

Combining Renewable Eleostearic Acid and Eugenol To Fabricate Sustainable Plasticizer and Its Effect of Plasticizing on PVC

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Abstract

The recent studies on sustainable plasticizer mainly focus on raw material source, synthesis method and plasticization, but the effect of chemical functional groups (epoxy group and ester group) of sustainable plasticizer on compatibility and thermal stability of plasticized polyvinyl chlorid (PVC) materials has been ignored. In this study, we synthesized two kinds of sustainable plasticizer, eleostearic acid eugenol ester(EAEE) and epoxidized EAEE. PVC films plasticized with EAEE were investigated and compared with epoxidized EAEE. PVC plasticized with epoxidized EAEE showed more flexible and thermal stability than EAEE. More hydrogen bonds were formed between PVC chains and epoxidized EAEE than that of PVC chains and EAEE, which caused the that epoxidized EAEE played more efficient plasticizing effect on PVC than EAEE. Epoxidized EAEE containing the flexible alkane chains and polar group (ester groups and epoxy groups) has stronger intermolecular interaction force than EAEE, causing homogeneous and smooth surface of plasticized PVC films.

1. Introduction

Polyvinyl chlorid(PVC) has been widely used in many different fields as early as 1926.^[1] Due to its good physical properties, excellent thermochemical resistance and low cost, it is second only to polyethylene (PE) and polypropylene (PP) in the global plastics market.^[2] In order to obtain better performance, such as thermal stability, flexibility, flame retardancy, etc. via adding some specific additives. Plasticizer is one of the most common plastics additives.^[3] It is used to make PVC obtain better performance, softer and more ductile.^[4]

Phthalates are commonly used as plasticizers, in particular, the dioctyl phthalate (DOP) and dibutyl phthalate (DBP), account for 80% of the global plasticizer market.^[5] Phthalate are fully derived from fossil oil.^[6] Phthalates are easy to diffuse out of PVC products, which reduces the performance of PVC and increases the harm to the human body and the environment. Studies have shown that it destroys the body's normal endocrine, and it causes carcinogen.^[7-9] When plastic is discarded and flows into rivers and lakes, it will be broken into small pieces under solar radiation, temperature changes and biological action, also known as microplastics.^[10] These microplastics can adsorb pollutants in the water, and when unfortunately enter the human body, it will cause inflammation, immune damage and even death.^[11] In order to solve the existing problems, Navarro and his team have developed various non-migration plasticizers by connecting with plasticizing molecules on the PVC chain through highly active functions.^[12-14] Chung and his group using a plasticizer composed of alkyl-terminal high-branched polyglycerol to produce non-toxic, phthalate-free flexible of PVC.^[15] Because of its harmfulness, various countries' government restrict the addition of DOP to PVC products including children's toys, food packaging, etc.^[16, 17] As early as two decades ago, both European and American regulations defined six banned phthalates derivatives.^[18] Due to recent stricter bans, the proportion of phthalate use is expected to dropping from 65% in 2017 to 60% in 2022.^[19]

Safe bio-based plasticizers have become the mainstream of research, which are made from vegetable oils, citrates, and sugar derivatives.^[20] There are sustainable, largely available and low cost. There is a lot of research on the use of soybean oil,^[21–23] tung oil,^[24] sunflower oil,^[25, 26] cardanol,^[27, 28] waste cooking oil and other bio-based plasticizers. Dekai Liu reported that oleic acid based ester derived from vegetable oil is a renewable environmentally friendly plasticizer with good cold resistance.^[29] Before using vegetable oil synthetic plasticizer, it must be modified, because vegetable oil has limited compatibility with PVC. Cardanol is often modified and then used as a potential plasticizer, and its unsaturated bonds are often epoxidized. Greco and his team developed an epoxidation method, discarding the general *m*-chloro benzoic acid and dichloromethane, and using environmentally friendly reagents to modify cardanol. The experimental results showed that the strength of PVC with 70 phr cardanol plasticizer was similar to that of 50 phr DEHP. However, the performance drops rapidly after aging, and the waist anti-migration performance is poor.^[30] In most cases, natural unsaturated bonds are usually epoxidized to obtain better heat resistance. At this time their anti-migration performance is improved.^[31]

However, due to the complex and cumbersome reaction and harsh conditions, it is difficult to apply to large-scale industrial production.^[32] Foreign chemical giants have launched related products, such as EASTMAN's TIXB (2,4-trimethyl-1, 3-glycol diolates) and other environmentally friendly plasticizer products. Witold Brostow comparing the performance of toxic plasticizers and non-toxic bio-based plasticizers in dynamic friction, found that non-toxic plasticizers are comparable to traditional toxic plasticizers.^[33]

In this study, we will use eleostearic acid and eugenol to synthesize two kinds of bio-based plasticizers. The product will be epoxidized using meta-oxy benzoic acid. These two products will be added to PVC in different proportions, and the performance of the plasticized PVC films will be investigated. The effect of chemical functional groups (epoxy group and ester groups) of biomass based plasticizer on compatibility and thermal stability of plasticized polyvinyl chloride (PVC) materials are investigated in detail.

2. Experimental

2.1 Materials

Eleostearic acid was purchased from Refined Oil And Fatty Co., Ltd. (Anhui, China). Eugenol, ethyl acetate, oxalyl chloride, triethylamine, sodium hydroxide, sodium chloride and tetrahydrofuran Aladdin Co., Ltd. Polyvinyl chloride (PVC) with K value 65.0 and degree of polymerization $1,300 \pm 100$ was procured from Hanwha (KM-31, South Korea).

2.2 Synthesis of eleostearic acid eugenol ester (EAEE)

Eleostearic acid (50 g, 0.18 mol) and 150 ml dichloromethane were dissolved in 500 mL three-necked flask equipped with a magnetic stirrer and a reflux condenser. Then oxalyl chloride (23 g, 0.18 mol) was added in the flask, and the reaction was continued at 25°C for 3 h. After the mixture of eugenol (27 g,

0.16 mol), trimethylamine (18 g, 0.18 mol) and 50 ml dichloromethane was slowly added into the system at 25°C. Then the reaction was heated to 50°C for 12 h. Finally, precipitate was removed by suction filtration and the filtrate washed several times with 7 wt% sodium bicarbonate solution and saturated NaCl solution cleaned to neutral pH by a separating funnel. The organic layer was collected and dried with anhydrous sodium sulfate and filtered. The methylene chloride was removed by a rotary evaporator and stored in a refrigerator at 4°C for later use.

2.3 Synthesis of epoxidized EAEE

EAEE (50 g) and ethyl acetate (100 ml) were added into a 500 ml flask, and perform magnetic stirring in an ice-water bath (< 5°C). 200 ml of ethyl acetate dissolved with 3-chloroperoxybenzoic acid (92 g) was dropped into the reaction system through a constant pressure separatory funnel and the temperature was controlled to be lower than 5°C. Then the reaction was heated to 25°C for 2 h, benzoic acid precipitated during the reaction. The product was washed several times with 7 wt% sodium bicarbonate solution and saturated NaCl solution cleaned to neutral pH by a separating funnel. The organic layer was collected and dried with anhydrous sodium sulfate and filtered. The methylene chloride was removed by a rotary evaporator to obtain epoxidized EAEE.

2.4 Preparation of plasticized PVC materials

PVC and plasticizer (epoxidized EAEE and EAEE) was dissolved in 40 mL of THF at 40°C. The mixture was fully dissolved by magnetic stirring, and then sonicated for 30 minutes to remove air bubbles. The samples were poured into petri dishes (d = 12 cm) followed by slowly air drying at ambient temperature for 1 days then under reduced pressure for 1 days to remove traces of THF and to obtain thin films. The formulations are shown in Table 1.

