The Effect of 4,4′-Methylene-bis-(2,6-di-tert-butylphenol) on Properties of Polyvinyl Alcohol /Chlorinated Polyethylene Composites

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Abstract. A series of damping composites were prepared by adding 4,4′-Methylene-bis-(2,6-di-tert-butylphenol) (AO 4426) to a mixture of chlorinated polyethylene (CPE) and polyvinyl alcohol (PVA) with a mass ratio of 80:20. The damping properties and molecular structure of the composites were measured, characterized and analyzed by means of DMTA, DSC and FT-IR. The results show that there is only one damping peak in the PVA/CPE composite. However, a new damping peak appeared above the glass transition temperature of CPE with the addition of AO 4426 because of phase separation which caused by the aggregation of AO 4426 microcrystal under the action of hydroxyl hydrogen bonds. The corresponding temperature of this new damping peak is determined by glass transition temperature of AO 4426. Fourier infrared spectrum show aromatic ether and aromatic ester formed by dehydration between PVA and AO 4426.

Keywords: Chlorinated polyethylene; Polyvinyl alcohol; Damping property; Phase separation.

1. Introduction

Noise and vibration as a physical phenomenon are affecting people's life quality, affecting measurement accuracy of precision instruments and even endangering the safety and lifespan of public facilities with the rapid development of the social economy. Development of damping materials, which can effectively control and reduce noise and vibration, has become a hot spot for researchers in various countries with continuing to grow the noise and vibration [1-3].

Polymer has become one of the most widely used matrix for high performance damping composites due to its unique viscoelasticity. However, the application of pure polymer is limited in the damping field because of the low damping performance or the narrow damping temperature range. Some researchers have been committed to improve the damping properties of polymer by means of blending [4-5], copolymerization [6-7], interpenetrating polymer networks (IPN) [8-9], and organic hybridization [10-13]. The damping performance of the blend composites depends on the glass transition of each component. Only one damping peak or multi-damping peaks would appear according to the compatibility or incompatibility between components. The improvement of the damping peak will lead to the narrowing of the damping temperature range, and vice versa. However, the improvement of one attribute came at the expense of another attribute. So, the damping improvement of blends could not be achieved in essence. The damping peaks appear respectively near the glass transition temperature of each component for incompatibility blends which will effectively expand damping temperature range. IPN is an effective
method for the preparation of wide temperature domain damping materials. However, there are series of problems such as lack of increasing the damping peak value, complicated processing technology and difficult production. Organic hybrid method can not only adjust the damping peak but also broaden damping temperature range because of obtaining a multi-peak platform which caused micro-phase separation by hydrogen bond formation, as long as the appropriate substrate and organic small molecules are chosen.

Polyvinyl alcohol (PVA), which acted as an excellent sizing agent in textile, has become a serious environmental contaminant due to poor biodegradation performance; strict environmental controls targets mean that PVA is facing elimination and replaced by others in the process of textile manufacturing. However, it provides the possibility of hybridization for the blends between PVA and polar rubber due to polyols characteristics of PVA. Meanwhile, its cost is much lower than that of rubber. So, it offers the possibility for preparation low-cost high performance damping composites.

A series of low-cost damping high composites were prepared by adding 4,4’-Methylene-bis-(2,6-di-tert-butylphenol) (AO 4426) as the filler to a mixture of chlorinated polyethylene (CPE) and polyvinyl alcohol (PVA) with a mass ratio of 80:20 as the matrix(In the previous study, CPE/PV A damping material with 80:20 of mass ratio between CPE and PVA had a high cost performance). The effect of AO 4426 on damping characteristics and structural analysis is investigated in PVA/CPE-AO 4426 composites.

2. Experimental

2.1. Raw Materials

The raw materials used for the low-cost high damping composites were CPE with 36% chlorinated degree (Trademark: CM 0836, The Dow Chemical Company, American), PVA with polymerization degree of 500 and the alcoholysis degree of 88 % (Japan Kurary). PVA/CPE blends with mass ratio of 20:80 were acted as the matrix and AO 4426 with double hydroxyl structure, white powder and a melting point of 115℃ as the filler was a commercial antioxidant (supplied by Jinhai Albemarle Chemical and Industry Co., Ltd., Ningbo, Zhejiang, China).

2.2. Composites Fabrication

The formulation of PVA/CPE-AO 4426 damping composites is PVA, CPE and AO 4426 with mass ratio of 20:80:0 (as a reference example), 18:72:10, 17:68:15, 16:64:20, 15:60:25, 14:56:30, respectively. They are correspondingly denoted as PCA-0, PCA-10, PCA-15, PCA-20, PCA-25, PCA-30 by means of combining abbreviated PVA/CPE-AO 4426 to PCA with the mass fraction of AO 4426 for the convenience of the description below.

