Effect of Dynamic Vulcanization on Properties of Linear Low Density Polyethylene/Natural Rubber Filled with Calcium Carbonate

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Abstract The effect of dynamic vulcanization with different loading of calcium carbonate (CaCO₃) on linear low density polyethylene/natural rubber using N,N’-m-phenylene bismaleimide (HVA-2) vulcanized and dicumyl peroxide (DCP) vulcanized as a cross-linker were investigated. Optimum ratio of LLDPE/NR blends was chosen is 70/30 in this study. Calcium carbonate loading was varied at 0wt%, 5wt%, 10wt% and 20wt% as filler in LLDPE/NR blends. The study showed that the tensile properties of the un-vulcanized LLDPE/NR blends were deteriorated with increasing in CaCO₃ content. The dynamic vulcanization approach by using the HVA-2 and DCP dynamic vulcanization agents was applied on the LLDPE/NR blends in order to compensate the deterioration properties caused by the incorporation of CaCO₃. According to the results, the addition of HVA-2 and DCP showed the composites were better in water resistance and tensile properties as compared to the standardized counterpart. The morphological analysis by using the scanning electron microscopy (SEM) found out that the interfacial adhesion and dispersion of CaCO₃ was improved in both vulcanization systems.

1 Introduction

Thermoplastic elastomers (TPE) are polymers that exhibit the property of cross-linked elastomer at ambient temperature and plastic properties at elevated temperature [1]. This effect is associated with certain inter-chain secondary valence forces of attraction, which have the effect of typical ordinal covalent cross-links, but at elevated temperature, the secondary bond dissociates, and the polymer possess thermoplastic behavior [2]. Thermoplastic elastomers are composed of two phase that is a soft phase (amorphous domains) and hard phase (crystalline domains), which provides elastic properties and thermoplastic segment respectively [3]. Thermoplastic elastomers provide both processing ease and full recyclability to the material.TPEs can be produced by a unique skill known as dynamic vulcanization. Dynamic vulcanization (DV) involves a choosing cross-linking of rubbers component and dispersing finely in molten thermoplastic continuous phase through intensive mixing to produce thermoplastic vulcanizate [4]. Compatibilization between the matrix and

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the modifier occurs in the extruder allowing a finer dispersion of the latter [5]. This results in greater adhesion between the two phases. Simultaneously, another reaction stabilizes the morphology of the impact modifier by cross-linking. DV can promote characteristics such as tensile characteristics, heat resistance and fluid resistance [6]. The use of filler in the TPE was due to the advantage that can be obtained, such as improvement in process-ability, cost reduction of the product and achievement of specific [7-12]. Generally, fillers become the minor dispersed phase in a polymer matrix. Various fillers have been employed in polymer blend such as kaolin and calcium carbonate. Mineral filler is used to produce lower cost and promote the mechanical properties of polymer blend [13].

2 Experimental

2.1 Materials

Linear low density polyethylene (LLDPE) was purchased from Lotte Chemical Titan Malaysia with density 0.920 g/cm³. Standard Malaysian Rubber - 10 (SMR - 10) was purchased from the Kilang Hevea Bukit Perak (KHBP) in Perak with T_g -69°C. Calcium Carbonate (CaCO_3) in odorless and fine white powder was purchased from Sigma Aldrich Chemical Company, St Louis, USA with density 2.83g/cm³. N, N-m-phenylenebismaleimide (HVA-2) and dicumyl peroxide (DCP) were supplied from Aldrich Chemical Company, St. Louis, USA.

2.2 Preparation of the sample

2.2.1 Preparation of LLDPE/NR/CaCO_3

The LLDPE was added into the heated two roll mill until all the LLDPE pellets were molten. The NR was then added to blend together with the molten LLDPE until homogeneous. The CaCO_3 was incorporated into the LLDPE/NR blend and processed until the CaCO_3 was homogeneous and well dispersed into the matrix. The compounding recipes for the HVA-2 dynamic vulcanized system and DCP dynamic vulcanized system were as shown in Table 1. The compounding process was processed using heated two roll mill with speed 15rpm at 140°C for 15 minutes. The compounding was then molded into a 1mm sheet by using compression molding machine at 140°C for testing and characterizations purpose.

| VULCANIZATION SYSTEM                      | INGREDIENTS               | PARTS PER HUNDRED (PHR) |
|-------------------------------------------|---------------------------|-------------------------|
| Un-vulcanized system                      | LLDPE/NR/CaCO_3           | 100                     |
| HVA-2 dynamic-vulcanized system           | LLDPE/NR/CaCO_3           | 100                     |
|                                           | HVA-2                     | 2                       |
| DCP dynamic-vulcanized system             | LLDPE/NR/CaCO_3           | 100                     |
|                                           | DCP                       | 2                       |
3 Characterization and Testings