Table 1
Formulation of the PVC films

PVC films	PVC (g)	EAEE (g)	Epoxidized EAEE(g)
PVC	2	-	-
PVC-25wt% EAEE	2	0.5	-
PVC-50wt% EAEE	2	1	-
PVC-25wt% epoxidized EAEE	2	-	0.5
PVC-50wt% epoxidized EAEE	2	-	1

2.4 Characterization

FTIR spectroscopy was performed on a Nicolet IS 10 IR spectrometer (Nicolet Co., USA) in a range of 4000 ~ 500 cm⁻¹ and the resolution of 4 cm⁻¹. ¹H NMR spectra were confirmed by a Bruker ARX 300 nuclear magnetic resonance spectrometer with CDCl₃ as the solvent and tetramethylsilane as the internal

standard. TGA measurements were performed NETZSCH TG 209F1 (Netzsch Instrument Crop., Germany) in a nitrogen atmosphere was used with a heating rate of 10°C/min and a temperature range of 35–600°C. Microstructure of PVC films was investigated using Leica DM750M(Leica Co., Germany).The glass transition temperature (T_g) of PVC films was investigated using a NETZSCH differential scanning calorimeter (DSC) 200 PC analyzer under N₂ atmosphere. The temperature ranged from – 40 to 120°C at a heating of 10°C/min. Tensile properties test was measured by a CMT4000 universal testing machine (according to ISO 527-2: 1993) with stretching rate of 20 mm/min. Each named sample need test at least five times.

3. Results And Discussions

The obtained biomass based plasticizers epoxidized EAEE and EAEE were characterized with FTIR and ¹H NMR, and compared with raw materials eugenol and eleostearic acid. As seen froure 2(a), the peak at 3533cm⁻¹ attributed to -OH of eugenol, the peak at 3010cm⁻¹ corresponded to -CH=CH-, the peak at 1515cm⁻¹ attributed to -CH₂-O-CH₂.^[34,35] Figure 2(b) shows the FTIR of eleostearic acid, the strong peak at 1796cm⁻¹ attributed to C=O group. In the Figure 2(c), the peaks at 6.8-6.9ppm attributed to protons of benzene ring, the peaks at 5.0-6.0ppm corresponded to protons of -CH₂-CH₂-, the other peaks at 3.43ppm and 3.91ppm attributed to other protons of -CH₂-.^[34,35] As seen from Figure 2(b), the peaks at around 5.4-5.9ppm corresponded to protons of conjugated double bond from eleostearic acid, the peak at 4.2-4.4ppm attributed to protons of -CH₂- connecting to the conjugated double bond. The peak at 2.43ppm corresponded to protons of CH₂- connecting to ester groups. The peak at 0.91ppm attributed to protons of -CH₃.^[36] After esterification, there is no peak at 3010cm⁻¹ in the FTIR of EAEE, as seen from Figure 3, and new peak corresponding to ester group appeared at 1761ppm, which indicated that EAEE was obtained. When the epoxidation reaction finished, there is not peak at 3010cm⁻¹ corresponding to -CH=CH- in the FTIR of epoxidized EAEE, indicating epoxidized EAEE was prepared.^[36] ¹H NMR of EAEE and epoxidized EAEE were also characterized to investigate their chemical structure, as seen from Figure 4, the peaks at 6.72-70ppm attributing to protons of benzene ring appeared in the ¹H NMR of EAEE, the peaks corresponding to protons of conjugated double bond appeared at 5.31-5.5ppm,which indicated that EAEE was obtained. In the ¹H NMR of epoxidized EAEE, there is not any peak at 5.31-5.5ppm corresponding to protons of conjugated double bond, which indicated that epoxidized EAEE was obtained.^[36]

In the processing of PVC resin, epoxidized plasticizer not only has plasticizing effect on PVC, but also has the function of stabilizer, because the epoxy group in its structure can absorb the hydrogen chloride degraded by light and heat, which prevents the decomposition of PVC dehydrochlorination, thus prolongs the service life of PVC products.^[37,38] In addition, epoxidized plasticizer has a cross-linking and toughening effect on PVC products, which can improve PVC's resistance to light, heat, aging, impact and lubrication. In this study, TGA was used to evaluate the thermal stability of PVC materials plasticized with epoxidized EAEE and EAEE. Figure 5 and Figure 6 show the TGA and DTG curves, and the related

TGA data 5%, 60% mass loss temperatures ($T_{-5\%}$, and $T_{-60\%}$), and char yield at 600 °C are summarized in Table 2. With more epoxidized EAEE and EAEE added in PVC films, $T_{-5\%}$ increased from 171.0°C to 237.3°C for PVC plasticized with EAEE, and $T_{-5\%}$ increased from 171.0°C to 244.1°C for PVC plasticized with epoxidized EAEE. In addition, $T_{-60\%}$ of PVC-50wt% EAEE and PVC-50wt% epoxidized EAEE reached 349.1°C and 372.9°C, respectively. The results showed that both epoxidized EAEE and EAEE improved the thermal stability of PVC films, and epoxidized EAEE was more effective to improve the thermal stability of PVC films than EAEE. This is mainly because the epoxy group of epoxidized EAEE can react with HCl, the epoxy group in its structure can absorb the hydrogen chloride degraded by heat, which prevented the decomposition of PVC dehydrochlorination. In addition, epoxidized EAEE has a cross-linking and toughening effect on PVC films, which can improve PVC's resistance.

Table 2. TGA dates of PVC and plasticized PVC films

Samples	$T_{-5\%}/^{\circ}\text{C}$	$T_{-60\%}/^{\circ}\text{C}$	char yield/%
PVC	171.0	302.8	11.4
PVC-25wt% EAEE	178.1	330.6	7.5
PVC-50wt% EAEE	237.3	349.1	9.3
PVC-25wt% epoxidized EAEE	198.2	347.8	14.5
PVC-50wt% epoxidized EAEE	244.1	372.9	14.6

It has been reported that plasticized PVC films with lower Tg will show more excellent plasticizing property and compatibility.^[36] In this study, DSC was employed to investigate the Tg of plasticized PVC films. Figure 7 shows the DSC curves of PVC plasticized with epoxidized EAEE and EAEE. Tg value for PVC films is 82.5°C, which has been reported in our previous study.^[36] Tg value for PVC-25wt% EAEE, PVC-50wt% EAEE, PVC-25wt% epoxidized EAEE and PVC-50wt% epoxidized EAEE was 36°C, 27°C, 24°C and 7°C, respectively, which showed that epoxidized EAEE and EAEE played efficient plasticizing effect on PVC, and the plasticizing effect of epoxidized EAEE was more efficient than EAEE. In addition, all of the plasticized PVC films showed only one endothermic peak, which illustrated that epoxidized EAEE and EAEE are all compatible with PVC, there is no free plasticizer in PVC films.

Figure 8 shows the stress-strain curves of all PVC films. With more epoxidized EAEE added in PVC films, PVC-50wt% EAEE showed increased elongation at break and decreased tensile stress than PVC-25wt% EAEE, and PVC-50wt% epoxidized EAEE showed increased elongation at break and decreased tensile stress than PVC-25wt% epoxidized EAEE. This indicates that epoxidized EAEE and EAEE improved the flexibility and movement ability of the PVC molecular chain to a certain extent. When PVC contained same mass of EAEE and epoxidized EAEE, PVC-50wt% epoxidized EAEE showed more flexible than PVC-50wt% EAEE, which indicated that epoxidized EAEE played more efficient plasticizing effect on PVC than EAEE.

