Effect of peroxide cross-linking on viscoelastic behaviour and thermal properties of zeolite filled ethylene vinyl acetate composite

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Abstract

In this research, both crosslinked and uncrosslinked zeolite/ethylene vinyl acetate (EVA) composites were prepared by a melt-mixing process followed by compression molding using a hot press machine according to standard test specimen. For the crosslinking process, dicumyl peroxide (DCP) was used as a crosslink agent in the composites. Dynamic mechanical analysis (DMA) was performed in order to study the viscoelastic properties of the composites and the results indicated that the transition temperatures of crosslinked composites were greater than those of uncrosslinked composites. The values of storage modulus and loss modulus were improved while that of loss tangent was reduced with the presence of DCP in the composites. Earlier, 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 decreased. Furthermore, the study of thermal properties of the composites was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results from TGA and DSC showed that the zeolite loading as well as the presence of DCP, had an influence on the thermal stability and crystallinity of EVA/zeolite composites.

Keywords: chemical crosslinking, dynamic mechanical analysis, thermal properties, 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]. Among the popular inorganic fillers are alumina, calcium carbonate, silica, feldspar and also clay minerals, particularly zeolite. In this study, zeolite was chosen as filler as it provides many advantages such as being economical and less harmful compared to other synthetic fillers. Plus, zeolite is commercially attractive due to its unusual crystalline structures yielding unique chemical properties. Zeolite consists of a tetrahedral network of oxygen and silicon atoms where aluminium replaces some of the silicon in order to form aluminosilicates. Zeolite is also known in widespread applications such as molecular sieves, catalysis, ion exchange materials and most importantly as mineral filler in polymer matrices [2].

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

Apart from the incorporation of coupling agents and compatibilizers into the polymer composites, crosslinking of polymer is also considered to be a promising method for yielding a composite with superior strength. Recently, there are two main methods that are extensively used in crosslinking of ethylene vinyl acetate (EVA), namely high-energy irradiation (gamma-rays or electron beam) crosslinking and chemical crosslinking (peroxide and silane crosslinking). Because of several shortcomings of high-energy crosslinking, such as high investment, complicated operation and critical requirement for safety and radiation protection, chemical crosslinking using dicumyl peroxide (DCP) was used in this research. Indeed, some researchers had found the usefulness of peroxide crosslinking in enhancing the interaction between matrix and filler [4–6]. Nogellova et al. observed an improvement in mechanical properties of LDPE/wood flour composites after modification of peroxide (2, 5-dimethyl-2, 5-ditertbutyl peroxy hexyne-3) [4]. A similar observation was made by Gul who studied the comparison of peroxides in cross-linking ultra-high molecular weight polyethylene (UHMWPE) [5]. Munusamy et al. evaluated the effect of different crosslinking system on the properties of EVA/natural rubber/organoclay composites [6]. However, there is no report on the use of DCP as a cross linking agent particularly in zeolite filled EVA composites.

The goal of this study is to investigate the effect of peroxide crosslinking on the thermal properties and viscoelastic properties of zeolite/EVA composites. All results will be discussed and compared with the uncrosslinked zeolite/EVA composites.
2 Experimental procedure

In this study, ethylene vinyl acetate (EVA) with specification Cosmothene Eva H2020 was used as polymer matrix. The melt flow rate and vinyl acetate content of this EVA is 1.5g/10 min and 15wt.%, respectively. Meanwhile, mordenite type of zeolite mineral species was used as natural filler. Zeolite is basically a hydrous alumino-silicate having a density of 1.914 g/cm³ and in the form of white color grains. Its chemical formula is (Ca,Mg₂,K₂)Al₂Si₁₀O₂₄.7H₂O with orthorhombic crystal system. Besides, dicumyl peroxide (DCP) was used as crosslinking agent and was supplied by Bayer (M) Inc., Malaysia. Prior to compounding process, zeolite was grinded into powder form using a ring mill machine. After the grinding process, the exact particle size was determined by Malvern Mastersizer particle size analyzer. The result obtained was 5.62 μm.

2.1 Compounding technique

Prior to compounding, zeolite powder and EVA were dried in an oven at 80°C for 24 hours. The composites were compounded using an internal mixer Thermo Haake Polydrive with Rheomix, R600/610 model. The processing conditions were set at 130°C with 7 min of mixing time and 50 rpm of rotor speed. After that, the samples were compressed molded for the required test pieces.

2.2 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed using a DMA instrument (Mettler Toledo DMA 861e) under oscillating flexural loading. Specimens of dimensions 63×12×3 mm³ were used for testing at a frequency of 1 Hz. The temperature was scanned from –70 to 100°C with a heating rate of 5°C/min.

2.3 Thermogravimetric analysis

A Perkin Elmer Pyris TGA-6 thermogravimetric analyzer was used to measure the weight losses and decomposition temperature of pure EVA and its composites in the temperature range of 20–600°C with a heating rate of 20°C/min and under a flow of nitrogen.

2.4 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) analysis was carried out with a Perkin Elmer Pyris DSC-6. 5 mg of sample were heated from 30 to 190°C at a rate of 10°C/min and held at 190°C for 2 minutes then they were cooled to 30°C at 10°C/min and reheated under the same conditions to 190°C. The crystallinity degree for the composites is determined by the ratio \( \Delta H_m/\Delta H_{m100} \), where \( \Delta H_m \) is the heat of fusion in joule per gram polyethylene segments in the EVA samples, while \( \Delta H_{m100} \) is the heat of fusion in joule per gram pure polyethylene with 100% crystallinity. The \( \Delta H_{m100} \) is 281 joule per gram pure polyethylene with 100% crystallinity [7].
3 Results and discussion

3.1 Dynamic mechanical analysis

The dynamic mechanical properties of the composites were analyzed in order to obtain further information on the viscoelastic behavior of the zeolite/EVA composites. The effect of chemical crosslinking on storage modulus of EVA and zeolite/EVA composites at 25 vol. % zeolite loading is depicted in fig. 1. It can be clearly observed that crosslinked EVA and its composites exhibited marginal improvement in the value of storage modulus compared to the uncrosslinked ones.