Water absorption test was performed by following ASTM D570 standard. The samples were dried and each sample was weighed by using electronic balance. The samples were then submerged in distilled water at room temperature and the samples were weighed at 1, 2, 3, 5, 10, 15, 20, 25, 30 days. For each composition ratio, an average out of five samples were prepared for measurement. Instron tensile test machine 3366 was used to analyze the mechanical properties of the blends. The specimens were cut into a rectangular shape, with the dimension of total length 100mm, 50mm gauge length, 30mm width and 1mm thickness for the tensile test under the ISO 527-3. The cross-head speed was set at 50mm/min under an ambient temperature. An average value was taken out of 5 samples in order to get an accurate value of tensile strength, modulus of elasticity and elongation at break. The morphological studies was carried out on the tensile fracture surface by using the Analytical Scanning Electron Microscopy (SEM) (Model JEOL JSM-6460LA) with the supply of accelerating voltage at 10kV. The tensile fracture sample was coated with palladium layer at about 1.5-3.0nm thickness with aid of utilizing the Auto Fine Coater (Model JEOL JFC 1600) in order to prevent the charging effect on the surface morphology. Fourier transform spectroscopy (FTIR) (Model Perkin Elmer Spectrometer 2000) was used to inspect structural changes at a resolution of 4cm⁻¹ and in the range of 4000-650cm⁻¹. The samples were scan for 32 times for a good resolution on the reading.

4 Discussion

4.1 Water Absorption Test

The water absorption test is conducted for 30 days, where reading of LLDPE/NR/CaCO₃ composites is weighted at 1, 2, 3, 4, 5, 10, 15, 20, 25, 30 days. The outcome of water absorption for un-vulcanized LLDPE/NR/CaCO₃ composites was shown in Figure 1(a). The curve depicts classic sorption performance with a quickly water absorption for the first few days of submerged for all the samples. This is mostly assigns to the storage of water absorption at the LLDPE/NR/CaCO₃ composites interphase [14]. Lack of wetting between hydrophilic natures of calcium carbonate and hydrophobic LLDPE/NR blend phase produces more voids that cause water molecules to store and flow in the polymer sample [15]. Excessive water take up described as the driving force between the dissimilar in water content and concentration point in the samples [16]. Higher water take up rate at 30% filler content can be described with the large aggregate of calcium carbonate increase the affinity of the sample with water molecules. The outcome of water take up for DCP and HVA-2 vulcanized systems are shown in figure 1 (b) and (c), respectively. From the figures, it is clearly showed that the vulcanized system shows better water resistance if compared with un-vulcanized (controlled) system. This is because capacity of DCP and HVA-2 to attach itself at the LLDPE/NR/CaCO₃ composite interphase and improved the interaction between CaCO₃ and LLDPE/NR matrix. Well embedded and dispersed calcium carbonate in the vulcanized LLDPE/NR matrix reduces the particle expansion and restricted water accumulation within the calcium carbonate phase [17]. HVA-2 vulcanized system shows better water resistance when compared to DCP vulcanized system. This is because DCP vulcanized system tended to undergo decomposition upon processing at high temperature and so the polymer chains would undergo chain scission into shorter...
chains and this made the DCP vulcanized system to be inferior to that of HVA-2 vulcanized system [18].

![Graph](image1)

**Fig. 1.** Water absorption percentage for (a) un-vulcanized, (b) DCP vulcanized, and (c) HVA-2 dynamic vulcanized LLDPE/NR/CaCO₃ composites.

### 4.2 Tensile properties

Figure 2 depicts the tensile strength of LLDPE/NR/CaCO₃ composites for un-vulcanized, HVA-2 vulcanized and DCP vulcanized systems. The graph showed that the increasing in calcium carbonate content will decrease tensile strength of the LLDPE/NR/CaCO₃ composites for all cases. This was due to the incorporation of calcium carbonate content leaded to poor adhesion with LLDPE/NR blends. The formation of agglomeration of calcium carbonate acted as the stress concentration...
point and caused the LLDPE/NR blend broke easily when the load was applied [19]. Its due to the composite was unable to bear the high stress and transfer the stress effectively between the LLDPE/NR/CaCO$_3$ phases [20]. The distribution and dispersion of the calcium carbonate particles were the main reason of adhesion and tensile properties of the blend. Thus, the higher the calcium carbonate content, the higher was the tensile properties deterioration and these resulted in the sample being broken easily when the external force was applied. The same trend of deterioration of mechanical properties could be observed when the HVA-2 vulcanized system and DCP vulcanized system were used when calcium carbonate content increase from 0wt% to 20wt%. However, there was an interesting found-out that the tensile strength of both HVA-2 dynamic vulcanized system and DCP dynamic vulcanized systems was higher than that of un-vulcanized system. The improvement in tensile strength was as outcome of the better adhesion between the LLDPE/NR phases by the formation of cross-linking in the NR phase [21]. The reduction of tensile strength as a result of increasing the calcium carbonate content was also less significant in vulcanized system [22]. This is because the calcium carbonate content were becoming smaller and distributing better well in the LLDPE/NR matrix, thus, the formation of weak concentration points would not be crucial [23]. Furthermore, the vulcanized rubber phase could prevent the chain slippage and provided better dimensional stability to the blend.