Firstly, powders of PVA weighted according to the process design formula were added in the self-made mixing device (in Fig.1) with appropriate amount of water at speed 20rpm without heating for 20min, and then PVA was dissolved in water until size(slurry) with viscosity stability was formed at 100℃ temperature and speed 60rpm for 120min.

Secondly, CPE and AO 4426 were been added into the solution of PVA in turn and stirred until even dispersion.

Thirdly, even dispersion mixtures were pulled into space between the rollers with 70℃ of a two roll mixing mill (X(S)K-160B, Chuangcheng Rubber &Plastic Machinery Co., Ltd, Wuxi, China) and then the mixtures were mixed by using the cutter for ensuring homogeneity after the water was evaporated.

Fourthly, evenly sheeted mixtures placed in the mold with thickness 1mm were molten at 135℃ for 20 min and then pressed at 135℃ for 30 min under the pressure of 10 MPa on plate vulcanizing press machine (QLB-D 400×400×2, Chuangcheng Rubber &Plastic Machinery Co., Ltd, Wuxi, China).

Finally, molded samples were taken-out, and then cooled them by ice water quenching to obtain a series of PVA/CPE-AO 4426 damping composites with a thickness of about 1mm.
2.3. Performance Characterization

2.3.1. Damping Property. DMTA of the composites was conducted on the DMA 8000 manufactured by Perkin Elmer Company, USA. For this, 12mm ×5mm×1.0mm dimension specimens were prepared. The damping properties of the composites were measured under the tensile mode, with the heating rate of 2 °C/min and frequency 1 Hz.

2.3.2. Thermal Behavior. DSC measurements were implemented on a Pyris-1 type DSC manufactured by Perkin Elmer Company, USA. Samples of about 5mg in weight and sealed in aluminum pans were heated from 30 to 180°C at a heating rate of 2°C/min under a high purity helium atmosphere with a gas flow rate of 20 ml/min.

2.3.3. Structural Analysis. The FTIR spectra of PVA/CPE-AO 4426 composites were received from scanning the specimens within the wavenumber range from 400 to 4000 cm⁻¹ for 64 times with a resolution of 2 cm⁻¹ by using Nicolet-5570 continuum Fourier transform infrared spectrometer and attenuated total reflection (ATR) technique.

3. Result and Discussion

3.1. Effect of AO 4426 on the Damping Performance of PVA/CPE

As shown in Fig.2, there is only one damping peak in the PVA/CPE composite indicating compatible system between CPE and PVA. Interestingly, a novel damping peak (the second peak of tan δ) appeared above the glass transition temperature (the first peak of tan δ) of CPE in PVA/CPE-AO 4426 composites with the addition of AO 4426. With the increase of AO 4426 content, the second peak increased and the first peak declined while the temperature corresponding to each damping peak barely changed.

Aromatic ether was formed by dehydration reaction between hydroxyl of PVA and hydroxyl of AO 4426 and aromatic ester was obtained by chemical reaction between acetate radical in the PVA and hydroxyl of AO 4426 in the process of hot-pressing with the addition of AO 4426. The excess AO 4426 would be precipitated in the material by microcrystal of AO 4426 with the continuous addition of AO 4426. So, aromatic ether, aromatic ester and microcrystal of AO 442 coexist in PVA/CPE-AO 4426 composites.
Figure 2. Temperature dependence of tan δ for CPE and PVA / CPE -AO 4426 composites with varied content of AO 4426. On one hand, they formed the steric-hindrance effect by hindering the movement of large chains of matrix molecules, but on the other hand, they caused large friction between them and matrix when the composites suffer external vibration. The former lead to decrease of damping, the latter resulted in the improvement of damping property. The first peak decreased with increase of AO 4426 content, which is obvious that the former's influence has prevailed. The temperature corresponding to the first damping peaks was determined by the glass transition temperature of CPE, so the damping peak corresponding temperature didn’t change. And the novel damping peak suggests that PVA / CPE -AO 4426 composites show the micro-phase separation \cite{13}, which is caused by a rich phase of AO 4426 microcrystalline under interaction of self-hydrogen bonding force. The hydrogen bond is formed between the hydroxyl in the exterior of microcrystal. In addition, the more the content of AO 4426 is in the composite, the more microcrystal is, the deeper the degree of AO 4426 enrichment is, the stronger the phase separation is \cite{13}. On one hand, the matrix of the composite is split and the first damping peak is declined. On the other hand, the second damping peak, which arises from the glass transition of AO 4426, is improved. The further proof is provided.

