Self-Plasticized PVC Prepared by Introducing Fatty Acid to the PVC with Triglycidyl Isocyanurate as an Intermediate Bridge

Tianxiang Deng, Shouhai Li, Puyou Jia, Na Yao, Haiyang Ding, Lina Xu, Yan Zhang, Xiaohua Yang, and Mei Li*

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ABSTRACT: The phthalate-free self-plasticization of poly(vinyl chloride) (PVC) conforms to the concept of green chemistry. In this work, phthalate-free, biocontaining, self-plasticized PVC with nonmigration (4-an-TG-X-PVC; X = R, P, or O) was prepared by covalent attachment of ricinoleic acid, palmitic acid, and oleic acid, respectively, to the PVC matrix with 4-aminothiophenol and triglycidyl isocyanurate (TGIC) as intermediate bridges. 4-Aminothiophenol and TGIC acted as the nucleophilic reagent and the thermally stable substance, respectively. The 4-an-TG-X-PVC was observed by diverse characterization methods. Specifically, Fourier transform infrared spectra, ^1H nuclear magnetic resonance, gel permeation chromatography, and migration stability tests proved the successful synthesis of 4-an-TG-X-PVC. Compared to the neat PVC, the mechanical property of 4-an-TG-X-PVC is better. The glass transition temperature (T_g) of PVC is 81.24 °C, while that of 4-an-TG-X-PVC decreased to 41.88, 31.49, and 46.91 °C. The 4-an-TG-X-PVC showed higher elongation at break and lower tensile strength than neat PVC. Simultaneously, the thermal property of 4-an-TG-X-PVC got a boost. Thermogravimetry−infrared and thermogravimetry−mass spectrometry showed that 4-an-TG-X-PVC released less HCl than neat PVC in a thermal environment. Discoloration experiments demonstrated that 4-an-TG-P-PVC had better heat stabilization and better color than 4-an-TG-O-PVC and 4-an-TG-R-PVC. This work provides a viable solution to the dependence on phthalates, reduced human health and ecological risks, and endowed PVC with improved thermal stability and nonmigration performance.
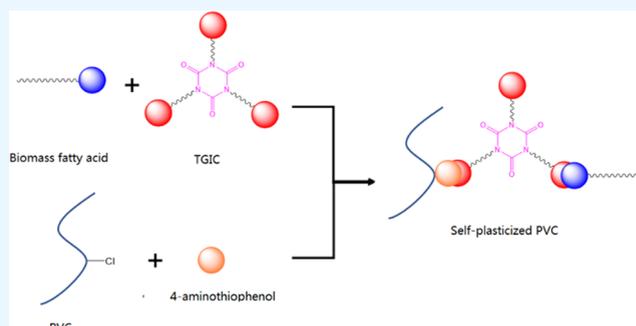
1. INTRODUCTION

Poly(vinyl chloride) (PVC) with low cost and high mechanical strength is the second common polymer worldwide. It is extensively used in medical treatment, construction materials, and toys.[1] Many polar chlorine atoms in pure PVC make it rigid at room temperature with a high T_g and low thermal stability. Thus, pure PVC is of little or no value. This problem is solved through the use of plasticizers and thermal stabilizers. Dioctyl phthalate (DOP), the mainly used plasticizer of PVC in China, is a toxic substance that migrates to the environment from the PVC substrate and then causes profound impact on human health.[2] Though some nontoxic plasticizers are prepared (e.g., oleate plasticizers,[3] ricinoleate plasticizer,[4] ester-amide based on ricinoleic acid,[5] triester-amide based on thiophene and ricinoleic acid[6]), the preparation methods are still limited owing to the problem of plasticizer migration. Therefore, it is very important to inhibit the migration and precipitation of plasticizers. The most effective way to prevent precipitation is to covalently connect plasticizers to PVC. Covalent grafting of flexible chains on PVC can achieve the desired results of plasticization and nontoxicity simultaneously, which is also called self-plasticization. Internal plasticization extends the distance between PVC chains and weakens the interaction between main chains by grafting long flexible chains. This process effectively prevents the migration of the plasticizer, makes PVC flexible, and promotes the movement of PVC chains. The inner plasticizer with flexible branch chains and polar groups is grafted onto PVC chains and thereby stabilizes the properties of modified PVC materials for a long time. This method completely avoids the migration of the plasticizer, further reduces the toxicity to human body, and prevents environmental pollution.[7] Nucleophilic substitution is the first step in modifying PVC and is commonly finished by mercaptan substitution[8] and azide substitution,[9] which both replace the active chlorine atoms on PVC and covalently connect the substitutes at the same time. Then, the active groups on the substitutes covalently connected to PVC can

