Loading on Curing Characteristic and Tensile Properties of Palygorskite Natural Rubber Nanocomposites

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Abstract

This work investigates the effect of filler loading on curing characteristics and tensile properties of palygorskite (PAL) natural rubber (NR) nanocomposites. The nanocomposites were prepared by using a combination of melt mixing and latex compounding method. Five different samples with different filler loading namely PAL2 (2 phr), PAL4 (4phr), PAL6 (6phr), PAL8 (8phr) and PAL10 (10 phr) were prepared in this work. All the samples were subjected to curing and tensile test. All the results were compared with pure gum of natural rubber. The curing characteristics of PAL/NR nanocomposites such as minimum and maximum torque were higher at optimum filler loading, PAL4. It means that the optimum filler loading would produce higher rigidity of the sample. Thus, PAL4 had higher stiffness compared to other filler loading. The scorch time and cure time of the sample that had undergone melt mixing and latex compounding method were higher compared to NR. The increase in both scorch time and cure time revealed that the presence of PAL could increase the curing process of the nanocomposites. Furthermore, PAL4 showed 18% increment in tensile strength. These results showed the optimum filler loading can increase the compatibility between PAL and NR. The size and shape of the PAL and the combination of melt mixing and latex compounding method might also contribute to this improvement. The morphology characteristics of all PAL/NR nanocomposites sample showed thicker tear line and rougher surface compared to control sample, NR. This might due to the homogenous dispersion of PAL which contains optimum filler loading. Thus, 4phr of palygorskite loading found to be the optimum filler loading with a combination of melt mixing and latex compounding methods.

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Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: Palygorskiteclay; Natural rubber,;Filler loading

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1. Introduction

Nanocomposites are one of the well-known advanced engineering materials. Nanocomposites are formed by the presence of filler such as silica[1], carbon black[2] and montmorillonite[3] and matrix in one system. It occupies outstanding mechanical properties, which are not present in individual components. Nowadays, nanocomposites based on natural reinforcement fillers are receiving a wider interest among researchers. The study on clay/rubber nanocomposite had drawn more attention due to their unique properties with better eco-performance at a lower price and renewability[4, 5]. In this study, palygorskite clay (PAL) was chosen as a filler. Palygorskite is a type of natural fibrillar silicate clay. It was chosen due to the excellent physical and chemistry properties. It also has special structure and shape that is needle like shape[6]. The shape and size of this clay result in unique colloidal properties. When it is thermally activated, it will give high surface area and high porosity particle in the structure[7]. Palygorskite is a family of fibrous hydrous magnesium silicates. The structure was introduced in early 1940 by Bradley[8]. The unit cell formula of PAL is $Si_8O_{20}Mg_5(Al)(OH)_2(H_2O)_4.4H_2O$ which represent the two types of water in the formula; magnesium coordinated water and adsorbed water. The smallest structural unit of PAL is fibrillar single crystal with a high aspect ratio with the length of 500-2000 nm and 10-25 nm in diameter[9] .It contains ribbons of a 2:1 phyllosilicate structure which is different from other layered silicates such as montmorillonite.

However, incorporation of clay into a rubber matrix does not always give significant improvements in the mechanical properties. This is due to the poor dispersion of the clay in the rubber matrix. It is also caused by the insufficiency of affinity between the clay and the organic polymers. Hence, to obtain the optimum reinforcing effect of this nanocomposites, two important conditions are needed; the strong interfacial adhesion between clay and rubber and the uniform dispersion of filler in the rubber matrix to form high-performance polymer–clay nanocomposites. Hence, in this study, melt mixing and latex compounding method was chosen because melt mixing method is more environmental friendly and most compatible with current industry while for latex compounding method many researchers reported the clay layers can be exfoliated and homogeneously dispersed in polymer matrix at a nanolevel by the latex compounding method[10,11,12]. The corresponding benefits of both methods; had led the authors to prepare the nanocomposites by a combination of these two methods.

Based on the published literature, very limited studies had been conducted using a combination method of melt mixing and latex compounding with the presence of PAL in the NR matrix. Thus, in this study, the incorporation of NR with PAL was carried out with a combination of latex compounding and melt mixing method. The goal of this work was to investigate the effect of filler loading on the curing properties and tensile properties of PAL/NR nanocomposites via melt mixing and latex compounding methods.