Plasticizing mechanism was explored with optical microscope. As seen from Figure 9, it can be observed that rough and irregular microstructure on surface of PVC-25wt% EAEE, with more EAEE added in PVC film, PVC was dissolved in EAEE, which caused the surface of PVC-50wt% EAEE less rough and irregular than PVC-25wt% EAEE. For PVC-25wt% epoxidized EAEE and PVC-50wt% epoxidized EAEE, which showed less rough and more smooth microstructure compared with PVC-50wt% EAEE, which is attributed to the strong interaction of the polar groups of epoxidized EAEE (ester group and epoxy groups) with polar groups of PVC. The plasticizing mechanism based on compatibility can be explained that epoxidized EAEE containing the flexible alkane chains and polar group (ester groups and epoxy groups) has stronger intermolecular interaction force than EAEE. PVC was easier to dissolve in epoxidized EAEE than EAEE, which caused that the microstructure of PVC-50wt% EAEE was more homogeneous and smooth than PVC-25wt% EAEE and PVC-50wt% EAEE.

The compatibility of PVC and plasticizer (epoxidized EAEE and EAEE) was investigated by FT-IR. It has been reported that FT-IR is a facile method to investigate the compatibility of PVC and plasticizers.^[39,40] Dipole-dipole interaction of polar groups(ester carbonyl groups and epoxy groups) and α -hydrogen of PVC will lead to carbonyl group infrared absorption peak of plasticizer (epoxidized EAEE and EAEE) to lower position. As seen from Figure 10, with more plasticizer (epoxidized EAEE and EAEE) added in PVC films, the position shift of ester groups of EAEE shifted from 1758cm^{-1} to 1756cm^{-1} , while the position shift of ester groups of EAEE shifted from 1757cm^{-1} to 1755cm^{-1} , which indicated that the miscibility between epoxidized EAEE and PVC is better than EAEE.

The formation of hydrogen bond between plasticizer (epoxidized EAEE and EAEE) and PVC chains will reduce interaction between PVC macromolecule themselves, it can be observed in Figure 11, the distance of PVC chains will be increased due to the formation of hydrogen, which will promote the mobility of PVC chains easily. More hydrogen bonds were formed between PVC chains and epoxidized EAEE than that of PVC chains and EAEE due to more epoxy groups in the chemical structure of epoxidized EAEE, which caused the that epoxidized EAEE played more efficient plasticizing effect on PVC than EAEE.

4. Conclusions

In this study, we synthesized two kinds of biomass based plasticizer, eleostearic acid eugenol ester(EAEE) and epoxidized EAEE. Performance of PVC plasticized with EAEE and epoxidized EAEE were investigated. The results showed epoxidized EAEE was more effective to improve the thermal stability of PVC films than EAEE, because the epoxy group can react with HCl and absorb the HCl degraded by heat, which prevented the decomposition of PVC dehydrochlorination. T_g value for PVC-25wt% EAEE, PVC-50wt% EAEE, PVC-25wt% epoxidized EAEE and PVC-50wt% epoxidized EAEE was 36°C , 27°C , 24°C and 7°C , respectively, which combining with the tensile results showed that epoxidized EAEE and EAEE played efficient plasticizing effect on PVC. More hydrogen bonds were formed between PVC chains and epoxidized EAEE than that of PVC chains and EAEE, which caused the that epoxidized EAEE played more efficient plasticizing effect on PVC than EAEE. The obtained efficient plasticizers based on eleostearic acid and eugenol will have wide application prospect in PVC products.