Figure 1. (a) Typical synthetic routes of TG-X (X = R, P, or O) and (b) 4-an-TG-X-PVC (X = R, P, or O).

access long branched chains so as to achieve the effect of plasticization.

Recently, self-plasticization of PVC was achieved by modification with waste edible oil,[10] triethyl citrate,[11] aminated tung oil methyl ester,[12] cashew phenol,[13] and P-containing castor oil-based derivatives.[14] The modified PVC has a lower glass transition temperature than neat PVC and becomes more flexible after grafting with long-chain substances. With cheap trichlorotriazine as the starting material, Navarro covalently connected PVC with different aliphatic hydrocarbons and monoamino groups functionalized with ethylene oxide (EO)/propoxy oligomer to improve the flexibility and migration inhibition of PVC.[15,16] Vahid Najafi grafted five nontoxic plasticizers (e.g., tributyl citrate, propyne ether, tributyl citrate, oleic acid, polydimethylsiloxane diglycidyl ether) onto PVC without migration in petroleum ether and other environments to realize PVC internal plasticization.[17] These methods with the use of phthalates provide feasible alternatives to reduce human health threats and environmental risks.

There are many literature reports on the self-plasticization of PVC, which all have achieved good plasticization effect. On the basis of meeting the self-plasticization, however, the graft modification of PVC also shall help maintain the stability of the PVC substrate. Due to the low thermal stability of the abnormal structure, PVC easily gets rid of HCl, and HCl can promote the degradation of PVC. Therefore, absorbing HCl is very important in protecting PVC. The epoxy groups can react with HCl to form chlor alkali. Lerke et al. used diglycidyl ether of 2,2-bis(4-hydroxy-3-methylphenyl)propane, diglycidyl ether of 1,1-bis(4-hydroxyphenyl)cyclohexane, and butyl-cis-9,l0-epoxystearate to stabilize PVC.[18] Boussaha Bouchoul used epoxidated biomass such as isosorbide diesters and epoxidized sunflower oil to stabilize and plasticize PVC.[19] However,

because the epoxy additives are blended rather than being covalently connected, migration of additives is inevitable. If the epoxy group can be covalently connected to PVC, the PVC substrate can achieve the effects of self-plasticization, thermal stability, and antimigration at the same time.

Triglycidyl isocyanurate (TGIC) is a triazine epoxy compound with three epoxy groups, which provide opportunities for grafting PVC and long branched chains and absorbing hydrogen chloride. Meanwhile, the triazine ring has excellent thermal stability and is used in flame retardant research.[20−22]

