Preparation and Application of Triglyceride Plasticizers for Poly(vinyl chloride)

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ABSTRACT: A series of triglyceride plasticizers were prepared from glycerol, acetic acid, and benzoic acid through a two-step reaction to develop potential uses of glycerol. The optimum reaction conditions were determined by the esterification of glycerol and acetic acid to produce glyceryl triacetate. When the molar ratio of glycerol to benzoic acid to acetic acid was 1:1:3.5, a novel plasticizer triglyceride mixture (GTM) was successfully synthesized; it had a good plasticizing effect on poly(vinyl chloride) (PVC). The elongation at break of PVC composites containing 80 phr GTM increased around 350%; the corresponding hardness (Shore D) and tensile strength decreased to around 35 D and 20 MPa, respectively. Moreover, the glass-transition temperature (T_g) of PVC composites containing 40 phr GTM decreased to around 50°C. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Poly(vinyl chloride) (PVC) is used extensively as a kind of plastic material because of its outstanding advantages; the performance can be changed according to the amount of different kinds of fillers and additives, and it has a low cost and a broad range of properties. Therefore, it is widely applied in wall coverings, cables, medical devices, and computers.[1–3] Furthermore, the great part of PVC is used as plasticized PVC. Hence, the plasticizer is a vital part of PVC; it can improve the flexibility and processing of PVC and overcome its inherent brittleness without changing the chemical properties of the PVC matrix.[4–6] There are many kinds of plasticizers, including aliphatic dicarboxylic acids, benzoate, citrate, epoxides, and triglycerides.[7–10]

In recent years, glycerol has been used widely because of its low cost and because it is a surplus source as a byproduct from the production of biodiesels.[11,12] Recently, many attempts have been made to develop potential uses of glycerol as an industrial chemical for plasticizers, such as triglyceride plasticizer for polymer.[13,14]

There are two kinds of these triglyceride that are widely used: glyceryl tribenzoate (GTB) and glyceryl triacetate (GTA).[15,16] GTB, whose plasticized performance to vinyl resins and allyl resin is similar to that of phthalates, has good compatibility with many kinds of polymers, and it exhibits a high thermal stability. Hence, it is an important plasticizer.[17] However, it is easily crystallized at overdosed; this is harmful to processes, so it is not widely used in the PVC field. GTA, a sort of water-white liquid, is widely used as a solvent and plasticizer in perfumes, cellulose, and food additives for its nontoxicity and low cost.[18,19] However, its poor compatibility with PVC has seriously limited its use in the field of PVC plasticizers. Therefore, it cannot be used as a primary plasticizer for PVC.

From the revelation of the properties of GTB, an assumption, the introduction of a benzene ring into GTA to endow it with compatibility with PVC, promoted us to explore some relevant research. Thus, we used benzoic acid to replace some of the acetic acid to react it with glycerol. By changing the molar ratio of glycerol to benzoic acid to acetic acid, we obtained a series of triglycerides. Then, a novel plasticizer triglyceride mixture (GTM) was synthesized through a two-step reaction when the molar ratio of glycerol to benzoic acid to acetic acid was 1:1:3.5; the benzene ring structure of this plasticizer was characterized by FTIR, UV, and ^{1}H-NMR. After that, PVC composites plasticized by the synthesized triglycerides as previously were tested to examine the glass-transition temperatures (T_g's) and mechanical properties, such as hardness, tensile strength, and elongation at break. Compared with the properties of PVC composites plasticized by di-(2-ethylhexyl) phthalate (DOP), the results show that GTM has a large potential for applications as primary plasticizers for PVC.

EXPERIMENTAL

Materials

Analytically pure glycerol, anhydrous acetic acid, benzoic acid, toluene, sodium hydrogen sulfate, *p*-toluene sulfonic acid, DOP, cyclohexane, and amino acid were purchased from Kelong Chemical Reagent Co. (Chengdu, China). Isopropyl acetate was supplied by Tianjin Bodi Chemical Co. (Tianjin, China). PVC powder (SG-III) was provided by Tianyuan Co., Ltd. (Yibing, China). An industrial-grade compound stabilizer (Baeropan SMS 318) was obtained commercially from Beijing YingTai HuanYa Trade Co. (Beijing, China).

