Research Article

Enhancement of the Thermomechanical Properties of a Fly Ash- and Carbon Black-Filled Polyvinyl Chloride Composite by Using Epoxidized Soybean Oil as a Secondary Bioplasticizer

Toan Duy Nguyen,1,2 Chinh Thuy Nguyen,3 Van Thanh Thi Tran,3 Giang Vu Nguyen,3 Hai Viet Le,4,5 Lam Dai Tran,2,3 Giang Long Bach,6 and Hoang Thai2,3

1Viet Tri University of Industry, No. 9 Tien Son, Tien Cat, Viet Tri, Phu Tho, Vietnam
2Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
3Institute for Tropical Technology, Vietnam Academy of Science and Technology, No. 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
4Laboratory of Advanced Materials Chemistry, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh City, Vietnam
5Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam
6Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

Correspondence should be addressed to Lam Dai Tran; trandailam@gmail.com and Hoang Thai; hoangth@itt.vast.vn

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Plasticized polyvinyl chloride (PVC) was fabricated using epoxidized soybean oil (ESBO) as a secondary bioplasticizer with dioctyl phthalate (DOP). The PVC/MFA/CB composites were prepared by melt mixing of the plasticized PVC with modified fly ash (MFA), carbon black N330 (CB), and polychloroprene (CR) in a Haake Rheomix mixer using a rotation speed of 50 rpm at 175°C for 6 min and then compressed by Toyoseiki pressure machine under 15 MPa. The effect of ESBO content on morphology, melt viscosity, tensile properties, and flame retardancy of PVC/MFA/CB composites was investigated. The obtained results showed that the incorporation of ESBO has significantly enhanced the processing ability, Young’s modulus, tensile strength, and elongation at break of the PVC/MFA/CB composites. The torque of PVC/MFA/CB composites was increased to approximately 12% when 50 wt% of DOP was replaced by ESBO. When ESBO was 20 wt% in comparison with DOP weight, the elongation at break, tensile strength, and Young’s modulus of the composites were increased to 48%, 24%, and 4.5%, respectively. Correspondingly, thermogravimetric analysis results confirmed that ESBO had improved the thermostability of the PVC composites. The ESBO have potential as a secondary bioplasticizer replacement material for DOP owing to their better thermomechanical stability.

1. Introduction

Dioctyl phthalate (DOP) was utilized widely as a plasticizer in polyvinyl chloride (PVC) plastic; however, this substance has been interdicted in many countries due to its high degree of toxicity [1–4]. Nowadays, epoxidized soybean oil (ESBO) was dedicated as an alternative bioplasticizer partially replacing phthalates in PVC applications thanks to its low cost, nontoxicity, renewability, and biodegradability [5–7]. In addition, ESBO has a high epoxy number making it a good HCl scavenger. The stabilization mechanism of PVC by ESBO involves the reaction of the epoxide ring in ESBO and hydrochloride generated during the PVC degradation process, leading to the unstable chlorine atoms returning into the PVC chains [8, 9]. This reaction prevents the further dehydrochlorination of PVC as well as its color and limits
the reduction in properties of plasticized PVC at high temperatures [8]. The use of ESBO as a secondary stabilizer for PVC in combination with DOP has been investigated in many reports. Mehta et al. indicated that the ratio of ESBO/DOP influences the tensile strength and elongation at break of PVC/DOP/ESBO compounds [10]. The hardness and glass transition temperature of PVC were also increased as the content of ESBO in the composites [11] increases.

In the recent decade, polymer composites based on PVC and low-cost fillers such as fly ash (FA) and carbon black (CB) have attracted many efforts to improve the mechanical properties of PVC [12, 13]. These fillers have the potential of improving mechanical properties such as ultimate tensile strength, percentage of elongation, yield strength, Poisson’s ratio for PVC due to its low density, good dispersion, and strong interaction with the PVC matrix [14–17].

So far, the effect of ESBO-DOP plasticized mixture on properties and morphology of PVC/MFA/CB composites has not been investigated. Therefore, in this paper, a combination of ESBO and DOP with different ratios of ESBO/DOP has been used to plasticize PVC and prepare the composites based on plasticized PVC, MFA, and CB N330. The effect of ESBO content on the melt viscosity, mechanical properties, thermal oxidation stability, and flame retardancy of the PVC/MFA/CB composites was studied and discussed.