With respect to the comparison between DCP dynamic vulcanized system and HVA-2 dynamic vulcanized systems, the tensile strength of the HVA-2 dynamic vulcanized systems was better than DCP dynamic vulcanized system. The highest tensile strength of HVA-2-0% was 14.42MPa while for DCP-0% was merely 8.76MPa as shown in Figure 2. The better in strength was assign to the substantial cross-links formation in the HVA-2 vulcanized blends [24]. This indicated that the HVA-2 dynamic vulcanized system was more efficient cross-linkers to be used in this vulcanization system as compared to using DCP dynamic vulcanized system [22].

Similar trend happened to the modulus of elasticity of the LLDPE/NR/CaCO$_3$ blends as shown in the graph, whereby the increase in calcium carbonate content would reduce the modulus of elasticity of the blends. The modulus of elasticity of controlled-0% un-vulcanized system, DCP-0% and HVA-2-0% dynamic vulcanized system without calcium carbonate content was 77.50MPa, 82.00MPa and 93.00MPa and reduced to 29.33MPa, 43.00MPa and 52.33MPa respectively when the calcium carbonate content was increased up to 20wt%. The incorporation of calcium carbonate would interfere the LLDPE/NR chains allignment and give the the softening effect to the blends. However, the application of dynamic vulcanization approach compensated the loss in the modulus of elasticity values as a result from the calcium carbonate incorporation. The vulcanized rubber phase could prevent the chain slippage and provided better dimensional stability to the blends. The graph also shows the effect of calcium carbonate loading on the elongation at break for the un-vulcanized, DCP and HVA-2 dynamic vulcanized systems in LLDPE/NR blends. The percentage of elongation at break would reduce with increasing the calcium carbonate content. The major reason to the reduction in elongation at break value was due to the weak dispersion and distribution of the calcium carbonate within LLDPE/NR blends [24]. The higher the amount of calcium carbonate content would lead to more weak stress concentration points, thus it broke easier when the tensile force was being applied. It could further be based on the data obtained from the elongation at break for controlled-0%, DCP-0% and HVA-2-0% vulcanized blends which were 459.62%, 463.84% and 473.34% and reduced to as
low as 339.75%, 359.34% and 437.87% respectively when the calcium carbonate content was increased up to 20wt%. However, there were some improvements whereby all the dynamic vulcanized blends showed better elongation at break than un-vulcanized blends. The contribution was as an outcome of the cross-linked NR in the rubber phase thereby improving the flexibility of the blends and restricted the deformability of the LLDPE/NR phase.

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Fig. 2. Tensile properties of different vulcanization system of LLDPE/NR/CaCO$_3$ composites.
4.3. Morphological Study

The surface morphology of the polymer sample was conducted by Scanning Electron Microscopy (SEM) in order to analyze the interfacial interaction and phase separation of the dispersed phase. The SEM micrographs with x500 magnification of fractured surfaces of LLDPE/NR blends were shown in Figure 3. All the LLDPE/NR blends showed phase separated morphology where the rubber phase occurred as a small droplets in LLDPE matrix. The phase morphology evidently showed poor interfacial adhesion evidences by the voids on the surface. Due to the incompatibility between the LLDPE and NR, this would create some voids and holes on the blends surface. Holes formation could also be as a result of rubber pull out during the tensile testing. In Figure 3(a), there was an incorporation of 20wt% of CaCO$_3$ into the LLDPE/NR blend. The incompatibility of CaCO$_3$ with the LLDPE/NR blend would create more and larger void formations and this explained why there was a reduction in the mechanical properties when the CaCO$_3$ content was increased [25]. On the other hand, it could be observed that the HVA-2-0% had a smoother surface than that of HVA-2-20% as shown in Figure 3 (b). The HVA-2-0% had lesser void formation and better interfacial interaction as a result from the cross-linking formation in NR phase and made the blend being more compact. It could be observed that the DCP-0% had also a smoother and compact surface than un-vulcanized system (Figure 3 (c)). As the calcium carbonate content was higher, there would be more incompatible in the phase structure due to the poor mixing creating more void formations and agglomeration [21]. It could also be observed that the controlled-20% had a larger void formation than HVA-2-20% and DCP-20%. Without the addition of curing agents, the interfacial bonding between the LLDPE/NR/CaCO$_3$ composites was weak [26]. With the incorporation of curing agent, the elastomer polymer chains will undergo cross-linking which control the chain mobility and increasing in viscosity in the rubber phase resulting in high shear which lead to the better dispersion and distribution of calcium carbonate [27].

