

Mechanical properties of zeolite filled ethylene vinyl acetate composites crosslinked by peroxide

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ABSTRACT

The effects of filler content and chemical crosslinking on mechanical properties of ethylene vinyl acetate (EVA) filled with zeolite particles in various volume fractions (5-25 vol. %) were investigated. The results of flexural tests illustrated that the incorporation of dicumyl peroxide (DCP) as crosslinking agent into the composites led to enhanced flexural modulus and also flexural yield strength compared to the composites in the absence of DCP. Besides, both uncrosslinked and DCP crosslinked EVA/zeolite composites exhibit increasing trend of flexural modulus and flexural yield strength with increasing volume percentages of zeolite. Meanwhile the results of DMA indicated that the transition temperatures of crosslinked EVA/zeolite composites were greater compared to that of uncrosslinked composites. Moreover, the value of storage modulus and loss modulus were improved while that of loss tangent was reduced with the presence of DCP in the EVA/zeolite composites. It was also found that the addition of higher content of zeolite particles had increased the magnitude of elastic modulus and loss modulus of both uncrosslinked and crosslinked composites. However, the intensity of loss tangent peaks was decreased.

KEYWORDS

Chemical crosslinking, Flexural properties, Dynamic mechanical analysis, Ethylene vinyl acetate, Zeolite

1. INTRODUCTION

The application of polymers filled with inorganic component has gained considerable attention mainly because of their excellent strength-to-weight ratios. In fact, enhanced properties arise from incorporating

inorganic mineral fillers into polymers, such as increased modulus, heat deflection temperature and fire retardant properties [1]. In this study, zeolite is chosen as filler as it provides many advantages such as economical and less harmful compared to other synthetic fillers. Plus, zeolite is commercially attractive due to its unusual crystalline structures yielding unique chemical properties [2].

However, most mineral fillers including zeolite exhibit hydrophilic ionic nature which contributes to a major problem in ensuring the hydrophobic polymer matrix to interact interfacially with the filler. Therefore, a modification method has to be performed in order to improve the adhesion and compatibility between the filler and matrix, thus obtaining composites with better properties. This is essential as the mechanical performance of polymer composites is greatly depends on the effectiveness of the bond between polymer matrix and filler in transferring stress across the interface [3].

Many investigators have been studied several modification methods in enhancing the polymer-filler interaction [4] [5] and [6]. Liu et al found that the combination of a coupling agent and a compatibilizer has led to a dramatic increase in mechanical properties of the composites [4]. Apart from that, crosslinking of polymer is also considered to be a promising method in yielding a composite with superior strength. They found that the limitations caused by poor interaction between constituents could be overcome by crosslinking [5,6]. Indeed, some researchers have found the usefulness of peroxide crosslinking in enhancing the interaction between matrix and filler [7] [8] and [9]. They proposed the improvement of mechanical properties is attributed to the formation of covalent bonds between the filler surface and polymer chains as the effect of crosslinking.

This work mainly deals with the study of dicumyl

peroxide crosslinking on the mechanical properties of EVA/zeolite composites. In order to evaluate the composites mechanical properties, flexural strength and modulus were obtained through a 3-point bend flexural test. Besides, dynamic mechanical properties like storage modulus, loss modulus and tan delta were determined. Plus, the influences of zeolite loading on the composites mechanical properties were discussed. The uncrosslinked EVA/zeolite composite has also been subjected to an identical test to enable comparative study.

2. EXPERIMENTAL METHOD

2.1. Material preparation

Ethylene vinyl acetate (EVA) was used as polymer matrix. Mordenite type of zeolite mineral species was used as natural filler. Meanwhile dicumyl peroxide (DCP) was used as crosslinking agent and was supplied by Bayer (M) Inc. Malaysia.

Zeolite was grinded into powder form using a ring mill machine. The size of zeolite particles used in this project was about 5.62 μ m. The compounding technique was done by using an internal mixer Thermo Haake Polydrive with Rheomix, R600/610 model. The processing conditions were set at 130⁰C with 7 min of mixing time and 50 rpm of rotor speed. The samples were then preheated at 130⁰C for 8 minutes followed by compression for 2 minutes. Finally, the samples were cold press for 4 minutes.