In our work, ricinoleic acid (Ra), palmitic acid (Pa), and oleic acid (Oa) were used to graft onto the PVC chain with 4-aminothiophenol and TGIC as intermediate bridges. First, 4-aminothiophenol was connected to the PVC chain by nucleophilic substitution, and three types of biological carboxylic acids were connected to TGIC to form thermally stable internal plasticizers (TG-X; X = R, P, or O). Finally, covalent connection was carried out through the reaction between the epoxy group and amino group on 4-amino-thiophenol. The chemical structure of the modified PVC was verified by Fourier transform infrared spectra (FTIR), H nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), and migration resistance tests. The mechanical property of the internally plasticized PVC was recorded by differential scanning calorimetry (DSC) and tensile tests, and the thermal property was studied by thermogravimetric analysis (TGA), thermogravimetry−infrared (TG-IR) and TG−mass spectrometry (TG-MS), and discoloration tests.
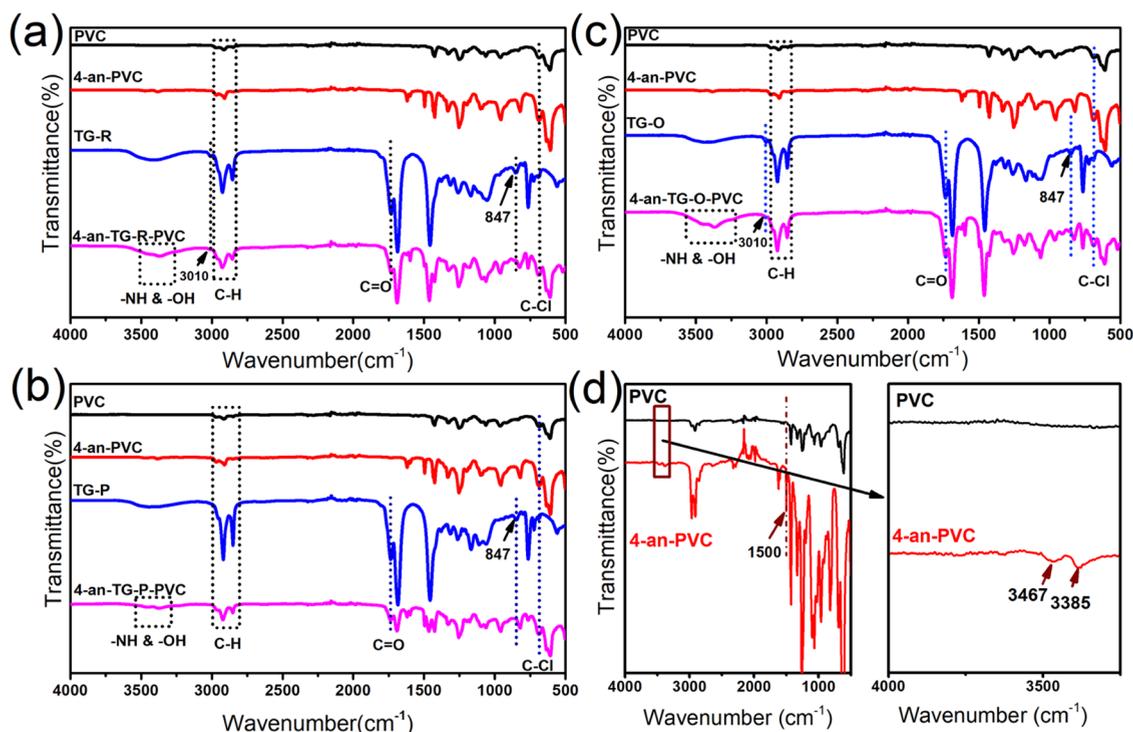
Figure 2. (a) FTIR spectra of 4-an-R-PVC, (b) FTIR spectra of 4-an-P-PVC, (c) FTIR spectra of 4-an-O-PVC, and (d) FTIR spectra of PVC and 4-an- PVC.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents were used as received. PVC was supplied from rhawn.cn (K value 59-55). 4-Aminothiophenol was purchased from Sigma-Aldrich Co., Ltd. (China). Ra, Pa, Oa, methanol, and benzyltriethylammonium chloride (TEBAC) were offered by Shanghai Macklin Biochemical Co., Ltd. (China). 1,3,5-TGIC was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). Potassium carbonate (K_2CO_3) and tetrahydrofuran (THF) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2. Synthesis of the Self-plasticization of Poly(vinyl chloride) Prepared by Covalently Linking Fatty Acid Groups Based on Triazine Ring (4-An-TG-X-PVC). Typical synthetic routes of the self-plasticization of poly(vinyl chloride) prepared by covalently linking fatty acid groups based on triazine ring(4-an-TG-X-PVC) are presented in Figure 1.