2. Experimental

2.1. Materials

PAL, anchoid, calcium chloride (CaCl) and potassium hydroxide (KOH) were purchased from Sigma Aldrich (M) Sdn Bhd. All materials for rubber compounding and 60% of HA latex were obtained from Zarm & Chemical Supplier Sdn Bhd. The recipe was tabulated in Table 1.

Table 1. Formulation of Rubber Compounds.

Materials	Functions	Parts per hundred rubber (Phr)
Natural Rubber, NR (SMR 20)	Acts as a matrix	100
Zinc Oxide (ZnO)	Acts as a activator	5
Stearic Acid	Acts as a activator	2
2,2'-Methylenebis(6-tert-butyl-4-methylphenol) (BKF)	Acts as an antioxidant	2
Zinc diethyldithiocarbamate (ZDEC)	Acts as an accelerator	0.5

Tetramethyl thiuram disulfide (TMTD)	Acts as an accelerator	1
Sulphur	Acts as vulcanising agent	2.5

2.2. Sample Preparation

2.2.1. Clay Dispersion

PAL/NR nanocomposite was prepared by the formation of PAL clay dispersion. The formulation was tabulated in Table 2. The clay dispersion was mixed using   for 60 minutes. After that, it was sonicated for 30 minutes. The dispersion underwent two dispersion processes to make the dispersion homogenous. After that, the PAL dispersion was mixed with high ammonia (HA) latex for 15 minutes using electric stirrer. Then, the mixture was co-coagulated by 10% calcium chloride solution then washed several times with water until it reached pH 7. Finally, the coagulated compound or masterbatch was dried in the oven for 2 hours until the weight was constant.

Table 2. Formulation of Palygorskite Clay Dispersion.

Materials	Parts per Hundred (Phr)
Palygorskite Clay	6
10% KOH	3
Anchoid	5
Water	86

2.2.2. Rubber Compounding

Compounding process was carried out by using a laboratory two-roll mill machine model XK-160 from Shanghai Rubber-Machine Worker, China. The masterbatch was compounded with rubber compounding materials as listed in Table 1. First, the SMR 20 was masticated through mastication process. Next, the masterbatch was added into two roll mill. The temperature of this machine was constant at 70°C. Afterwards, the activator, antioxidant, accelerator and lastly the vulcanizing agent were added into the compounding. The control sample, NR was also prepared by using two roll mill machine. No filler was added in the control sample. The sequence of adding ingredient in this sample was similar as masterbatch sample but no PAL masterbatch was added. This sample used to compare the properties between PAL/NR nanocomposites with different filler loading. The time taken to complete all process was about 25 to 30 minutes. Nip gap, the speed roll mill, time of mixing and the sequence of adding ingredient were kept constant for all formulations. The nip gap of the machine was range from 0.8-2.5 mm then followed by the step of mixing.

2.2.3. Preparation of Tensile Test Sample

The test specimen sheets of all compounds were produced using compression moulding. The temperature of the compression moulding machine was kept constant at 160°C. The time taken to produce the sheets specimen was based on the curing time (t_{90}) from the curing testing.

2.3. Testing

2.3.1. Curing Characteristics

The rubber compound were kept in the closed container before cured. The curing test was performed using Alpha Technologies moving die (MDR 2000). The respective results, maximum torque (M_H), minimum torque (M_L), scorch time (t_{s2}) and cure time (t_{90}) was obtained from curing testing at 160°C.

2.3.2. Tensile Properties

The tensile test of the PAL/NR nanocomposites was determined by Instron 3366 Machine. Dumb-bell shape was cut out, and the cross-head speed of this testing was 500 mm/min.

2.3.3. Field Emission Scanning Electron Microscope (FESEM)

The fracture surfaces of the PAL/NR nanocomposites were examined using field emission electron scanning microscopy (FESEM) instrument model Zeiss SUPRA 35VP FESEM. The fractured samples were coated with a thin layer of gold-palladium using a SEM sputter coater. The coating was necessary to prevent the occurrence of these superfluous electrons.