Synthesis of GTA

We added different molar ratios of glycerol to acetic acid (1:3.5, 1:4.0, 1:4.5, 1:5.0, and 1:5.5), sodium hydrogen, and isopropyl acetate into a three-necked flask equipped with a thermometer, thorn fractionating column, Allihn-type condenser, and water segregator.

Different kinds of catalyst (*p*-toluene sulfonic acid, amino acid, and sodium hydrogen) were added, respectively, to a three-necked flask equipped with a thermometer, thorn fractionating column, Allihn-type condenser, and water segregator; we then added glycerol, acetic acid, and isopropyl acetate to these three-necked flasks (the molar ratio of glycerol to acetic acid was 1:4.0).

Different kinds of azeotropic agents (toluene, cyclohexane, isopropyl acetate) were, respectively added to a three-necked flask equipped with thermometer, thorn fractionating column, Allihn-type condenser, and water segregator, then adding glycerol, acetic acid and sodium hydrogen into these three-necked flasks (the molar ratios of glycerol to acetic acid is 1:4.0).

All of these reactions were performed at about 110°C under stirring and reflowing; when there was no more water produced, the reactions ended.

Synthesis of the Novel Plasticizer

In the first step, set contents of glycerol, benzoic acid, *p*-toluene sulfonic acid, and toluene were added to a three-necked flask equipped with a thermometer, thorn fractionating column, Allihn-type condenser, and water segregator. Among these reagents, *p*-toluene sulfonic acid worked as a catalyst, and toluene was used as an azeotropic agent for the removal of water. The esterification reaction was maintained around 120°C under stirring and reflowing until the time reached around 3.5 h, when amount of separated water reached the theoretical quantity.

In the second step, the thorn fractionating column was replaced by a column filled with glass beads, and we added a certain amount of acetic acid according to the molar ratio of glycerol to acid. Sodium hydrogen sulfate worked as a catalyst, and isopropyl acetate was used as the azeotropic agent for water separation in the reactive three-necked flask. This reaction was also set at about 110°C under stirring and reflowing; when the time reached about 6 h and there was no more water produced, the reaction ended.
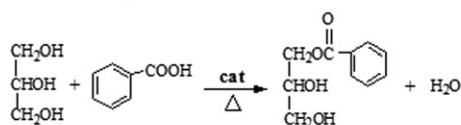
The molar ratio of glycerol to acid (benzoic acid and acetic acid) was 1:4.5 during the whole reaction. In the first step, the molar ratios of glycerol to benzoic acid were 1:0.0, 1:0.4, 1:0.8,
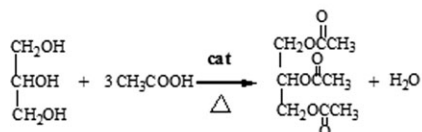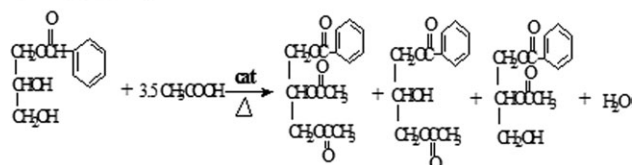

Scheme 1. Synthesis route of the main reaction.

and 1:1.0. In the second step, the molar ratios of glycerol to acetic acid were 1:4.5, 1:4.1, 1:3.7, and 1:3.5.

Toluene, isopropyl acetate, and some acetic acid were distilled off from the resulting mixture through heating *in vacuo*. Then, the mixture was washed to a neutral pH by saturated sodium bicarbonate and filtered to remove inorganic salts. Then, the product was obtained after drying at 60°C for 24 h.

The main reaction is shown in Scheme 1.

The equation of the esterification rate is as follows:

$$\text{Esterification rate} = \left(1 - \frac{n_{H_2O}}{3n_{C_3H_8O_3}}\right) \times 100\%$$

where *n* is the amount of substance.