2.2.1. Synthesis of the Adduct of Ra and TGIC(TG-R), the Adduct of Pa and TGIC(TG-P), and the Adduct of Oa and TGIC(TG-O). TGIC (10 g, 0.0337 mol) and 0.1 g of TEBAC were added to a 50 mL flask. Then, 10.034 g of Ra (0.0337 mol), 8.62 g of Pa (0.0337 mol), and 9.495 g of Oa (0.0337 mol) were slowly dripped into the mixture separately. And then, the reaction mixtures were stirred at 125 °C for 3 h under the N_2 atmosphere, forming TG-R, TG-P, and TG-O.

2.2.2. Synthesis of 4-An-PVC. PVC (15 g), 4.8 g (0.0383 mol) of 4-aminothiophenol, and 5.28 g of K_2CO_3 were dissolved in 240 mL of THF. After stirring at 60 °C for 4 h under N_2 conditions, the reaction system precipitated in a methanol/water mixture (1/1, volume), washed several times with methanol, and dried in a vacuum oven to form 4-an-PVC (~17 g).

2.2.3. Synthesis of 4-An-TG-X-PVC (X = R, P or O). Three 250 mL flasks were taken. Then, PVC (5 g), 1.6 g of 4-

aminothiophenol (0.0128 mol), 1.76 g of K_2CO_3, and 80 mL of THF were added to each flask and stirred at 60 °C for 4 h in a N_2 atmosphere. Then, 7.62 g of TG-R, 7.07 g of TG-P, and 7.4 g of TG-O were added into the mixture separately under stirring at 60 °C for 4 h. Then, the reaction systems precipitated in a methanol/water mixture (1/1, volume), washed several times with methanol, and dried in a vacuum oven to form 7.8 g of 4-an-TG-R-PVC, 9.11 g of 4-an-TG-P-PVC, and 11.13 g of 4-an-TG-O-PVC.

Given the neighboring effect, intrachain cross-linking of PVC chains is likely to occur. The typical structure of 4-an-TG-X-PVC(X = R, P or O) is presented in Figure 1c.

2.4. Preparation of 4-An-TG-X-PVC (X = R, P, or O) and PVC films. 4-An-TG-R-PVC (3 g), 3 g of 4-an-TG-P-PVC, and 3 g of 4-an-TG-O-PVC were dissolved in 50 mL of THF separately. The mixtures were fully agitated by a mechanical agitator at 200 rpm and room temperature for 1 h. The products were cast into Petri dishes and dried at 60 °C for 2 days to remove traces of the residual solvent and to form thin films.

PVC (3 g) was dissolved in 50 mL of THF, followed by sufficient mechanical agitation at 200 rpm and room temperature for 1 h. The resulting samples were cast into Petri dishes and dried at 60 °C for 2 days to get rid of traces of the residual solvent and to obtain thin films.

2.5. Characterization. The FTIR spectrometer (Nicolet iS50-Thermo Fisher Scientific) was operated within 4000−500 cm^{-1} at a resolution of 4 cm^{-1}.

The ^1H NMR spectrometer (ARX300, Bruker, Faellanden, Switzerland) was run with $CDCl_3$ as a deuterated solvent.