Declarations

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Figures

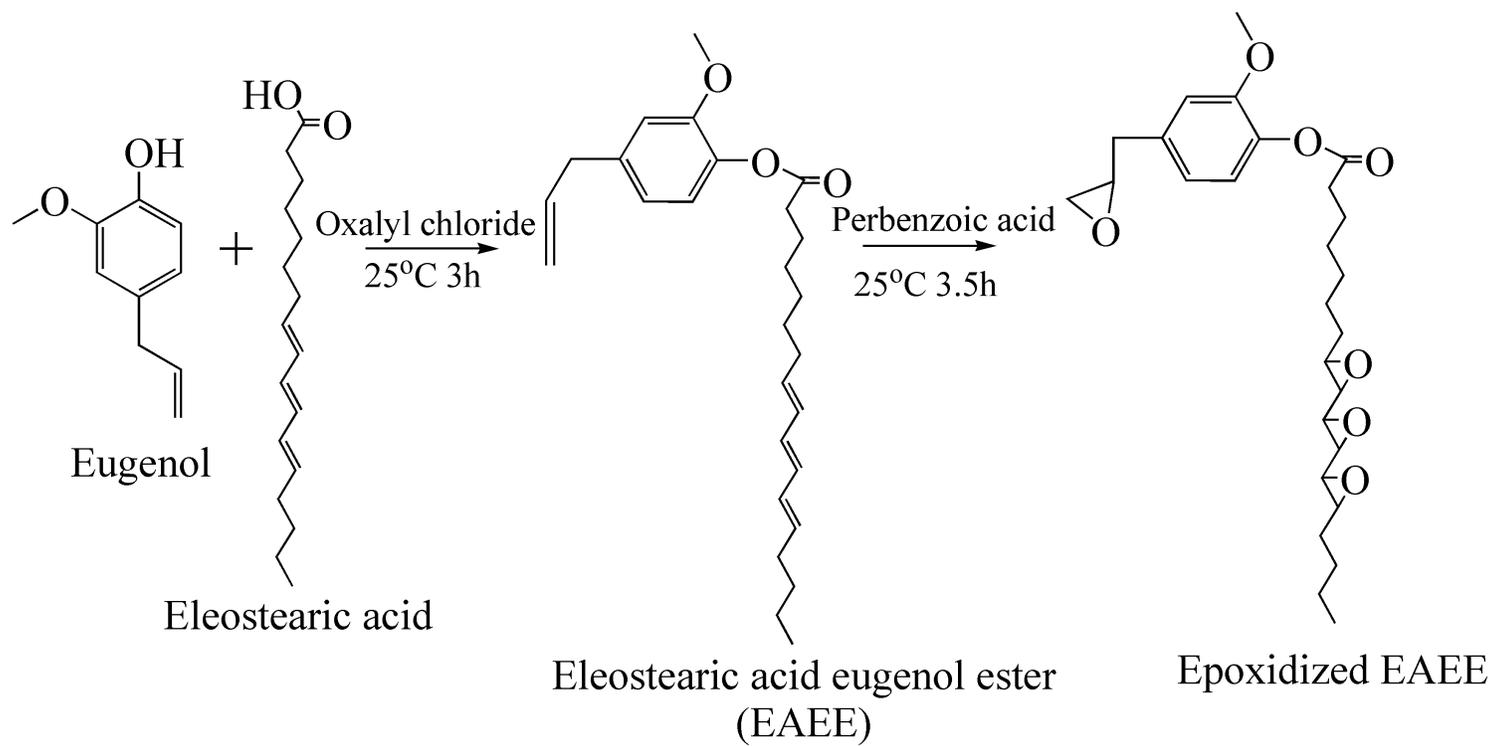


Figure 1

Synthesis of epoxidized EAE

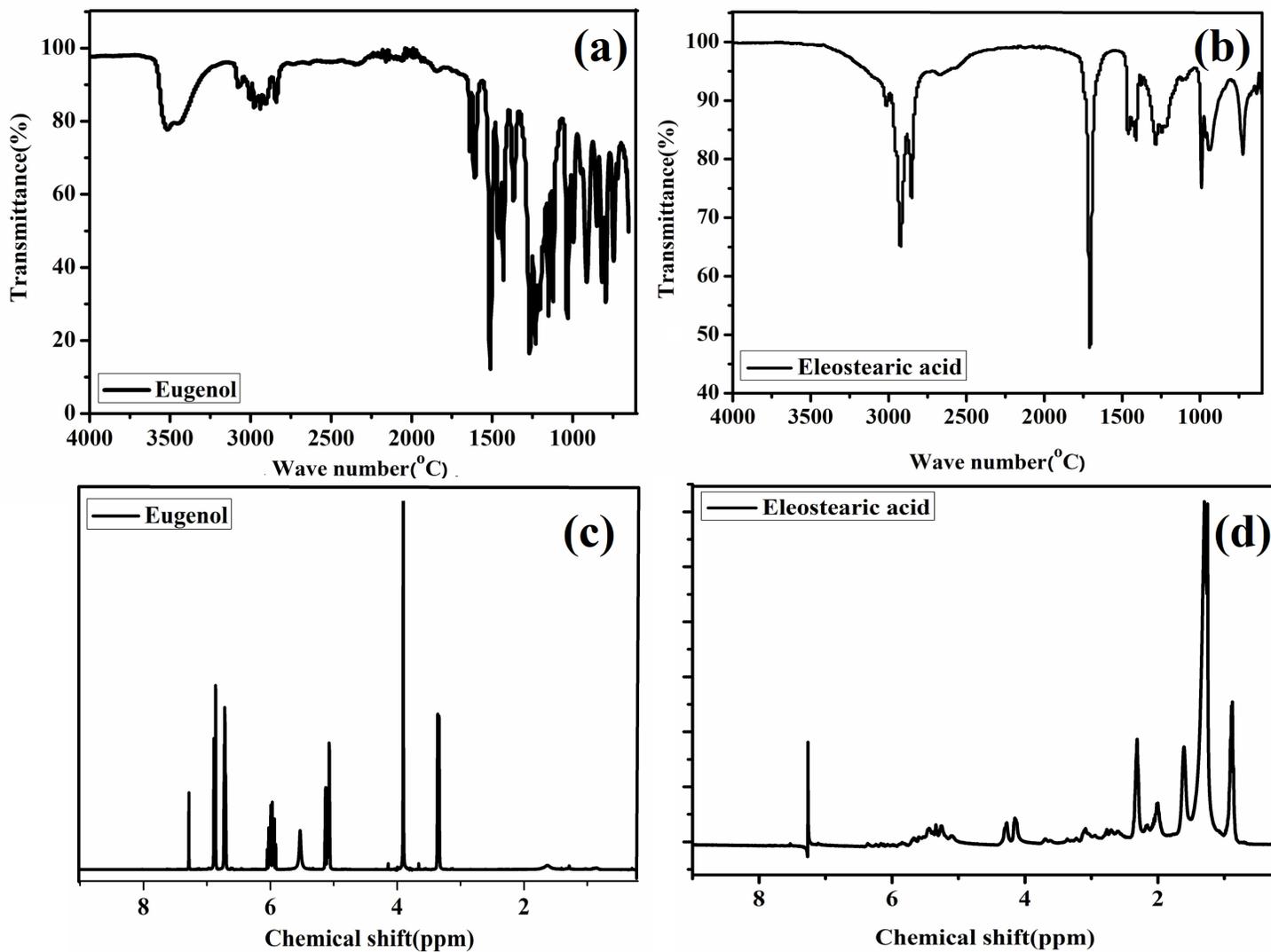


Figure 2

(a) FTIR of eugenol. (b) FTIR of eleostearic acid. (c) ¹H NMR of eugenol. (d) ¹H NMR of eleostearic acid.