Preparation of the Plasticized PVC

The PVC powder, synthesized triglyceride, and compound stabilizer were mixed at 80°C until the plasticizer sufficiently penetrated the PVC matrix. The resulting dried mixture was blended in a double-roll mill (SK-160R 160 × 320 mm², Shanghai rubber machinery factory, Shanghai, China) at 180°C for 10 min. Then, the plasticized PVC was molded into a 160 × 160 × 1 mm³ sheet and a 50 × 50 × 6 mm³ sheet by a vulcanizing machine (QLB-D400 × 400 × 2, Shanghai rubber machinery factory, Shanghai, China) at 175–180°C. The former was cut into a dumbbell shape with dimensions of 25 × 6 × 1 mm³ for tensile strength testing and a rectangle with dimensions of 35 × 4 × 1 mm³ for T_g testing. The latter was used for hardness testing.

Characterization

FTIR Spectroscopy, UV Spectroscopy, ^{1}H-NMR, and Dynamic Mechanical Analysis (DMA). The structures of GTM and GTA were characterized with a Nicolet 560 FTIR spectrometer (iS10 Thermo Nicolet Corp., Madison, America) with a resolution
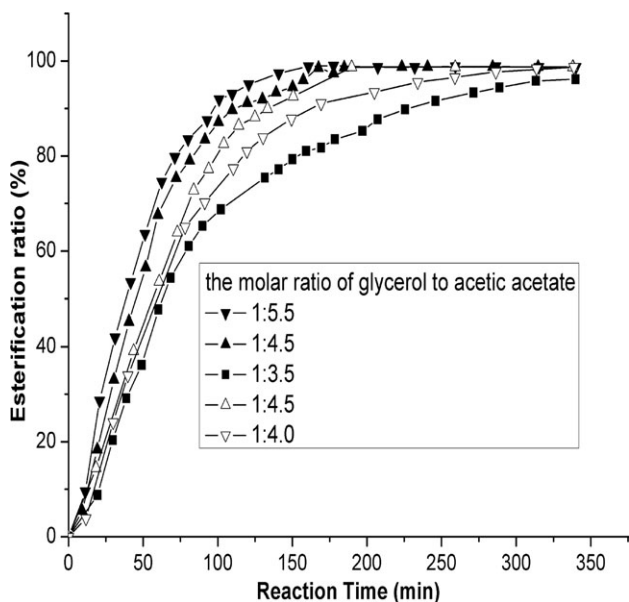
Figure 1. Effect of different molar ratios of glycerol to acid on the esterification rate of GTA.

setting of 4 cm^{-1} and a scanning range of 400–4000 cm^{-1}. We used a UV spectrometer (TU-1901, Persee Co., Beijing, China) with a scanning range from 190 to 350 nm and an ^{1}H-NMR instrument (Bruker Avance AV II-400NMR, Germany) with CDCl$_3$ as a solvent. DMA (Q800, American Ta Co. America) was used to test T_g with a heating rate of 3°C and the temperature ranged from −50 to 100°C in the stretching mode.

Mechanical Testing. The dumbbell-type specimen was used for the tensile tests with an Instron 4302 instrument (Instron Corp., America) at a tensile rate of 100 mm/min. The hardness of the composites was determined with a Shore hardness tester (LXA-D, cany Shanghai, China).
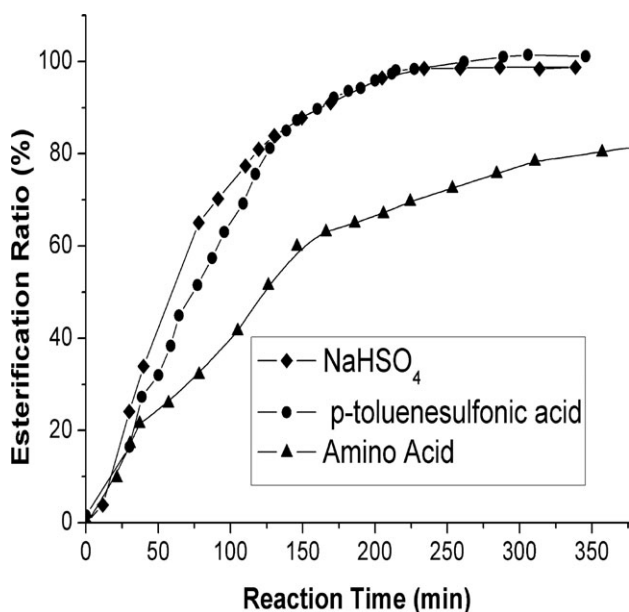
Figure 2. Effect of different catalysts on the esterification of GTA.