Molecular weights of 4-an-TG-X-PVC were detected on an efficient gel chromatograph (Waters1525) at 35 °C and at a flowrate of 1 mL/min (column: Aglient PLgel 5um MixED-C, made in GB) with THF as the solvent.
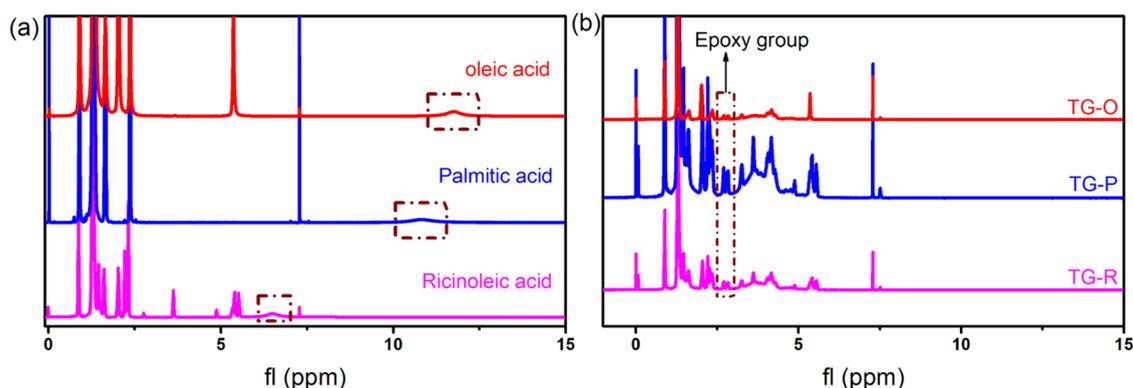
Figure 3. (a) ^{1}H NMR spectra of fatty acid and (b) ^{1}H NMR spectra of TG-X.
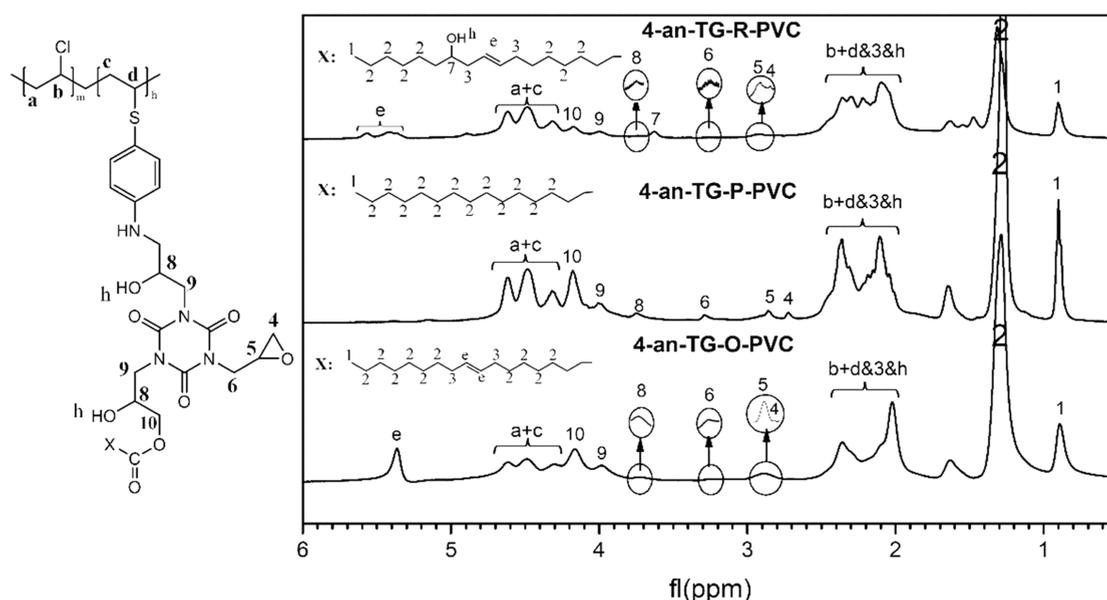

Figure 4. ^{1}H NMR spectra of 4-an-TG-X-PVC.

The migration stability of the plasticizer was measured at 25 °C according to ASTMD1239-98. 4-An-TG-X-PVC and DOP/PVC films were soaked in petroleum ether as the extraction medium. After 12, 24, or 48 h, the extracted 4-an-TG-X-PVC and DOP/PVC were dried and reweighed. The degree of migration was computed as follows

$$\text{degree of migration} = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 and W_2 are the primary and final weights of the tested 4-an-TG-X-PVC or DOP/PVC specimen, respectively.

Glass transition temperature (T_g) was detected with a NETZSCH DSC 200 PC analyzer from −40 to 120 °C at a heating rate of 20 °C/min.