2.2. Flexural test

The flexural test was carried out with a universal testing machine Instron 3366 according to ASTM D 790. The samples dimensions were 127x12x3 mm. A crosshead speed of 50 mm/min was used and the test was conducted at room temperature. The flexural properties such as flexural yield strength and modulus were recorded at the end of each test.

2.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed using a DMA instrument (Mettler Toledo DMA 861e) under oscillating flexural loading. Specimens of the dimensions 63x12x3 mm were used for testing at a frequency of 1 Hz. The temperature was scanned from -70 to 100⁰C with heating rate of 5⁰C/min.

3. RESULTS AND DISCUSSION

Flexural Properties

Figure 1 indicates the flexural yield strength and flexural modulus of uncrosslinked and DCP crosslinked EVA/zeolite composites at different zeolite loadings. The flexural yield strength for both uncrosslinked and crosslinked composites increased with increasing zeolite content. Thus, it is apparent that zeolite is favorable for

improving flexural yield strength of the EVA composites. The result of flexural yield strength also shows that the crosslinked EVA/zeolite composites exhibit slightly greater strength than the uncrosslinked ones. The composites yield strength is greatly dependent on the interfacial interaction between EVA and zeolite particles [13]. This clearly indicates that the higher flexural yield strength of DCP crosslinked EVA/zeolite composites is attributed to the available free radicals of DCP which initiate some interaction between EVA and zeolite particles hence improving the filler/matrix interfacial interaction. Moreover, the improved zeolite dispersion within the crosslinked EVA matrix may give rise to the composites mechanical properties [14].

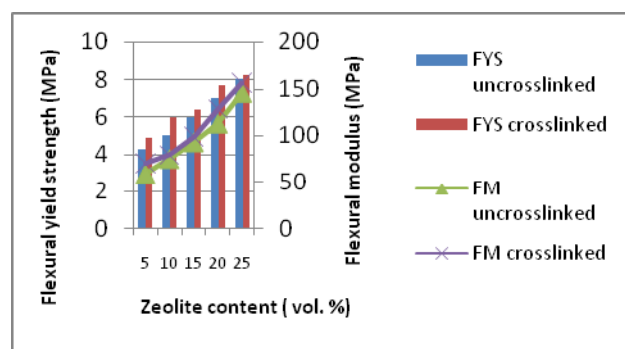


Figure 1: Flexural yield strength (FYS) and flexural modulus (FM) as a function of filler content for all studied composites

Figure 1 also shows that flexural modulus of the composites increased monotonically with increasing zeolite loading. This is probably because of the reinforcing effect and stiffness of zeolite in the EVA matrix. This is in perfect agreement as reported by Chen et al who stated that clay will enhance the composites modulus regardless of clay type including zeolite [15]. This modulus enhancement is due to the constraint of the polymer chains by their interaction with the zeolite surfaces. The overall increase in the flexural modulus with increasing zeolite content is expected since the addition of zeolite in particle form increases the stiffness of the composites [16]. The flexural modulus of the crosslinked composites was higher than those of the uncrosslinked composites as can be seen in Figure 1. This is believed to be associated with the better dispersion of zeolite particles throughout the crosslinked EVA matrix. Plus, the improvement in flexural modulus for crosslinked composites was mainly caused by the formation of interaction between EVA and zeolite which contributes to the enhancement in compatibility between the phases [14].

Dynamic Mechanical Properties

Figure 2 represents the variation of storage modulus values of EVA/zeolite composites according to changes in temperature. It can be seen that storage modulus decreases with increasing temperature. This is associated with softening of the polymer matrix at higher temperature [17]. Consequently, the polymeric chains have considerable flexibility and they tend to adopt conformations that lead to maximum entropy or minimum free energy, resulting in a reduction in the storage modulus with increase in temperature [18]. As expected, the storage modulus increased according to the increase in the contents of zeolite. This is obviously because zeolite is much stiffer than EVA. The presence of zeolite particles restrict the flow of EVA as a matrix and this restriction increases with increasing zeolite loading resulting greater modulus at higher loading of zeolite. Plus, the increase in storage modulus with increasing zeolite content proves that the stress was transferred from the matrix to the zeolite particles that introduced stiffness into the EVA [19].