Table I. Effect of Different Azeotropic Agents for the Removal of Water on the Esterification of GTA

Azeotropic agent	Reaction time (h)	Temperature (°C)	Esterification rate (%)
Toluene	4	112–128	94.8
Cyclohexane	5	80–92	79.2
Isopropyl acetate	4	108–123	98.9

RESULTS AND DISCUSSION

Study of the Optimum Factors of Plasticizer Synthesis

Molar Ratio of Glycerol to Acid in the Esterification of GTA. The specific impacts of different molar ratios of glycerol to acid on the esterification rate are shown in Figure 1 with the conditions that sodium hydrogen sulfate worked as a catalyst and isopropyl acetate worked as an azeotropic agent for water separation. When the molar ratios of glycerol to acetic acid were 1:3.5 and 1:4.0, the esterification yield just reached around 85% in 3.5 h; however, the esterification yield almost reached about 98.8% when the molar ratios were 1:4.5, 1:5.0, and 1:5.5 for the same time. Therefore, the optimum molar ratio of glycerol to acetic acid was 1:4.5.

Catalyst. The catalytic effects of several catalytic systems were inspected in the esterification of glycerol with acetic acid to produce GTA, these catalytic systems included *p*-toluene sulfonic acid, amino acid, and sodium hydrogen. As shown in Figure 2, amino acid did a remarkably bad job on this reaction. In reverse, sodium hydrogen sulfate and *p*-toluene sulfonic acid had good catalytic activities. However, it was difficult to remove *p*-toluene sulfonic after the reaction, which could make PVC degrade during processing. Therefore, sodium hydrogen sulfate was determined to be the optimal catalyst for the esterification of GTA, whereas it had inferior catalyst efficiency in the first-step reaction. Because of the poor dissociation capability of the aromatic acid (benzoic acid), sodium hydrogen sulfate did not tend to ionize in the first-step reaction system. What was more, for the conjugate effect of the benzene ring, it weakened the proton catalysis because of the sodium hydrogen sulfate ionizing proton associated with the carboxyl group of aromatic acid. Eventually, *p*-toluene sulfonic was used as the catalyst in the first-step reaction, and sodium hydrogen sulfate was used in the second-step reaction.

Azeotropic Agent. Tables I and II show the effect of different azeotropic agents for the removal water on the esterifications of the GTA and GTM, respectively. As shown in Table I, the use of isopropyl acetate as an azeotropic agent resulted in a short reaction time and moderate temperature; this could reduce the

Table II. Effect of Different Azeotropic Agents for the Removal of Water on the Esterification of GTM

Azeotropic agent	Reaction time (h)	Temperature (°C)	Esterification rate (%)
Toluene	3	118	91.3
Isopropyl acetate	2	118	0

Table III. Esterification Rate

Molar ratio of glycerol to benzoic acid and acetic acid	Esterification rate in the first step (%)	Esterification rate in the second step (%)	Esterification rate (%)
1.0 : 0.0 : 4.5	—	98.5	98.5
1.0 : 0.4 : 4.1	91.3	96.5	88.1
1.0 : 0.8 : 3.7	82.4	92.6	76.3
1.0 : 1.0 : 3.5	81.3	89.3	72.6

chance of side effects when the temperature was high. Moreover, under these conditions, the esterification rate reached the optimum value. The esterification rate was also high when toluene worked as the azeotropic agent. However, the temperature was so high that the side effects occurred easily. With cyclohexane as the azeotropic agent, the reaction temperature was too low. Thus, isopropyl acetate was the best choice for removing water in the esterification of GTA. However, as shown in Table II, the effect of toluene was clearly better than that of isopropyl acetate as the azeotropic agent for the separation of water. The reason may have been that the temperature in the first-step reaction was a little higher, so toluene was needed. Eventually, toluene was used in the first-step reaction, and isopropyl acetate was used in the second-step reaction.