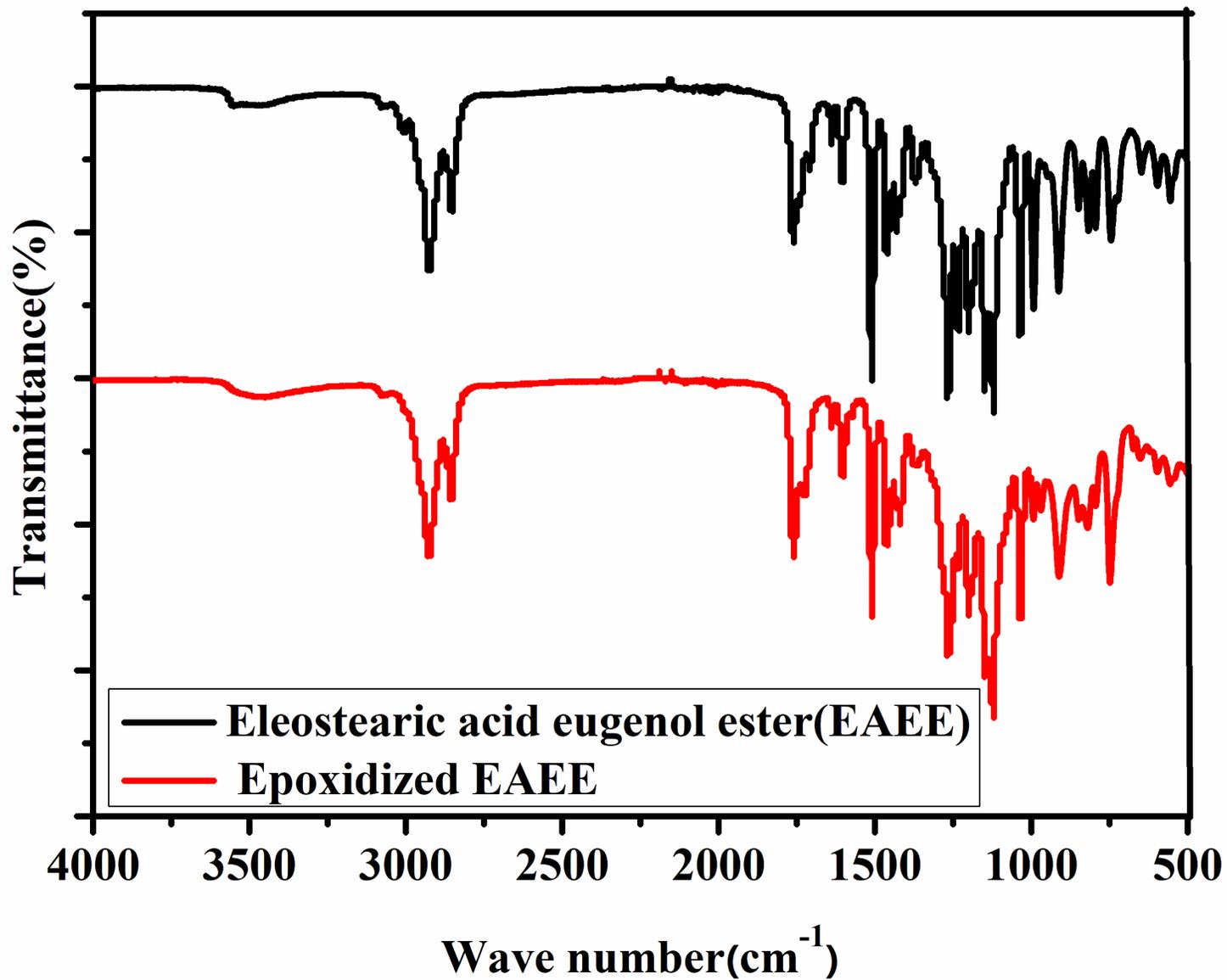


Figure 3

FTIR of EAE and epoxidized EAE

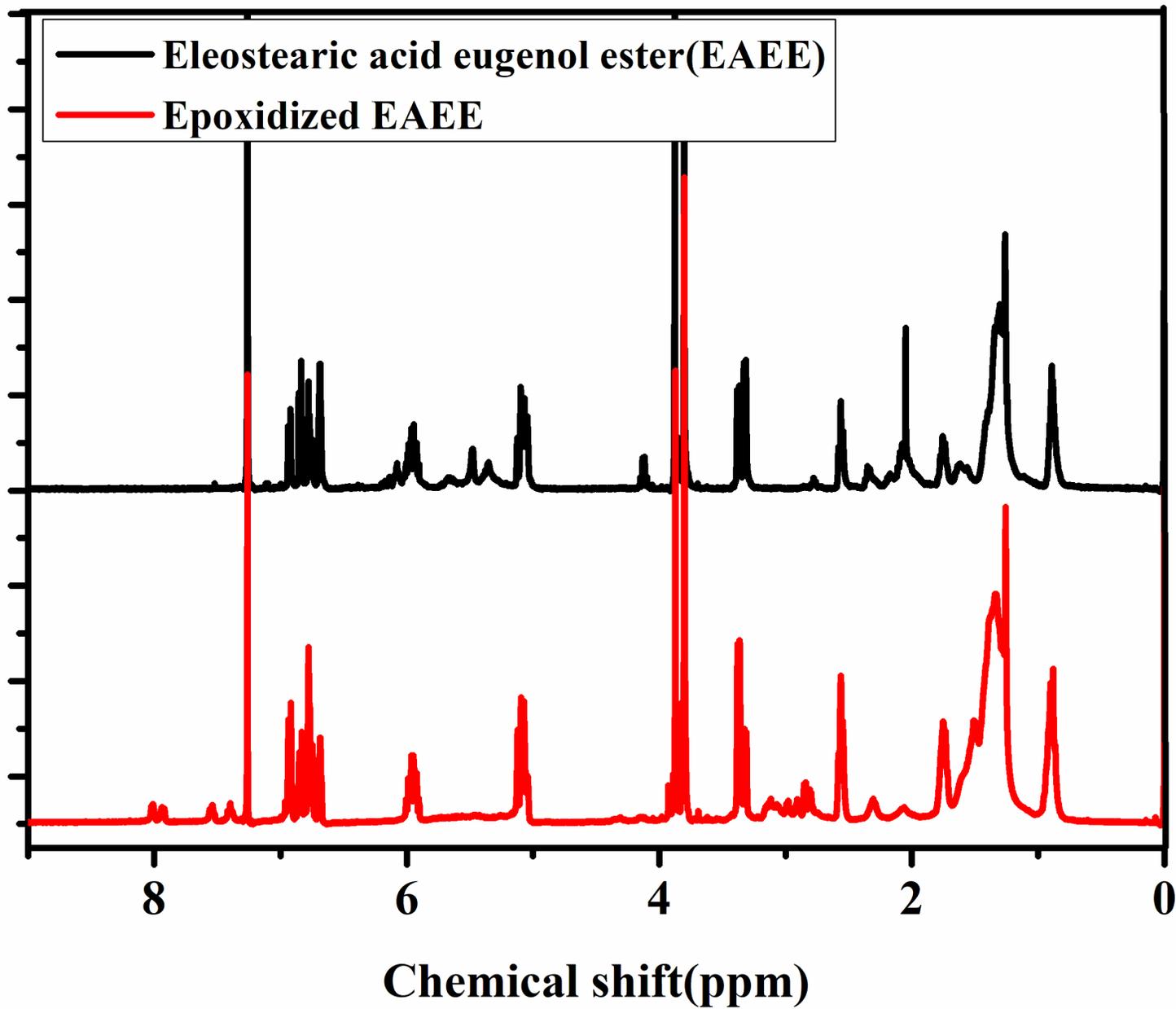


Figure 4

¹H NMR of EAE and epoxidized EAE

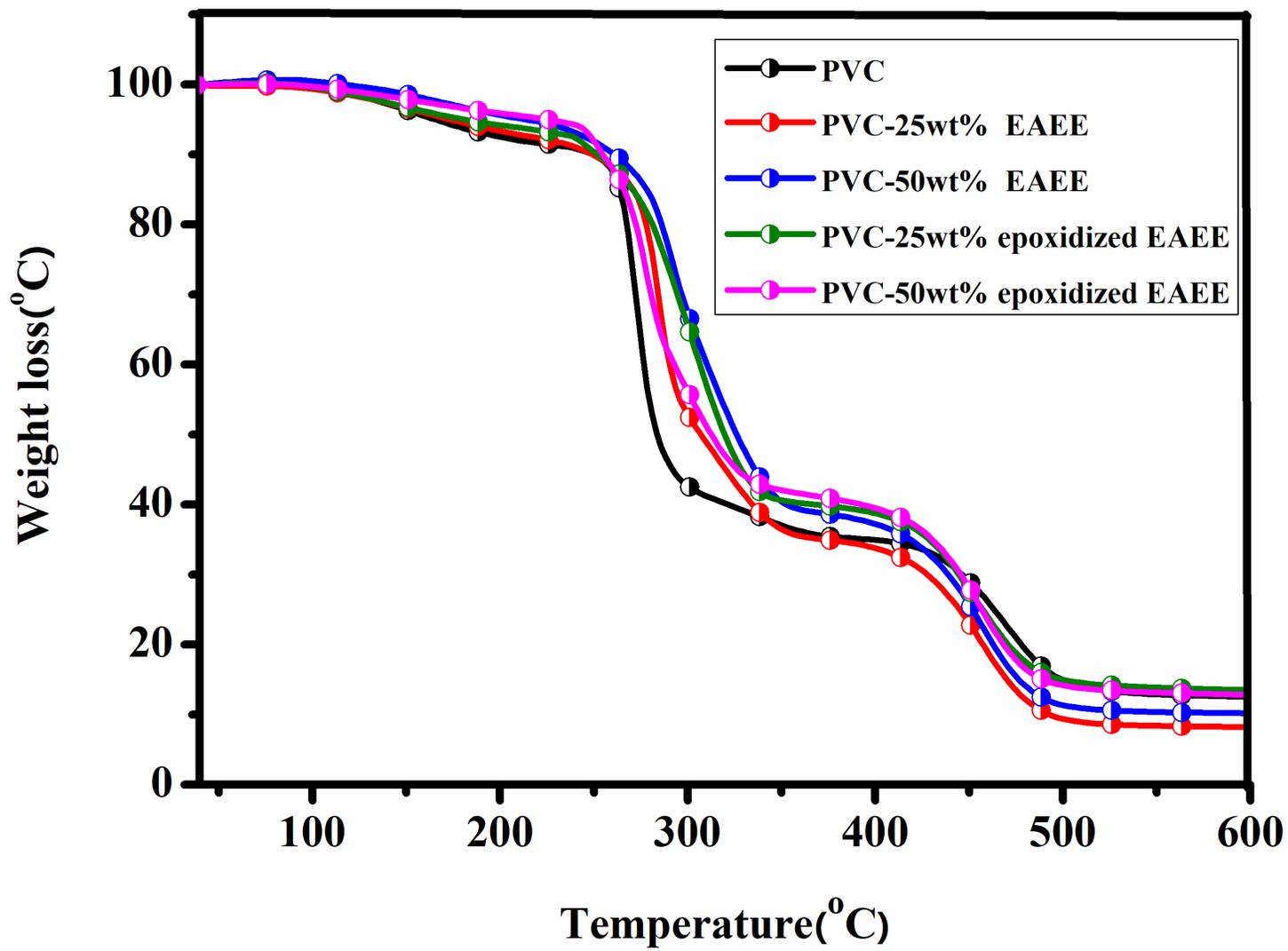


Figure 5