2. Experiment

2.1. Materials. Polyvinyl chloride (PVC) was produced in Vietnam with a K value of 65.0 and a degree of polymerization of 1300 ± 100. Dioctyl phthalate (DOP) was purchased from Korea. Epoxidized soybean oil (ESBO) with an epoxide group content of 15.2 was provided by Malaysia. Carbon black (CB, code N330), a commercial product made in China, had a density of 1.7–1.9 g/cm³ and a grain diameter of 26.0–38.0 nm. The fly ash (FA) was from the waste from Pha Lai Thermal Power JSC, Vietnam, and it contains SiO₂, Fe₂O₃, and Al₂O₃ with a total value higher than 86%, a moisture content of 0.3%, and a particle size of 3–10 μm. FA was modified with stearic acid (MFA) in which the weight of stearic acid was 3 wt% based on the weight of FA. Polychloroprene (CR) having a density of 1.23 g/ml and a Mooney viscosity of 48 ± 5 was purchased from Japan and used as a compatibilizer.

2.2. Instruments. The composites were prepared by a Haake internal mixer (Germany) and hot pressure machine (Toyoseiki, Japan). The tensile properties of the composites were analyzed on a Zwick Tensile 2.5 Machine (Germany), and the fractured surface of the sample was evaluated by field-emission scanning electron microscopy (FESEM) analysis using an S-4800 SEM (Hitachi, Japan). Thermal property studies were performed on a DSC-60 thermogravimetric analyzer (Shimadzu Co., Japan). The thermal oxidation stability of the composites was evaluated in a gravity convection oven (Memmert, Germany).

2.3. Plasticization of PVC with DOP and ESBO. Firstly, 60.0 grams of PVC powder was mixed with 30 wt% of plasticizers (ESBO + DOP total weight in comparison with PVC weight). The ratios of ESBO/DOP are 0/100, 10/100, 20/100, 30/100, 40/100, and 50/100 (wt%/wt%). Secondly, 0.9 gram of dibutyltin bis-(isooctyl thioglycolate) (1.5 wt% in comparison with PVC weight) was then added to the above mixture. Finally, the mixture was aged for 3 h at 85°C in a convection air oven to yield dry plasticized PVC powder. A proposed schema of plasticization of PVC with DOP and ESBO is demonstrated in Figure 1. Here, the plasticization externally plasticized PVC thanks to the formation of physical interaction between functional groups in DOP, ESBO, and PVC.

2.4. Preparation of PVC/MFA/CB Composites. The as-prepared dry plasticized PVC powder was mixed with CB powder and MFA fillers (CB + MFA total weight of 10 wt% in comparison with dry plasticized PVC powder weight). Next, 6.7 g CR is added to this mixture, and the above mixture was mixed in a Haake internal mixer at 190°C for 6 min, at a rotor speed of 120 rpm, and then pressed to form 1.0 mm thickness sheets. All samples were left to cool down to room temperature and stored at standard conditions for at least 48 h before characterizing their mechanical properties and morphology. The PVC/MFA/CB composite samples with ESBO/DOP ratios of 0/100, 10/100, 20/100, 30/100, 40/100, and 50/100 were denoted as P0, P10, P20, P30, P40, and P50, respectively.

2.5. Methods of Investigation. The melt viscosity or torque of the PVC/MFA/CB composites during melt mixing was recorded by using Polylab 3.1 software connected to the Haake internal mixer at 190°C for 6 min, at a rotor speed of 120 rpm. The tensile properties of the composites were determined according to the ASTM D638 standard on the Zwick universal mechanical measuring device at a speed of 100 mm/min and a temperature of 23 ± 2°C. The thermal oxidation stability of the composites was evaluated by comparing tensile properties before and after heating at 100°C for 72 h in a gravity convection oven (Memmert, Germany). Flame retardancy of the composites was tested according to UL-94VB method (Underwriters Laboratories Inc., USA). All tests were evaluated in triplicate to confirm the repeatability of the data.