Esterification Rate. Table III illustrates the esterification rate. As shown in this table, the esterification rate decreased with the increasing molar ratio of benzoic acid to glycerol because there were two α-hydroxyls and one β-hydroxyl in glycerol and the α-hydroxyl reacted easily with benzoic acid for its vivacity. However, as the reaction progressed, the steric hindrance of the spatial structure of the benzene ring was more obvious, and this reaction was more difficult.

UV Results
The UV spectra of GTA and GTM are shown in Figure 3. There was an absorption peak of carbonyl around 220 nm, shown in in Figure 3(a) for GTA and Figure 3(b) for GTM. However, compared with Figure 3(a), the new wide absorption peak

between 260 and 290 nm in Figure 3(b) was the characteristic absorption band of the benzene group. According to these, it was shown that the benzene ring was successfully added to GTA; this means that GTM was successfully synthesized.

FTIR Results
GTA and GTM were further confirmed by IR spectroscopy, as shown in Figure 4. Figure 4(a) shows the GTA spectra, an obvious absorption peak at 1745 cm^{-1} belonged to carbonyl. Also, there were two absorption peaks between 1099 and 1300 cm^{-1}, which were the characteristic absorption bands of the C—O—C stretching in GTA. The characteristic features near 2960 and 1373 cm^{-1} belonged to methyl groups. At 3472 cm^{-1}, a weak absorption band of —OH was also observed; this demonstrated a little unreacted hydroxyl in the glycerol. Compared with Figure 4(a), there were several characteristic absorption bands of the benzene group near 1453, 1605, and 3066 cm^{-1} in Figure 4(b), so the first-step reaction was completed, and GTM was successfully obtained.

^{1}H-NMR Results
The spectrum of Figure 5 corresponds to GTA [Figure 5(a)] and GTM [Figure 5(b)]. In Figure 5(a), with regard to the induction of the oxygen atom, the displacement of β-H was a little further than α-H in glycerol compared with that of the origin. Therefore, the characteristic peaks around 4.3 and 5.2 ppm belonged to α- and β-H, respectively, in the glycerol. At the 2.2 ppm, there was a strong peak belonging to the methyl of acetic acid because of the superimposed effect of equal protons in these methyls of acetic acid. In Figure 5(b), the peaks around 7–8 ppm represented benzene group, and the other displacement of hydrogen was similar to that shown in Figure 5(a). Therefore, GTM was successfully synthesized.