TGA curves of PVC films

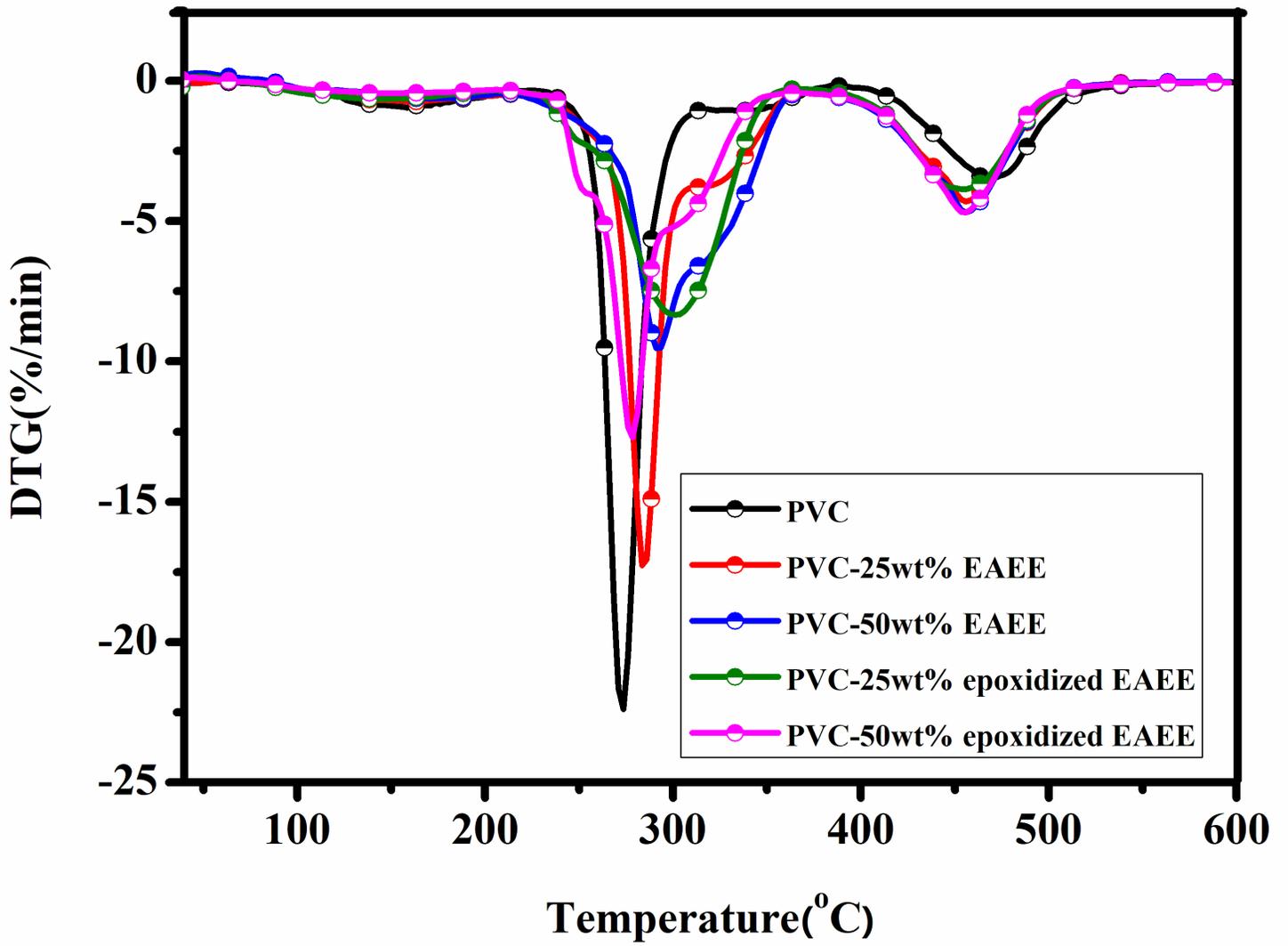


Figure 6

DTG curves of PVC films

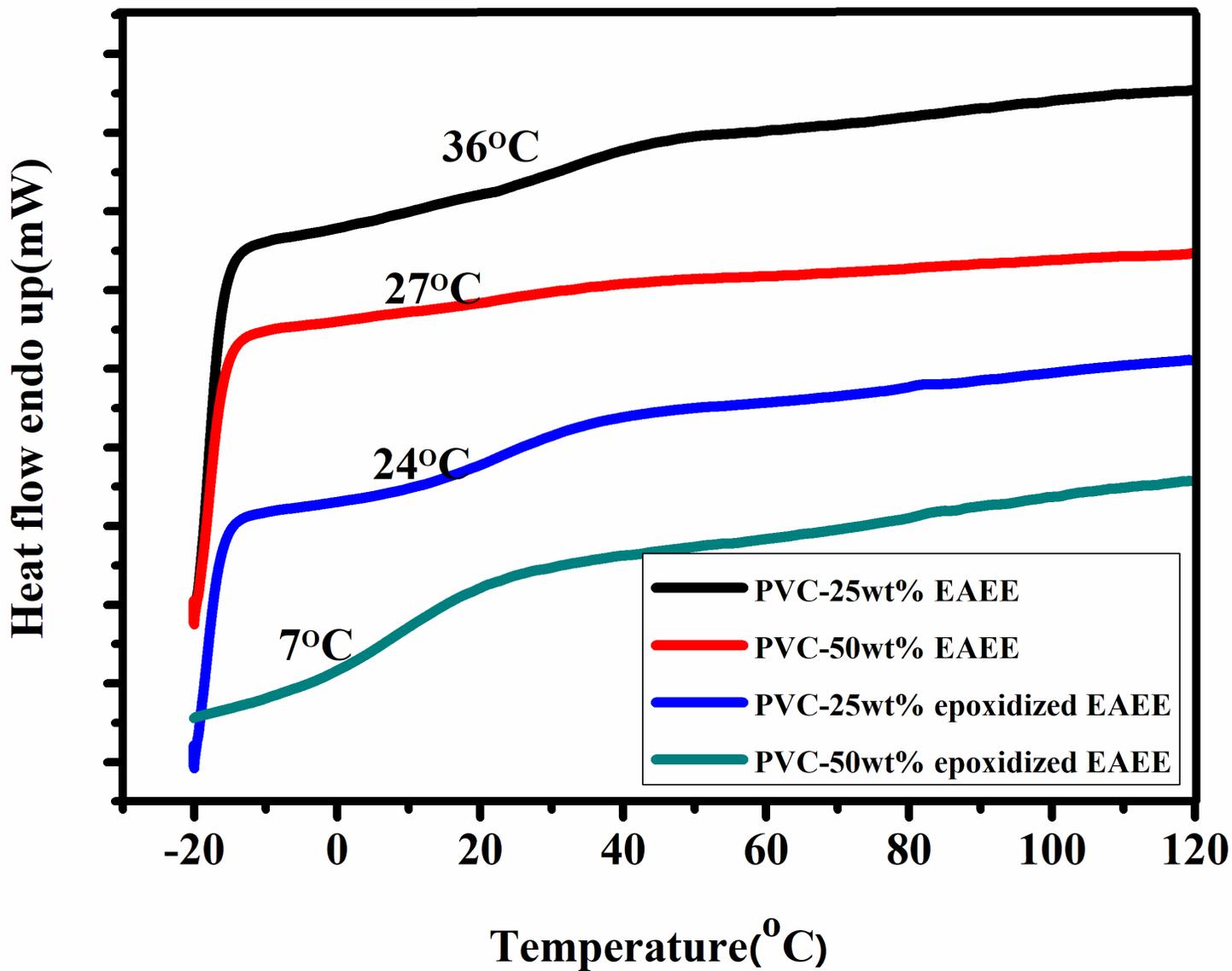


Figure 7

DSC curves of PVC films

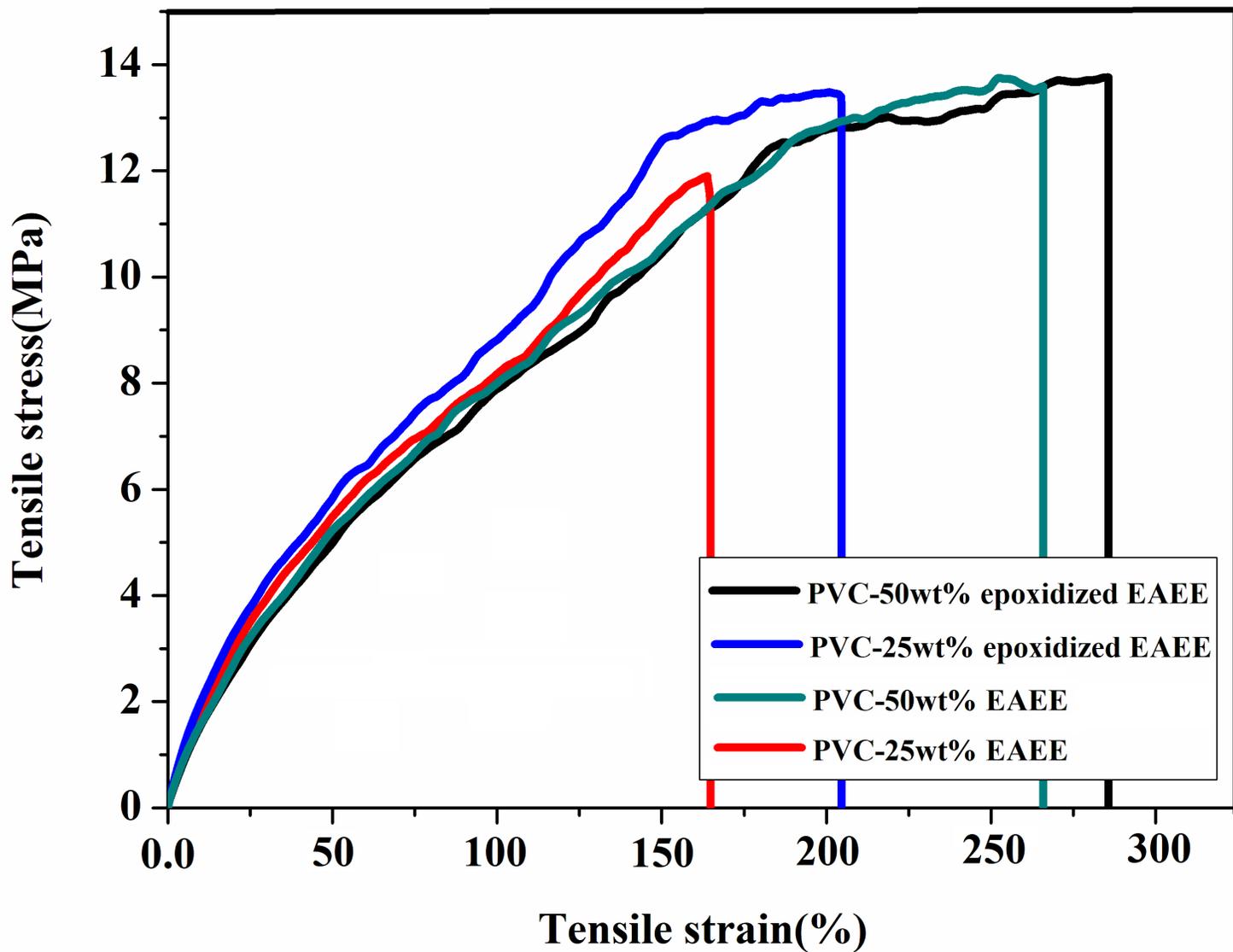