3. Result and Discussions

3.1. Cure Characteristics

The curing characteristics result of PAL/NR nanocomposites was illustrated in Table 3. All the data was discussed and compared with pure gum, NR. Table 2 shows that the filler loading of 4 phr (PAL4) PAL has a highest minimum (M_L) and maximum torque (M_H) compared to other filler loading. The increase in the torque showed PAL4 has higher stiffness compared to other filler loading samples. This result was due to the restriction of the molecular motion of the molecules in the sample. Thus, it shows that the optimum filler loading would produce higher rigidity of the sample. However, as the filler loading increased, the M_H value had decreased. It also might be due to the weaker bonding interaction between PAL and NR at higher filler loading.

Table 3. Cure Characteristics of PAL/NR Nanocomposites.

Sample	M_L	M_H	t_{s2}	t_{90}	Cure Rate Index (CRI)
NR	0.02	6.99	1.16	1.80	156.25
PAL2	0.03	5.77	1.31	1.85	185.19
PAL4	0.07	5.83	1.29	1.87	172.41
PAL6	0.03	5.45	1.35	1.89	185.19
PAL8	0.06	5.42	1.4	1.94	185.19
PAL10	0.03	4.23	1.42	1.91	204.08

It can also be seen that the samples that underwent melt mixing and latex compounding technique exhibited a higher cure time and scorch time than NR. The value of scorch time had increased as the filler loading increased. This is because the presences of the accelerator, ZDEC increase the scorch time. This accelerator has a medium scorch safety in the molecules. However, at the optimum filler loading, the scorch time was reduced. According to the Vijayalekshmi (2009)[13], the lower scorch time of the sample indicated better processing ability. The processing ability is related to the total amount of heat history which can be tolerated before the rubber is converted to a rubber cross link state. Attharangsan et al. (2012)[14] had reported that the scorch and cure time of their study were decreased as the carbon black content increased. This is because more heat generated from shear force during mixing due to higher viscosity. Rubber which has high molecular weight will produce high melt viscosities during melt mixing and this effects will generate high shear stresses for the shearing and breaking layers of filler[13]. It is also due to higher viscosity of the optimum filler loading, PAL4 which can shorten the scorch time of the rubber compounds compared to other filler loadings. Ismail et al. (2009)[15] have reported that the higher amount of HNT will increase the amount of active sulphurating agents. Those agents will generate more crosslinks in the nanocomposites. Thus, a shorter scorch time was obtained.

The higher cure time of all sample showed that the presence of PAL could prolonged the vulcanization process of the nanocomposites. The other reason is that the PAL can adsorb the vulcanizing and curing agents easily because of the high specific surface areas of the PAL and the charges on the lattice[16]. They also reported that a large number of bound water and hydroxyl groups on the surface of PAL caused the delay of the span of rubber compound. Chang et

al.[17] also reported that cure time of EPDM–organo-montmorillonite hybrid nanocomposites was prolonged with the addition of the organoclay in the compound. They believe that the cure time protracted due to the absorption of the curing agents on the filler surface. The cure index (CRI) indicating the rate of cure of the composite is defined as $100/(t_{90}-t_{s2})$. The CRI of PAL/NR nanocomposites is significantly increased in all samples as compared to control sample, NR. The CRI value increased as increasing filler. This is due to higher addition of PAL in the PAL/NR nanocomposites samples increase the levels of the hydroxyl groups which increasing rate of vulcanization. Thus, the crosslinking reaction was accelerated due to hydroxyl group[18].

3.2 *Tensile Properties*

The tensile strength, elongation at break and 300% tensile modulus for sample PAL2, PAL4, PAL6, PAL8 and PAL10 of PAL/NR nanocomposites are showed in Table 4. From the results of samples PAL2, PAL4, PAL6, PAL8 and PAL10 showed 13.15%, 17.99%, 10.16%, and 9.76 % and 11.75% increase in tensile strength, respectively. The results show the optimum filler loading, PAL4 has highest tensile strength compared to another sample. These results depict the optimum filler loading can increase the compatibility between PAL and NR. They also show that PAL can reinforce the NR matrix. A very good dispersion of PAL in the NR matrix had also contributed to this improvement of tensile strength results. According to Jinghua et al., (2012)[19], the mechanical properties of the nanocomposites can significantly increase due to the nano size and high aspect ratio of the filler. Thus, they also show that the size and shape of PAL had also influenced these excellent results. Wang and Chen (2013)[16] had also reported in their study that the lower amounts of PAL can easily disperse in the nanocomposites. Thus, it will produce to a significant improvement in the filer matrix-interfacial bonding. This improvement will lead to a better dispersion of the filler in the matrix. As a result, the efficiency of the stress transfer from matrix to filler phase had increase.