Mechanical Properties
The tensile strength and elongation at break of the plasticized PVC composites with these triglycerides and the other plasticizer (DOP) are shown in Figure 6. As shown in Figure 6, the elongation at break of the PVC composites sharply increased and the tensile strength decreased with triglyceride and DOP contents ranging from 20 to 80 phr. The reason was that the polar group of the plasticizer could combine with the polar chlorine atom in
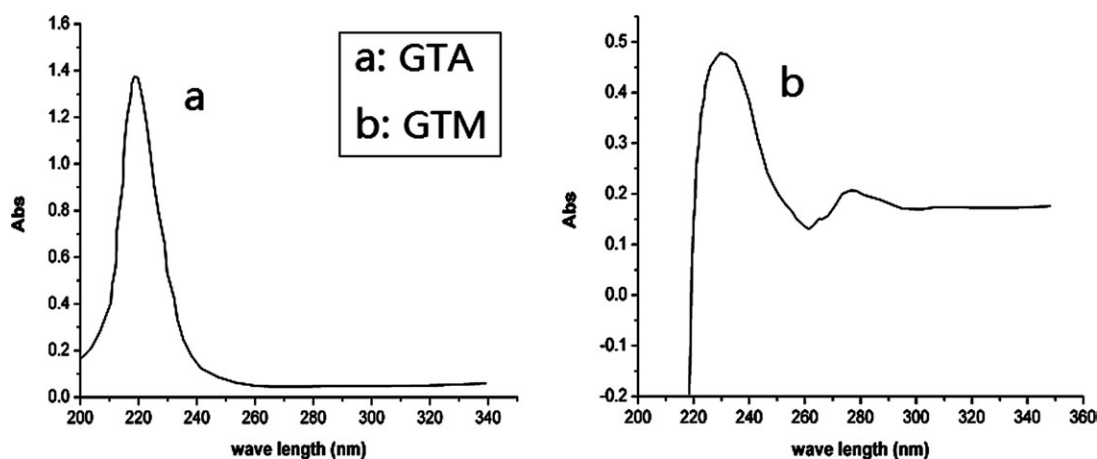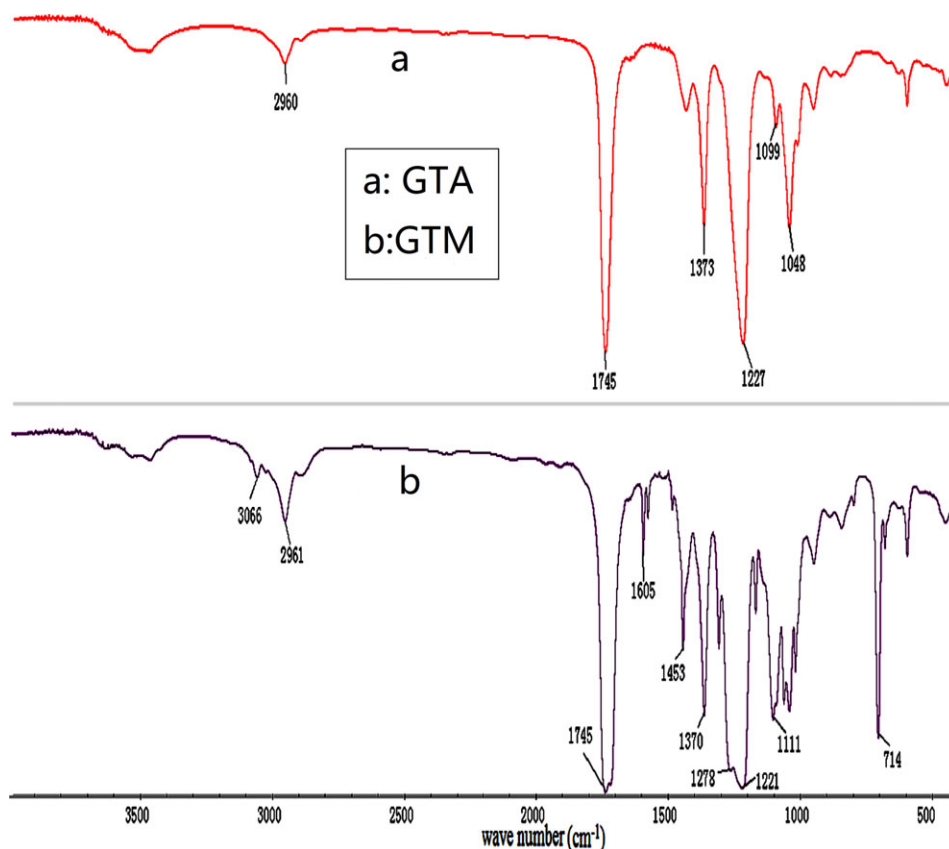

Figure 3. UV spectra of (a) GTA and (b) GTM.

Figure 4. FTIR of (a) GTA and (b) GTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PVC chain, which can reduce the physical crosslinking points between the chlorine atom and the chlorine atom in the PVC molecular chains; this shielded the polymer chains from interacting with each other and increasing the chain segmental motion in PVC. So, with the increase in the content of plasticizer, this effect was obvious. Moreover, with the increasing molar ratio of benzoic acid at the same triglyceride content, the results show that the elongation at break increased further and the tensile strength decreased further. Finally, when the molar ratio of benzoic acid to glycerol was 1:1, the elongation at break reached the maximum, and the tensile strength reached the min-