Figure 8

Tensile stress-tensile strain curves of PVC films

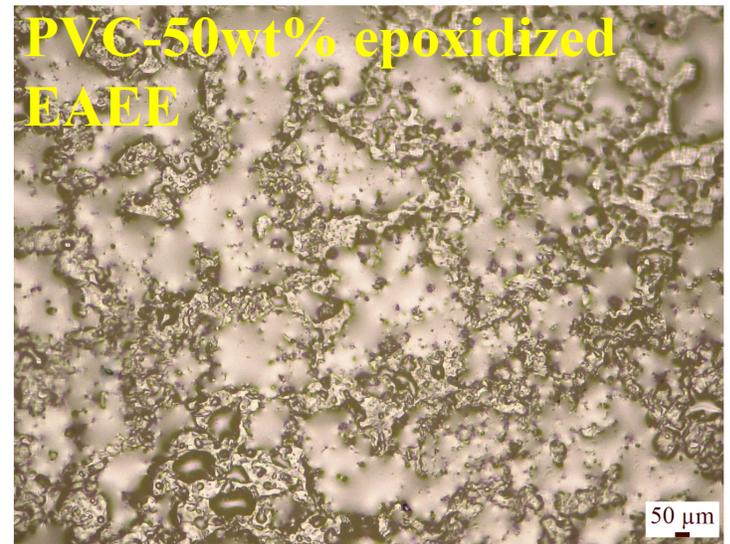
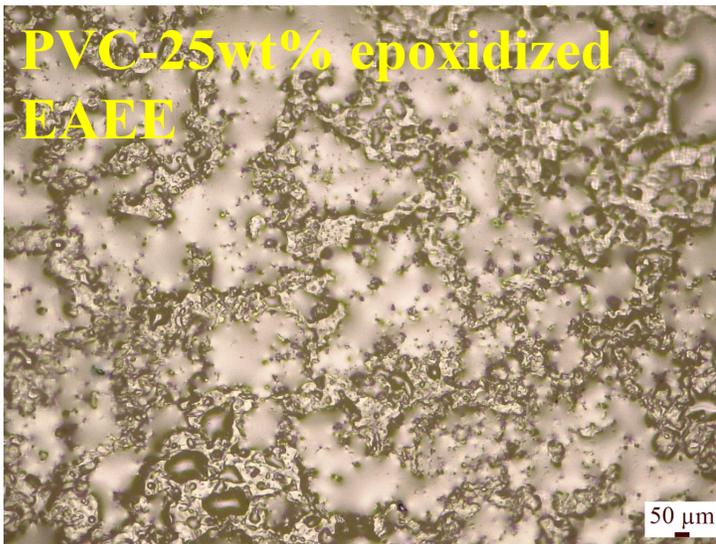
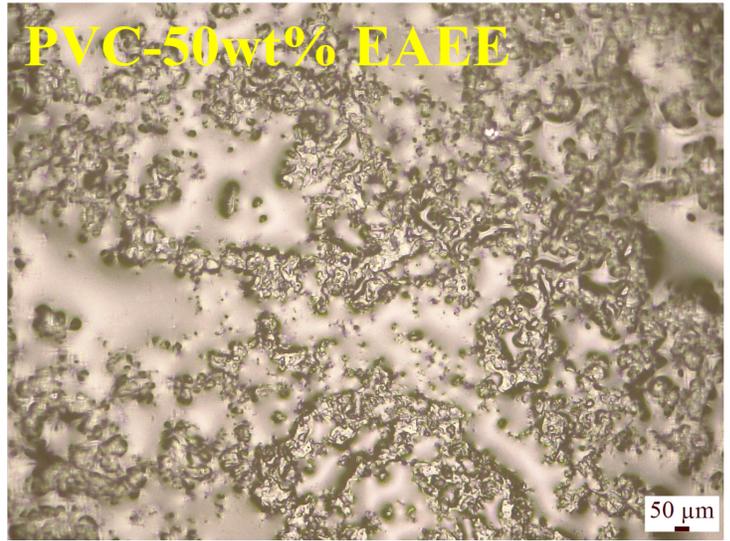
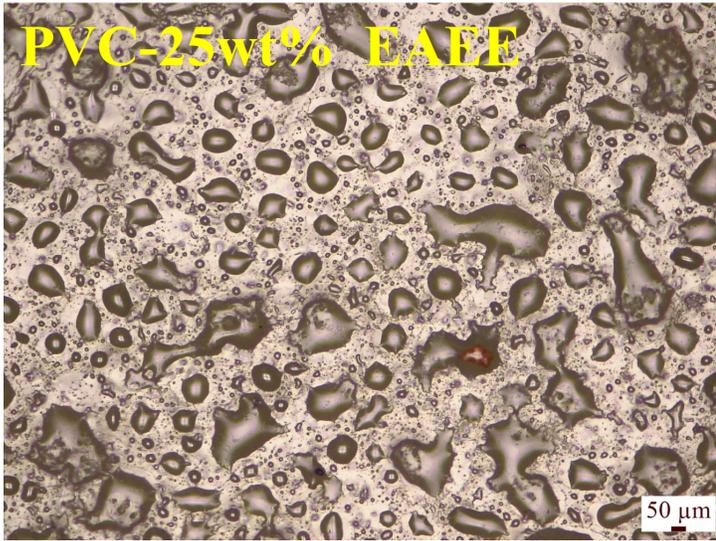