Fig. 3. SEM micrographs of un-vulcanized and vulcanized blends at x500 magnification with 20% CaCO$_3$ content for (a) un-vulcanized controlled system (b) HVA-2 vulcanized system (c) DCP vulcanized system
4.4 Structural Analysis

The infra-red spectra of LLDPE/NR blends were analyzed in order to investigate the structural changes after incorporation of CaCO₃. The FTIR test was carried out onto un-vulcanized LLDPE/NR blend with 0wt% and 20wt% of CaCO₃ is shown in Figure 4 (a). The most prominent peak to differentiate the controlled-0% and controlled-20% would be the band range occurring at 1650.81cm⁻¹ representing stretching vibrations of C=O groups. The controlled-0% and controlled-20% had the almost similar characteristics for the rest of the peaks. The band range occurring at 2900 cm⁻¹ correlating to the C-H streach and symmetry stretching vibrations of CH₂ group. The chemical structure of the LLDPE and NR constituted a lot of –CH₂ substituent leaving a lower %T. The absorption peak at 1451.58cm⁻¹ and 1446.44cm⁻¹ would be due to the methyl group –CH₃ bending vibration for controlled-0% and controlled-20% respectively. The absorption peak at 1451.58cm⁻¹ and 1446.44cm⁻¹ were attributed to the C=C single bond. Furthermore, the absorption peak at 710.86cm⁻¹ represent –CH₂-CH₂- (cis) and this constituted from natural rubber (NR) [21]. Another analysis was done to study the effect of vulcanization systems by using different vulcanizing agents of HVA-2 and DCP by comparing between controlled-20%, HVA-2-20% and DCP-20% with 20wt% of CaCO₃ as shown in Figure 4 (b). Both the HVA-2 vulcanized and DCP vulcanized samples showed a variation of spectra from un-vulcanized blends. It was found that the HVA-2 had a peak at 2906.32cm⁻¹ with highest percentage of transmittance representing C-H stretch and symmetry stretching vibrations of CH₂ groups and while the reduction of percentage of transmittance in DCP was due to the chain scission occurring into the blend causing the NR to be in a shorter chain, so more detections at this peak were observed. Besides that, after subjecting to dynamic vulcanization, the both systems were almost giving the similar absorption peak and the structural changes were varying slightly while comparing the un-vulcanized blends and vulcanized blends.

![Fig. 4(a). Infrared spectra of un-vulcanized LLDPE/NR and LLDPE/NR/CaCO₃-20% composites.](image-url)
5 Conclusions

In conclusion, the incorporation of CaCO₃ had influence on the reduction in tensile properties of the LLDPE/NR blend. By using the SEM, it could be observed that the decrease in tensile properties was due to the incompatibility and weak interfacial interaction of CaCO₃ with the LLDPE/NR blend which would create more and larger void formations as more CaCO₃ content was increased. The interaction between the CaCO₃ and the LLDPE/NR matrix was also studied by using the FTIR testing. The incompatibility was shown whereby no new formation or interaction between them in the un-vulcanized blend. The dynamic vulcanization was done to crosslink the rubber phase and the mechanical properties promoted greatly as differentiate to the un-vulcanized counterpart. The improvement in the tensile properties was mainly because of the promoted in crosslink density in the polymer. With respect to different vulcanization agents being used, it was found out that the HVA-2 dynamic vulcanized blends were greater than DCP dynamic vulcanized blends in the aspect of both properties. This was because HVA-2 was an effective cross-linking agent which was able to vulcanize NR even without the presence of free radical initiator at a sufficiently high temperature if compared with DCP. With the incorporation of curing agent, the elastomer polymer chains would undergo cross-linking which restricted the chain mobility and increasing in viscosity in the rubber phase resulting in high shear and therefore improved the dispersion and distribution of CaCO₃.

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