imum compared with that of the other products because the benzene group in the new product was similar to the benzene ring structure of universal plasticizer in the DOP and DBP, which increased the polarity of the plasticizer. Thus, the rigid benzene ring effectively reduced the interaction between the molecular chains of PVC and prevented the crystallization of PVC in the plasticizing process.[20] Moreover, the compatibility of GTM with PVC compared with that of GTA was improved with the addition of this polar benzene ring.[6,21] It also can be seen from Figure 6 that the elongation at break of the PVC composites plasticized by DOP with contents ranging from 20 to 80
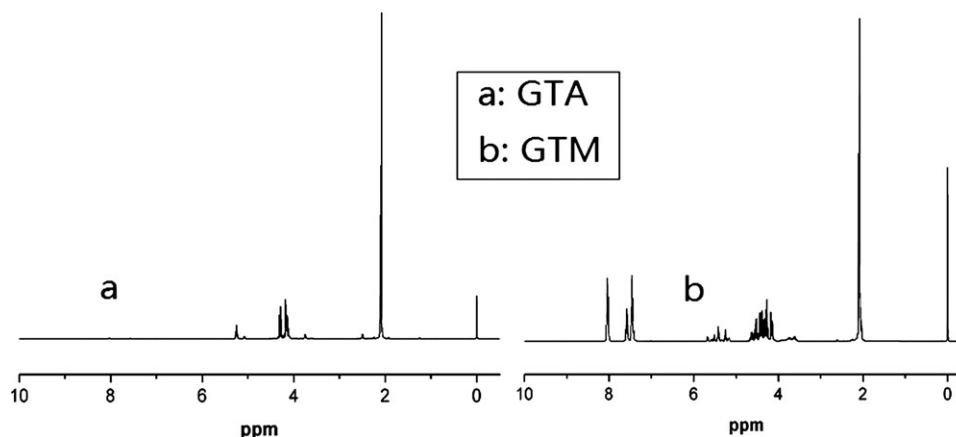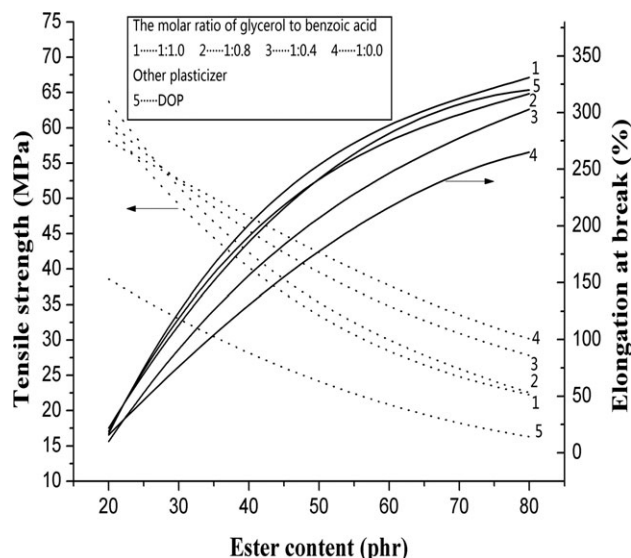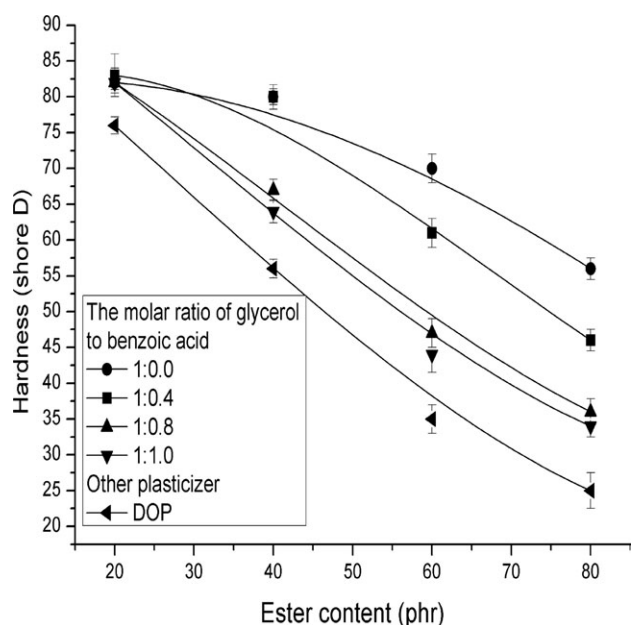