Tensile strength and elongation at break of PVC and 4-an-TG-X-PVC were recorded as per GB/T 13022-91 (China) on an E43.104 universal testing device (MTS Instrument Crop., China).

The 3D TGA-FTIR spectra of the gas phase during PVC thermal decomposition were recorded on a 409PC thermal analyzer (Netzsch, Germany) equipped with a Nicolet iS10 FTIR device (Nicolet Instrument Crop.).

The TG-MS analysis was performed using a 409PC thermal analyzer (Netzsch, Germany) coupled with a QMS403C

instrument (Netzsch, Germany). Under an N$_2$ atmosphere, ~10 mg of each specimen was put into the 409PC thermal analyzer; the temperature was increased from 40 to 600 °C at 10 °C/min.

Thermogravimetric analysis (TGA) was performed using a Q600 TGA device. Each sample was put into platinum pans under a nitrogen atmosphere and scanned from 30 to 600 °C at a rate of 20 °C/min.

A discoloration test was conducted according to ISO 305:1990 (E). The PVC strip films were first put into an oven (ZXRD-B5055) at 180 °C. The samples were taken out at a certain interval (one sample each time), and the color changes of the samples at adjacent time points were observed.

X-ray photoelectron spectroscopy (Thermo Fisher Scientific k-α) was used for testing. The vacuum degree of the analysis room was 5×10^{-10} Pa, the excitation source was Al kα ray ($h\nu$ = 1253.6 eV), the working voltage was 15 kV, the filament current was 10 mA, and the signal accumulation of 5−10 cycles was carried out. Passing energy was 50 eV, step size was 0.05 eV, and charge correction was carried out with C$_{1s}$ = 284.80 eV combined energy as the energy standard.
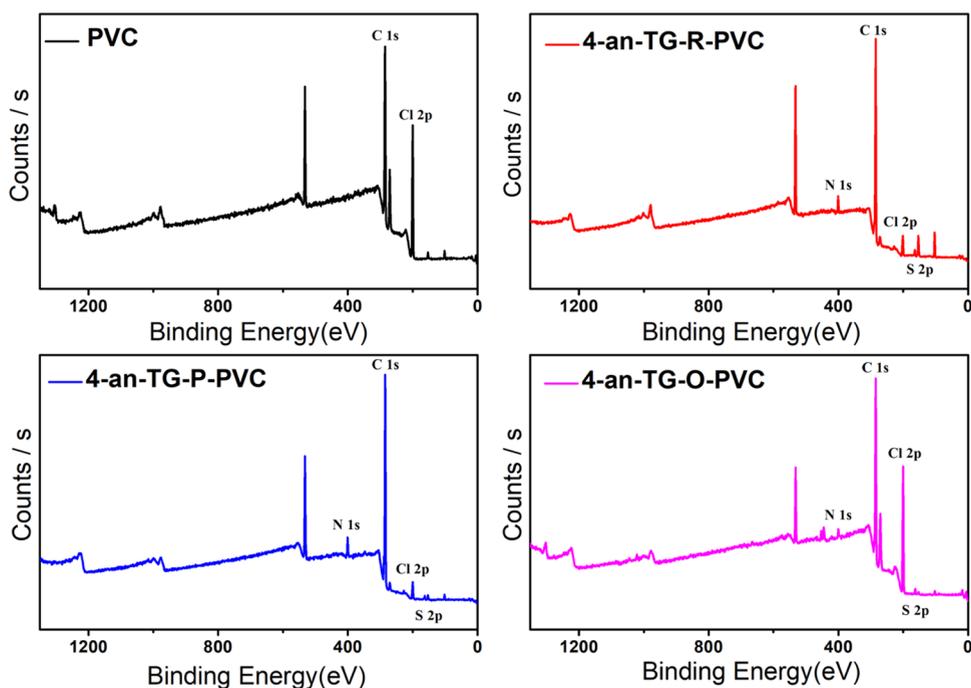
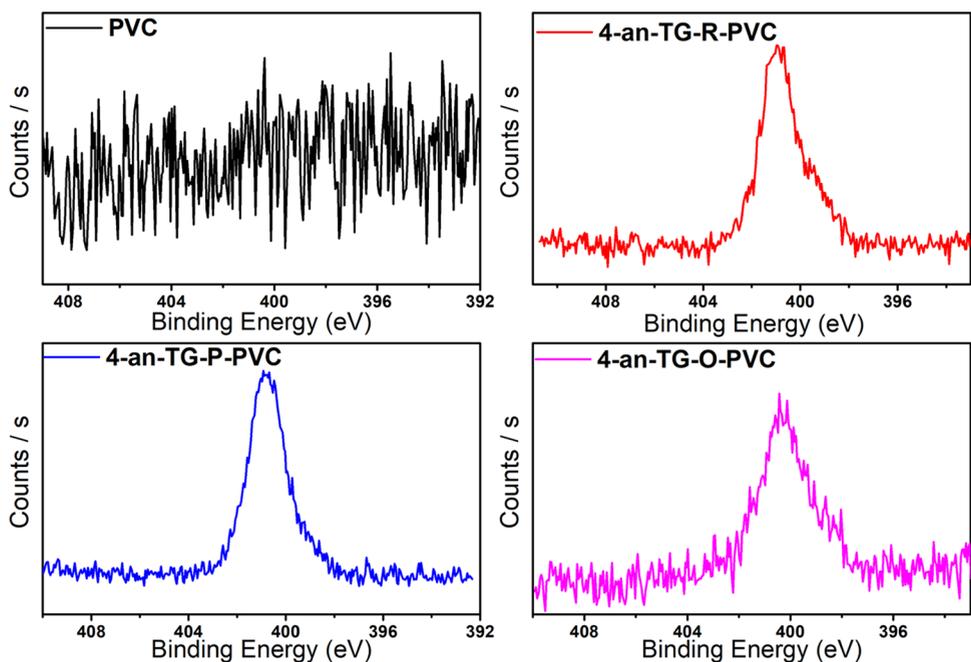**Figure 5.** XPS spectra of PVC and 4-an-TG-X-PVC with element type.