3. Results and Discussion

3.1. The Melt Viscosity of PVC/MFA/CB Composites. The melt viscosity of PVC/MFA/CB composites with ESBO/DOP ratios of 0/100, 10/100, 20/100, 30/100, 40/100, and 50/100 expressed by the change of mixing torque according to mixing time is demonstrated in Figure 2. It can be seen that the mixing temperature of the chamber is decreased, when the mixture of dry plasticized PVC powder, CB powder, MFA, and CR is added to the mixing chamber, because PVC powder and CR are still in the solid state. The mixing torque of all composites is increased to the maximum value. Then, the entire mixture is heated, and PVC and CR begin to melt, leading to the reduction in the mixing torque quickly after the first melt mixing for 4 min and slightly after another melt mixing for 5 min (Table 1). The ratio of ESBO/DOP affects slightly the mixing torque of PVC/MFA/CB composites during the mixing time.
From the data presented in Figure 2 and Table 1, all the investigated samples of the PVC/MFA/CB composites, except for the P50 sample, have a mixing torque a little higher than that of the P0 sample. These results can be explained by the lower viscosity of DOP which penetrates the outer surface of PVC faster than ESBO in the first stage of plasticization. Therefore, the plasticizing time of PVC by DOP is shorter than that by ESBO [11, 18]. Thus, the replacement of DOP by ESBO (from 10 wt% to 40 wt%) is more suitable for the processing ability of the PVC/MFA/CB composites. In particular, ESBO not only plays a role of a plasticizer but also as a suggestion can interact with both MFA and CB through hydrogen bonding as well as through dipole-dipole interactions between epoxide ring, C=O groups in ESBO and OH groups in CB, stearic acid in MFA, and Cl atoms in CR. Through the above physical interactions, MFA and CB can be dispersed into PVC, and thus, the internal friction of the melt mixing process to form the PVC/MFA/CB composites is decreased. As a result, the preparation process of PVC/MFA/CB composites using ESBO/DOP (10-40 wt% of ESBO in the ESBO + DOP mixture) is similar to that of the sample using only a DOP plasticizer. However, when using ESBO content in the ESBO + DOP mixture higher than 40 wt%, the redundancy amount of ESBO cannot interact with MFA and CB anymore, make a separate phase, and eliminate out samples in the melt mixing process (the boiling temperature of ESBO > 150°C), thus limiting the plasticization ability of ESBO. Therefore, the PVC/MFA/CB composite containing 50 wt% of ESBO has a torque higher than that of composites containing 10-40 wt% of ESBO.
3.2. Morphology of the PVC/MFA/CB Composites. SEM images of a fracture surface of the P30 composite (using 30 wt% of ESBO) are represented in Figure 3. It is clear that MFA particles adhere and disperse well to PVC and are not clustered (Figure 3(a)). At higher magnification, good adhesion and dispersion of CB can be observed, which are better than those of MFA in the PVC matrix (Figures 3(b)–3(d)). This is due to hydrogen bonding and dipole-dipole interactions between epoxide ring, C=O groups in ESBO and hydroxyl groups in CB, stearic acid in MFA, and Cl atoms in CR as mentioned above. On the other hand, the separation of the CR phase in the composite was not found which indicated that CR could improve compatibility of PVC and MFA and CB.

3.3. Tensile Properties of the PVC/MFA/CB Composites. The effect of the ESBO/DOP ratio on the tensile strength, elongation at break, and Young’s modulus of the PVC/MFA/CB composites is demonstrated in Table 2. The tensile strength and elongation at break of the composites using 10-50 wt% of ESBO are remarkably higher than those of the sample without ESBO. It can be explained by the plasticization role of ESBO to physical interactions between ESBO and MFA, CB, and CR in the PVC/MFA/CB composites as mentioned above. Young’s modulus of the PVC/MFA/CB composites is increased with increasing ESBO content to 30 wt%. Due to high physical interactions, the structure of the composites is closer and more regular, leading to the enhancement in hardness of the composites. In contrast, Young’s modulus of the PVC/MFA/CB composites is decreased with rising ESBO content over 30 wt%. Using a large amount of ESBO, it makes the composites become softer and less tight and the hardness of the composites is reduced. From the obtained

| Composite | Tensile strength (MPa) | Elongation at break (%) | Young’s modulus (MPa) |
|-----------|------------------------|-------------------------|-----------------------|
| P0        | 14.58                  | 64.47                   | 754.00                |
| P10       | 16.64                  | 79.63                   | 758.33                |
| P20       | 18.10                  | 95.47                   | 788.17                |
| P30       | 18.40                  | 91.73                   | 784.67                |
| P40       | 17.84                  | 89.20                   | 639.33                |
| P50       | 17.02                  | 87.35                   | 586.23                |