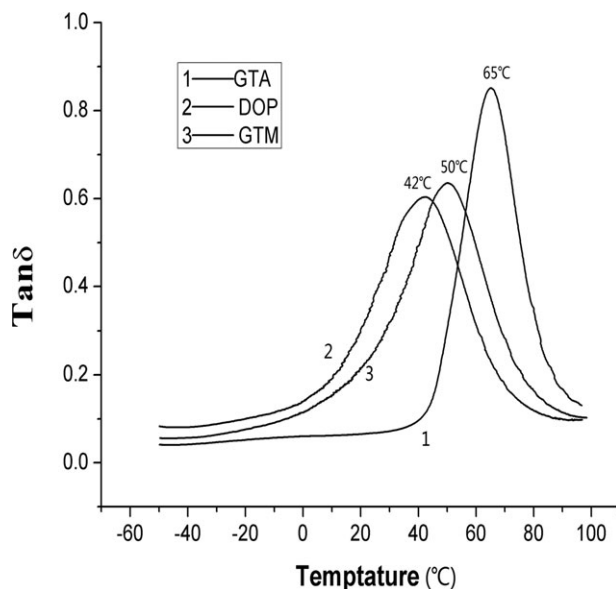**Figure 5.** ^{1}H-NMR of (a) GTA and (b) GTM.

Figure 6. Effects of the triglyceride content with different molar ratios of benzoic acid to glycerol on the tensile strength and elongation at break of the PVC composites.

Figure 8. Effect of three kinds of plasticizers on the T_g values of the PVC composites.

phr increased from about 20 to 320%; this was similar to the previous PVC composites plasticized by triglyceride when the molar ratio of glycerol to benzoic acid was 1:0.8. However, the tensile strength of PVC plasticized by the DOP decreased a little more than that of the PVC composites with triglycerides. Nevertheless, GTM was almost nontoxic compared to DOP, so GTM was a good plasticizer for PVC.

The influence of the plasticizer of the triglycerides and DOP on the hardness of the prepared PVC composites is shown in Figure 7. It was revealed that the hardness of the prepared com-

posites with increasing triglyceride content decreased continuously. At the same ester content, the hardness of the prepared PVC composites decreased with the addition of the molar ratio of benzoic acid to glycerol. Moreover, the PVC composites plasticized with GTM had the lowest hardness compared with the other triglycerides at the same content. However, the hardness of the PVC composites plasticized by DOP was a little lower than that of the PVC composites plasticized by triglycerides. In consideration of human health, this novel plasticizer is worth more study.

DMA Results

The variation of T_g is a very important factor in the evaluation of the plasticizer effects. The T_g value of the PVC composites without plasticizer was about 85°C. Figure 8 presents the DMA results, including tan δ; the temperature corresponding to the peak is the T_g. It can be seen that the T_g values of GTA, GTM, and DOP were 65, 50, and 42°C, respectively; this meant that all of these plasticizers showed some good plasticization for PVC. Compared those of the other two, the plasticization of GTA for PVC did not seem to be very good; the reason may have been its poor compatibility with PVC. The T_g values of GTM and DOP had little difference on each other. However, it is known that DOP is dangerous to human health,[22] so GTM is a potential plasticizer for the PVC composites.

CONCLUSIONS

The condition of esterification was successfully studied by the synthesis of GTA. When the molar ratio of glycerol to acetic acid was 1:4.5, sodium hydrogen worked as a catalyst, isopropyl acetate used as an azeotropic agents for the removal of water, and the reaction time was around 3.5 h, the esterification yielded 98.5%. GTM for PVC was successfully synthesized under these conditions through two steps when the molar ratio of glycerol to benzoic acid was 1:1, p-toluene sulfonic was used as

Figure 7. Effect of the triglyceride content with different molar ratios of benzoic acid to glycerol on the hardness of the PVC composites.

catalyst in the first-step reaction, and sodium hydrogen sulfate was used in the second-step reaction. With regard to the azeotropic agent, toluene was used in the first-step reaction, and isopropyl acetate was used in the second-step reaction.

The hardness (Shore D) and tensile strength of PVC plasticized by the synthesized mixture esters decreased, while the elongation at break increased. Moreover, when GTM was added to the PVC, the best mechanical properties were achieved. The T_g values of the PVC composites were tested to investigate the effect of this novel plasticizer. The results proved that PVC composites with excellent mechanical properties could be obtained by the addition of this novel plasticizer.

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