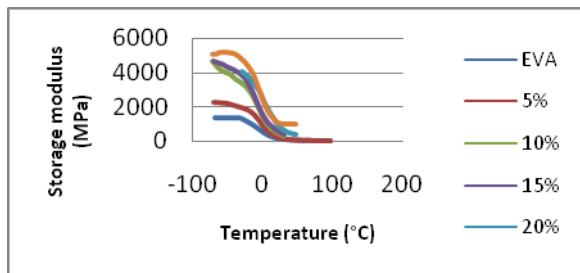


Figure 2: Storage modulus of pure EVA and EVA/zeolite composites versus temperature

The variation of loss modulus versus temperature for EVA/zeolite composites is shown in Figure 3. The highest peak of the loss modulus represents the γ -transition peak or glass transition temperature (T_g) of the composites [20]. By referring to Figure 3, the maximum value of loss modulus or also known as T_g slightly changes with the zeolite content. T_g of pure EVA is around -7.60°C and shifts to -6.34°C , -5.99°C , -4.12°C , -3.75°C and -3.01°C with increasing zeolite content from 5 to 25 vol. %, respectively. The shift in the value of T_g to a higher temperature indicates the presence of interaction between EVA matrix and zeolite. Also, T_g shift is evidence that the glassy behavior of filled EVA increases in the presence of an immobilized interfacial layer around the zeolite particles. Figure 3 also shows that the loss modulus increased according to the increase in the contents of zeolite. This suggests that the incorporation of zeolite has improved the ability of the EVA/zeolite composites to convert or dissipate the applied mechanical energy as heat.

The tan delta shown in Figure 4 provides the fractional energy lost in a system due to a deformation [4]. The incorporation of zeolite particles reduces the tan

delta as the presence of zeolite apparently restricted the mobility of the polymeric chains causing the immobilization of EVA matrix in the relaxation process which consequently reduces the damping of the composites.

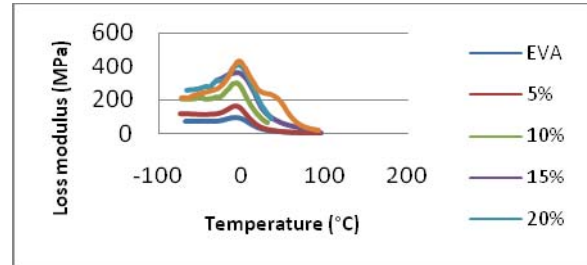


Figure 3: Loss modulus of pure EVA and EVA/zeolite composites versus temperature

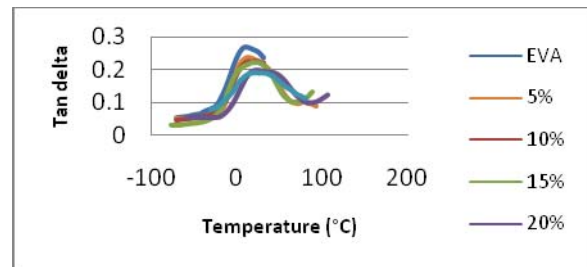


Figure 4: Tan delta of pure EVA and EVA/zeolite composites versus temperature

The effect of chemical crosslinking on storage modulus of EVA and EVA/zeolite composites at 25 vol. % zeolite loading is depicted in Figure 5. It can be clearly observed that both crosslinked EVA and 25 vol. % crosslinked EVA/zeolite composites exhibit marginal improvement in the value of storage modulus compared to the uncrosslinked ones. This is probably attributed to the presence of peroxide radicals from DCP which promote the formation of covalent bonding. The crosslinks formation in the EVA/zeolite system with the presence of DCP results in a reduction of the molecular chains mobility in the interfacial region which consequently improved the storage modulus of EVA/zeolite composites.