The value of tensile strength increased as the filler loading increased. However, the value of this property had dropped as it reached optimum value. At high PAL loadings, the aggregations and agglomeration of the filler in the NR matrix may have formed. Hence, it will reduce the tensile strength of the PAL/NR nanocomposites. The addition of PAL will increase the concentration of this filler in the NR matrix. As a result, it will cause the agglomeration and interruption the filer-matrix bonding. This behaviour is also adequately explained by the works of Sirichai et al., (2012)[20].

Table 4. The Tensile Properties of PAL/NR Nanocomposites.

Sample	Tensile Strength, MPa	Elongation at Break,%	300% Tensile Modulus, MPa
NR	18.18	818.90	2.33
PAL2	20.57	886.60	2.17
PAL4	21.45	938.33	2.31
PAL6	20.02	913.90	2.59
PAL8	19.95	895.57	2.46
PAL10	20.35	900.00	2.74

The elongation at break value of the sample that underwent latex compounding and melt mixing method were higher that NR. The increasing by 8.27%, 14.58%, 11.6%, 9.36% and 9.90% were recorded for PAL2, PAL4, PAL6, PAL8 and PAL10, respectively. As the filler loading increases, the elongation at break tend to decrease. The decreasing of elongation at break at higher filler loading is due to the enhancement in rigidity of the nanocomposites[13]. Ismail et al, (2013)[21] stated the similar explanation regarding the decrement of the elongation at break at higher filler loading. Azahari et al (2012)[22] stated that the reduction in elongation at break may possibly affected by the higher brittleness of PAL when added into the matrix and the attractive forces between the fillers and the polymer molecules[23]. They further explained that the forces restrict the free mobility of the polymer chains to form a crosslinked network. Thus, it will increase the resistance to stretching upon the application of strain. At 4phr of filler loading, the elongation at break value was higher due to strong rubber-filler interaction occurred in the system. The similar report was obtained by Azahari et al (2012)[22] which at low adding of PAL, the filler is

homogenously dispersed in the PVA matrix. The PAL structure which is needle-like shape has a high aspect ratio. This advantage give benefit to improve interfacial bonding and the formation of a filler-polymer interaction occurred because of the high specific surface area of the filler. Thus, it improved the elongation at break. However, the 300% tensile modulus of PAL/NR nanocomposites shows an increasing value as the filler loading increases. The results for 300% tensile modulus show the stiffness of the sample increases as the PAL loading increases. These results also show the PAL can influence the stiffness of the rubber nanocomposites. Besides, the latex compounding method had also contributed to the excellent result of PAL/NR nanocomposites. As reported by Jinghua et al., (2012)[19], the increase in the mechanical properties was due to the dispersed structure of the filler at nanolevel. In their study of rubber-Ca-MMT nancomposites, there was a significant improvement in mechanical properties. This improvement can be ascribed to the dispersed structure of modified Ca-MMT at the nanolevel. The high aspect ratio and the enhancement in polymer–filler interaction could be the reasons for the improvement. The dispersing of filler by latex compounding method had also contributed to these results.