Figure 3: SEM images of the P30 composite in different magnifications.
results, the composites using 20-30 wt% ESBO have tensile properties higher than those of the rest of the investigated samples. Therefore, partially replacement of DOP by ESBO may help to enhance the tensile properties of the PVC/MFA/CB composites.

3.4. Thermal Oxidation Stability of the PVC/MFA/CB Composites. The thermal oxidation stability of PVC/MFA/CB composites is determined by comparing the tensile properties of the materials before and after thermal oxidation testing. As shown in Figure 4, the tensile strength and Young’s modulus of the PVC/MFA/CB composites using different ESBO/DOP ratios before and after thermal oxidation testing.

\[
\begin{align*}
\text{(a)} & \quad \left(\text{CH}_2\text{CH}_2\right)_n \xrightarrow{\text{HCl}} \text{HCl} + \left(\text{CH}_2=\text{CH}\right)_n \\
\text{(b)} & \quad \text{HCl} + \text{ESBO} \rightarrow \text{Epoxide groups} \xrightarrow{\text{H}^+} \text{OH}
\end{align*}
\]

Figure 5: Mechanism of PVC degradation by thermal oxidation and removal of HCl (a) and reaction of epoxide groups in ESBO with HCl generated during the degradation process (b) [6].
Figure 6: DSC thermograms of the P30 sample before (a) and after (b) thermal oxidation testing.
Before and after thermal oxidation testing, we are able to mimic the changes in the composites after thermal oxidation testing can be caused by chemical and physical changes in the materials. Therefore, all PVC/MFA/CB composites reach a V0 level, besides the organic nature of ESBO with low flame retardancy. In other words, using different ESBO/DOP ratios does not change the flame retardancy of the PVC/MFA/CB composites.

### 3.5. Flame Retardancy of PVC/MFA/CB Composites

Flame retardancy of PVC/MFA/CB composites is significant. The data used to support the findings of this study are included within the article.

Based on the obtained results of the tensile strength and Young’s modulus of the PVC/MFA/CB composites before and after thermal oxidation testing, we are able to confirm that ESBO enhances thermal oxidation stability of the composites. Therefore, all PVC/MFA/CB composites reach a V0 level, besides the organic nature of ESBO with low flame retardancy. In other words, using different ESBO/DOP ratios does not change the flame retardancy of the PVC/MFA/CB composites.

### 3.5. Flame Retardancy of PVC/MFA/CB Composites

The flame time of the PVC/MFA/CB composites at different ESBO/DOP ratios is listed in Table 3. It can be observed that all samples are self-extinguishing after fire ignition (no smoke generated, no flame, and no flame drops falling). The total burning time \( t_1 + t_2 \) of all samples is small. This is explained by the presence of chlorine atoms in CR macromolecules which increases flame retardancy of the materials. Therefore, all PVC/MFA/CB composites reach a V0 level, besides the organic nature of ESBO with low flame retardancy. In other words, using different ESBO/DOP ratios does not change the flame retardancy of the PVC/MFA/CB composites.

### 4. Conclusion

Replacement of DOP by ESBO (10-50 wt%, in comparison to DOP weight) is suitable for the processing of PVC/MFA/CB composites. The elongation at break and tensile strength of the composites using 10-50 wt% of ESBO are remarkably higher than those of the composites using only 100 wt% of DOP. Young’s modulus of the PVC/MFA/CB composites is increased with increasing ESBO content to 30 wt% and decreased with rising ESBO content over 30 wt%. Thermal oxidation stability of the PVC/MFA/CB composites is improved by using ESBO as a secondary plasticizer. The different ESBO/DOP ratios do not change the flame retardancy of the PVC/MFA/CB composites. It can be prepared more friendly composites of PVC/MFA/CB using 20-30 wt% of ESBO.

### Data Availability

The data used to support the findings of this study are included within the article.

### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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