Figure 1: The effect of crosslinking on storage modulus of EVA and zeolite/EVA composites as a function of temperature.

This was probably attributed to the presence of peroxide radicals from DCP which improved the interaction between the EVA matrix and zeolite filler. The enhanced filler/matrix interaction resulted in a reduction of the molecular chains mobility in the interfacial region hence causing an increase interfacial stiffness which consequently improved the storage modulus of zeolite/EVA composites. Furthermore, Vijayabaskar et al. [8] mentioned that crosslinking hindered the segmental motion of polymeric chains and this required a higher temperature for the inception of rotation thus increasing the value of storage modulus. This means that the higher value of storage modulus for crosslinked composites is related to the formations of bonds between polymer chains through a crosslinking process [9].

In addition, Mishra et al. [9] obtained a similar result where there was an increase in storage modulus upon peroxide crosslinking, especially at the low frequency region, and it was accompanied by a decrease in terminal region slope.
They claimed that such lower terminal slope and higher storage modulus indicated a solid-like behavior of the peroxide modified blends, which was originated from the network structure of the blends as a consequence of the crosslinking of each phase as well as interchain crosslinking between the components in the blends.

Figure 2: The effect of crosslinking on loss modulus of EVA and Zeolite/EVA composites as a function of temperature.

A clear comparison of loss modulus of the uncrosslinked and DCP crosslinked composites is given in fig. 2. For both EVA and Zeolite/EVA composites, a shift in the peak temperature towards a higher temperature could be clearly observed for the DCP crosslinked ones. This was expected since the newly formed crosslinks restricted the segmental mobility of the EVA chains, and increased the energy requirements for the transition to occur thus raising 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. It is also well known that the improvement in the $T_g$ value indicates an enhanced polymer/filler interaction in the case of DCP crosslinked Zeolite/EVA composites.

This result is in line with those reported by Zurina [10], who stated that the introduction of crosslink into a polymer will proportionally increase the intermolecular network, causing a rise in the $T_g$. Furthermore, they reported that a shifted value of $T_g$ peak for EVA to a higher temperature in the presence of DCP crosslinking agent was attributed to the increase in crosslink density as also proved in the gel content result.

Moreover, the tan delta peaks of uncrosslinked and DCP crosslinked EVA and its composites at 25 vol. % can be distinctly observed in fig. 3. As can be seen, both crosslinked EVA and zeolite/EVA composites exhibit a lower magnitude of...
tan delta peaks than that of the uncrosslinked ones. This is associated with the restriction in molecular motion of EVA chains due to crosslinking which results in less dissipation of energy throughout the composites, hence lowers the tan delta values.

![Figure 3: The effect of crosslinking on tan delta of EVA and Zeolite/EVA composites as a function of temperature.](image)

### 3.2 Thermogravimetric analysis

The effect of peroxide crosslinking on the thermal degradation of zeolite/EVA composites is evident in figs 4 and 5. The crosslinked zeolite/EVA composites result in better thermal properties compared to uncrosslinked zeolite/EVA composites. For example, zeolite/EVA/DCP composites exhibit greater $T_5$, $T_{90}$ and also maximum degradation temperature ($T_{100}$) compared to those of uncrosslinked zeolite/EVA composites.

These results prove that the filler-matrix adhesion and also dispersion of filler within polymer matrix are important factors governing the thermal stability of the composites. Similar results were obtained by Zhang et al. [11] who reported that the well-dispersed filler in the polymer matrix could be more effective in hindering the diffusion of volatile decomposition products hence leading to the improved thermal stability.
Figure 4: TGA curve of peroxide crosslinked and uncrosslinked zeolite/EVA composites at various zeolite contents.

Figure 5: DTG thermogram of peroxide crosslinked and uncrosslinked zeolite/EVA composites at various zeolite contents.
3.3 Differential scanning calorimetry

The DSC heating curves of crosslinked and uncrosslinked zeolite/EVA composites at various zeolite loadings are shown in figs 6(a) and 6(b), respectively. The DSC curve of pure EVA shows an endothermic peak at around 94°C, which can be related to the melting temperature of the EVA phase.

Figure 6: The heating DSC curves of (a) uncrosslinked zeolite/EVA composites and (b) peroxide crosslinked zeolite/EVA composites with different zeolite content.

The melting temperature of crosslinked zeolite/EVA composites shifts to a higher temperature compared to uncrosslinked zeolite/EVA composites. However, the degree of crystallinity of crosslinked zeolite/EVA composites is lower due to the presence of DCP. The lower degree of crystallinity for DCP crosslinked composites can be explained by the improved interaction between EVA and zeolite which gives rise to more reduced chain mobility and hence the crystallization of EVA chains is more difficult to occur.
4 Conclusions

The dynamic mechanical properties of EVA and zeolite/EVA composites were dramatically improved in the presence of DCP as crosslinking agent. The DCP crosslinked zeolite/EVA composites exhibited higher value of storage and loss modulus but lower magnitude of tan delta peaks compared to that of the uncrosslinked composites. This is attributed to the presence of DCP which improved the dispersion of zeolite within the EVA matrix. In addition, the DMA results proved the presence of enhanced interaction between EVA matrix and zeolite filler, as evident from the shift in the value of $T_g$ to a higher temperature. Thus it can be concluded that the adhesion between polymer matrix and filler has a great influence on the visco-elastic properties of the composites.

References