3.3 Field Emission Scanning Electron Microscope (FESEM)

The micrographs of PAL/NR nanocomposites of NR, PAL2, PAL4, PAL6, PAL8, and PAL10 are shown in Fig.1(a), Fig.1 (b), Fig.1 (c), Fig.1 (d), Fig.1 (e) and Fig.1 (f), respectively. The magnification of NR figure was 1.00KX while for the other figures were 500X. In order to obtain good mechanical properties of PAL/NR nanocomposites, a good dispersion of palygorskite in the rubber matrix is required. Fig.1 (a) acted as a control sample which shows a clear and smooth surfaces while the other figures, Fig.1 (b), Fig.1 (c), Fig.1 (d), Fig.1 (e), and Fig.1 (f) show irregularity surfaces.
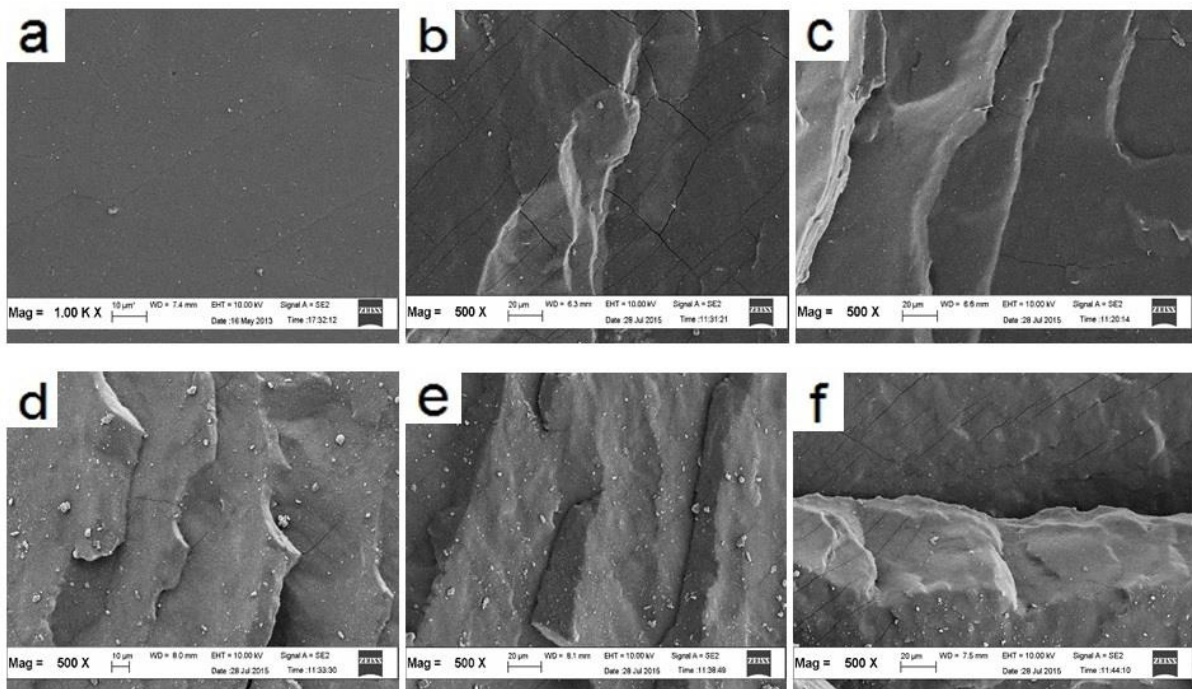

Fig.1. The Field Emission Scanning Electron Microscope (FESEM) of PAL/NR Nanocomposites; (a) Natural Rubber ;(b) PAL2 ;(c) PAL4 ;(d) PAL6 ;(e) PAL8 ;(f) PAL10.

The tensile fracture surface of Fig.1(b), Fig.1 (c), Fig.1 (d), Fig.1 (e), and Fig.1 (f) were compared and the results displayed that all PAL/NR nanocomposites samples had thicker tear lines and rougher surface. In Fig.1 (c), it can be seen that there are no flocculation occurred and the PAL structures were also not appear on the surface sample compared to Fig.1 (d), Fig.1 (e) and Fig.1 (f). This might be due to the homogenous dispersion of the palygorskite in the rubber matrix which contain the optimum loading of the palygorskite. Well dispersion of PAL in this sample hindered the agglomeration to occur. The thicker tear line and rougher surface formation was also due to the increasing in resistance of crack propagation and thus giving higher tensile strength or increasing in mechanical properties in comparison to the control sample. The non-homogenous dispersion of PAL in the rubber matrix contributed to the formation of the flocculation which had caused negative effects to the mechanical properties as shown in Table 4.

4. Conclusion

The effect of filler loading on curing characteristics and tensile properties of PAL/NR nanocomposites was examined. The following conclusion can be drawn: there was an improvement in the tensile strength and curing characteristics on the optimum loading filler, PAL4. These results might be due to the combination of melt mixing and latex compounding method to reduce the agglomeration in the nanocomposites. The strong interaction between NR and PAL had also contributed to these results.

Acknowledgement

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