3.2. Effect of AO 4426 on the FT IR of PVA/CPE
Fourier transformed infrared spectra of PVA / CPE -AO 4426 composites with varied content of AO 4426 are shown in Fig. 3.
There is a broad peak at the wavenumber range of 3200~3500 cm$^{-1}$ in the PVA/CPE composite indicating intermolecular hydrogen bonds between OH-OH of PVA and $\alpha$-H-OH of CPE and PVA. With the addition of AO 4426, the spectra of PVA / CPE -AO 4426 composites are the presence of two bands associate with hydroxyl stretching vibration. The bands at 3634 cm$^{-1}$ and 3598 cm$^{-1}$ are assigned to free hydroxyl stretching vibration (non-hydrogen bonded) showing “free” hydroxyl of AO 4426 in the composites, while the bands at the wavenumber range of 3200~3500 cm$^{-1}$ are assigned to intermolecular hydrogen bonds between OH-OH and $\alpha$-H-OH. Hydrogen bonds of OH-OH are hydrogen bonds between hydroxyl of PVA and AO 4426 and themselves, while hydrogen bonds of $\alpha$-H-OH are hydrogen bonds between $\alpha$-H of CPE and hydroxyl of PVA and AO 4426. Interestingly, there are some strong sharp peaks at 1730 cm$^{-1}$, 1230 cm$^{-1}$ and 1039 cm$^{-1}$. The former is mapping to carbonyl stretching vibration indicating aromatic ester formation by dehydration reaction between acetate radical of PVA and hydroxyl of AO 4426; the latter two are assigned to Ar-O stretching vibration and R-O stretching vibration of aromatic ether, which is formed by dehydration reaction between hydroxyl of PVA and hydroxyl of AO 4426. On the one hand, these confirmed the above conjecture, which there are aromatic ester and aromatic ether in the PVA/PVA-AO 4426 composites. On the other, these solved the problem of the service life due to characteristic of absorbing wet to sticky of aromatic ether and aromatic ester in the PVA/PVA-AO 4426 composites.

3.3. Effect of AO 4426 on the Storage Modulus of PVA/CPE

Fig. 4 shows the temperature dependence of storage modulus for PVA / CPE -AO 4426 composites with varied content of AO 4426.

![Figure 4](image)

**Figure 4.** The temperature dependence of storage modulus for PVA / CPE -AO 4426 composites with varied content of AO 4426.

It was found that there is only one phase transition in the storage modulus curves between CPE and PVA/CPE, and the modulus height of PVA/CPE is higher than that of CPE. This indicated that PVA/CPE is compatible systems, and PVA acts as reinforcement. The curves of PVA/CPE-AO 4426 can be divided in five domains: two phase transition regions in which $E'$ changes rapidly with temperature, and three platform regions that appear a gentle decrease in slope. The former transition at 0°C is corresponding to the glass transition of CPE phase. The latter phase transition at 60°C is a novel phase transition which is associated with the transition of AO 44 26 rich phase caused by phase-separation between PVA/CPE and AO 4426.
3.4. Effect of AO 4426 on the DSC of PVA/CPE

Fig. 5 shows DSC curves of AO 4426 and PVA / CPE - AO 4426 with varied content of AO 4426 at 2 °C min⁻¹, respectively.

As shown in fig. 5(b), there are two peaks in the PVA/CPE-AO 4426 except for PVA / CPE - AO 4426 with AO 4426 content of 10% at 112 °C, 51 °C, respectively. The former peak is corresponding to the crystal-melting endothermic peak of AO 4426, and the temperature corresponding to peak is only slightly lower than pure AO 4426 indicating imperfect crystals (i.e. microcrystalline) formed in the PVA/CPE-AO 4426 composites. The latter peak corresponds to the glass transition of AO 4426 (there is a glass transition in the pure AO 4426 in this temperature range as shown in fig.5(a)) which is cause by the enrichment of AO 4426 microcrystals by hydrogen bond force in the PVA/CPE-AO 4426 composites. This also confirmed that a novel damping peak at 51 °C is caused by the glass transition of AO 4426. Most of the AO 4426 is compatibility to PVA/CPE, and a few AO 4426 microcrystalline exists in the PVA / CPE - AO 4426 with AO 4426 content of 10%. So, there are only one peak at 112 °C in the PVA/CPE-AO 4426 with AO 4426 content of 10%.
4. Conclusion
(1) There are two damping peaks in the PVA/CPE-AO 4426 composites indicating formation of phase separation. The damping peak at low temperate corresponds to the glass transition of CPE while the damping peak at high temperature corresponds to the glass transition of AO 4426. This effectively improves the damping performance of the composite.
(2) The aromatic ether is formed by the dehydration between the hydroxyl group of PVA and the hydroxyl group of AO 4426 and aromatic ester is formed by the dehydration between acetate radical of PVA and the hydroxyl group of AO 4426. These solve effectively the problem of moisture absorption and sticky of PVA/CPE-AO 4426 composites and improve the functional lifespan of composites.
(3) Its crystals were clearly observed by DSC curves. However, this kind of crystals is imperfect. Meanwhile, the glass transition of AO 4426 was observed by DSC curve in the PVA/CPE-AO 4426 composites because of phase separation between PVA/CPE and AO 4426.

4.1. Declaration of Conflicting Interests
The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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