Figure 9

Microstructure of PVC films

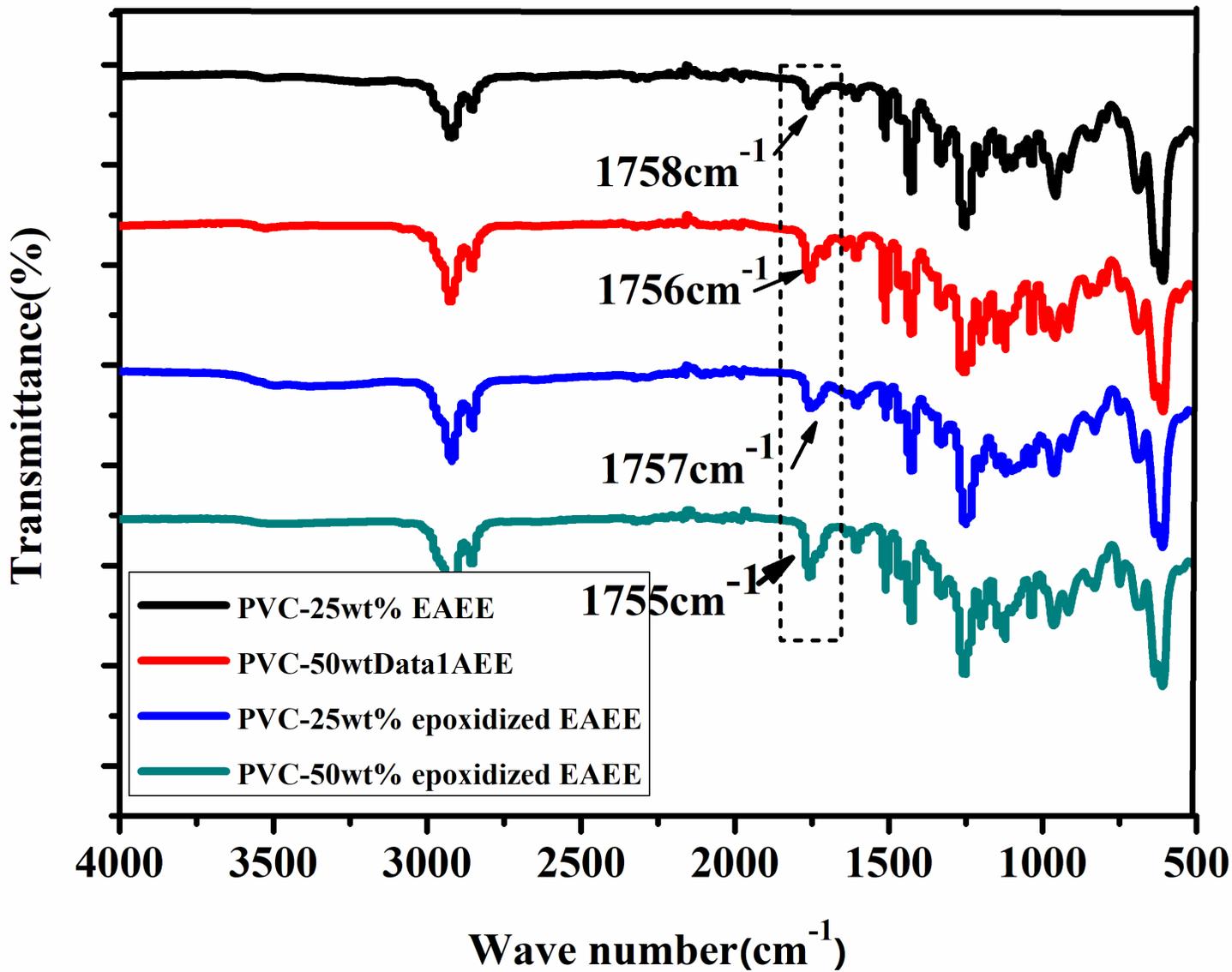


Figure 10

Shift of infrared absorption peak of ester group in PVC films

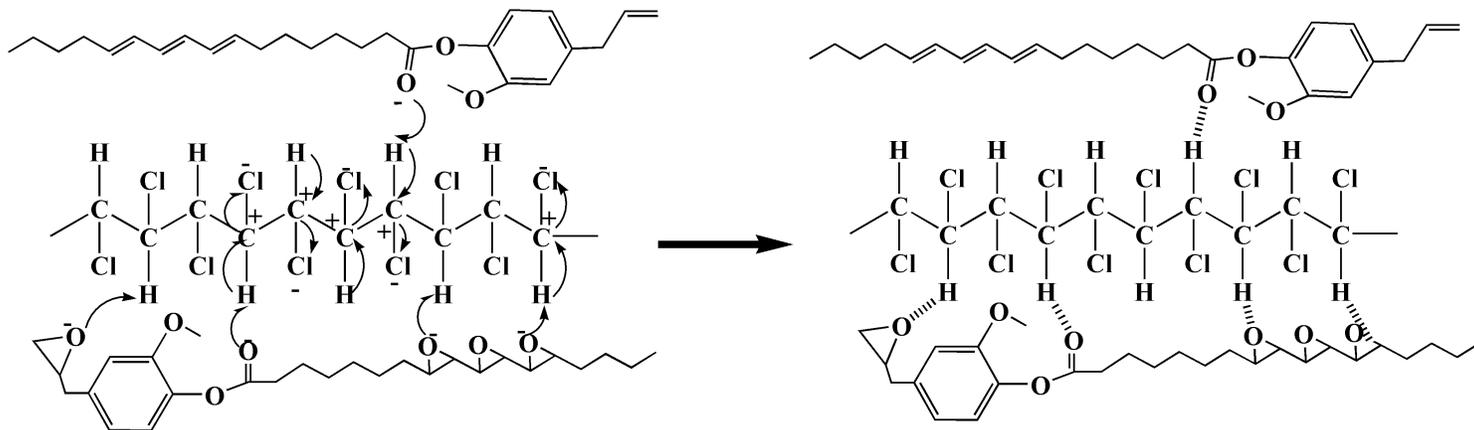


Figure 11

Formation of hydrogen bond between plasticizer (epoxidized EAEE and EAEE) and PVC chains

Supplementary Files

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- [GraphicalAbstract.tif](#)