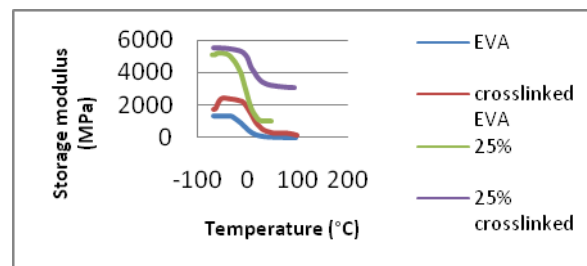


Figure 5: The effect of crosslinking on storage modulus of EVA and EVA/zeolite composites as a function of temperature

A clear comparison of loss modulus of the uncrosslinked and DCP crosslinked ones is given in Figure 6. The T_g of pure EVA changes from $-7.60\text{ }^{\circ}\text{C}$ to $3.61\text{ }^{\circ}\text{C}$ meanwhile that of 25% EVA/zeolite composites changes from $-3.01\text{ }^{\circ}\text{C}$ to $11.35\text{ }^{\circ}\text{C}$ in the presence of DCP crosslinking agent. This is as expected since the newly formed crosslinks will restrict the segmental mobility of the EVA chains, and increases the energy requirements for the transition to occur thus raises the T_g . In addition, the constraints imposed upon the amorphous phase by crosslinking exhibit a great influence on the T_g of a polymer composite [20].

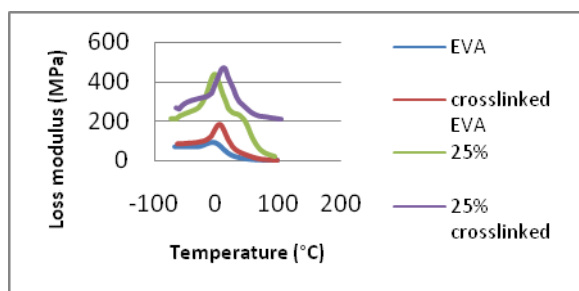


Figure 6: The effect of crosslinking on loss modulus of EVA and EVA/zeolite composites as a function of temperature

The tan delta peaks of uncrosslinked and DCP crosslinked EVA and its composites at 25 vol. % can be distinctly observed in Figure 7. As can be seen, both crosslinked EVA and EVA/zeolite composites exhibit lower magnitude of tan delta peaks than that of the uncrosslinked ones. The reduction in the damping behavior of the crosslinked composites indicates that the viscosity of the system is enhanced due to the incorporation of DCP into the EVA matrix.

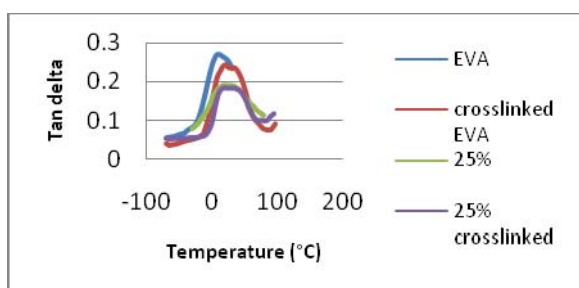


Figure 7: The effect of crosslinking on tan delta of EVA and EVA/zeolite composites as a function of temperature

4. CONCLUSIONS

The results of both flexural yield strength and modulus exhibit almost the same trend where the composites containing DCP crosslinking agent give higher values compared to that of uncrosslinked composites. The incorporation of zeolite particulate filler into the EVA matrix provides greater storage and loss

modulus. However, the value of tan delta or mechanical loss factor of EVA/zeolite composites decreases with increasing zeolite content. The dynamic mechanical properties of EVA and EVA/zeolite composites were dramatically improved in the presence of DCP as crosslinking agent. This is attributed to the formation of covalent bonds as the effect of crosslinking by DCP.

5. REFERENCES

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