Figure 6. XPS spectra of PVC and 4-an-TG-X-PVC with N element.

3. RESULTS AND DISCUSSION

3.1. Structures and Characterization of PVC, 4-An-PVC, TG-X, and 4-An-TG-X-PVC (X = R, P, or O). *3.1.1. FTIR and ^{1}H NMR Analysis.* The infrared spectra of PVC, 4-an-PVC, TG-X, and 4-an-TG-X-PVC are shown in Figure 2. The peaks at 2913 and 680 cm^{-1} are ascribed to C−H and C−Cl, respectively,[13,15,23] which both reflect the existence of PVC chain. In the FTIR spectrum of 4-an-PVC (Figure 2d), the peak at 1500 cm^{-1} indicates the aromatic C−C stretching, and the characteristic peaks of primary amine are observed at 3385 and 3467 cm^{-1}. That means the successful

grafting of 4-aminothiophenol onto PVC chain by nucleophilic reaction.[24] In the FTIR spectra of TG-R, TG-P, and TG-O (Figure 2a−c), the peak at 847 cm^{-1} is a characteristic of the epoxy group, which can react with the amino group to form a hydroxyl group.[25] Compared to the FTIR spectra of TG-R, TG-P, and TG-O, it can be seen that the characteristic peak of the epoxy group at 847 cm^{-1} almost disappeared, and the peak of the hydroxyl group at 3360 cm^{-1} appeared in the 4-an-TG-X-PVC (X = R, P, or O) spectra. Meanwhile, the absorption at 3010 cm^{-1} comes from the tensile vibration of C═C on the ricinoleic acid chain and oleic acid chain (Figure 2a,c). All of
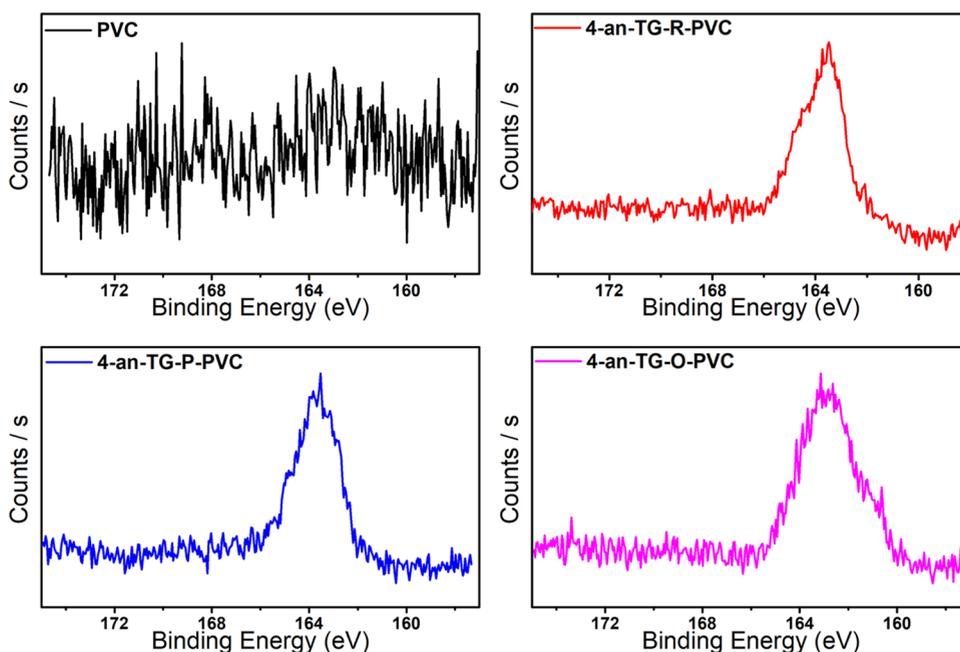
Figure 7. XPS spectra of PVC and 4-an-TG-X-PVC with S element.
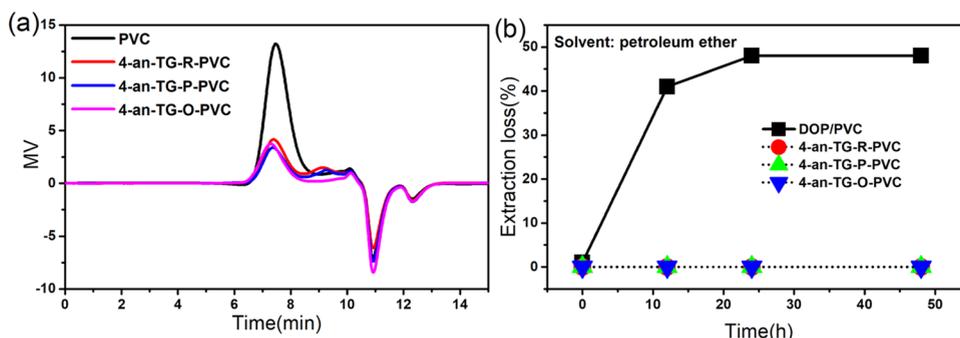
Figure 8. (a) GPC spectra of PVC and 4-an-TG-X-PVC and (b) degrees of migration of DOP/PVC and 4-an-TG-X-PVC.

these results indicate the successful synthesis of 4-an-TG-X-PVC.

The ^{1}H NMR spectra of fatty acids and TG-X (X = R, P, or O) are presented in Figure 3. There were wide peaks in the ^{1}H NMR spectra of fatty acids, which were the signals of carboxyl. Compared with the ^{1}H NMR spectra of fatty acids, these wide peaks disappeared and new peaks of the epoxy group appeared in the ^{1}H NMR of TG-X, which indicated that the carboxyl group was completely consumed by TGIC. The ^{1}H NMR spectra of 4-an-TG-X-PVC are presented in Figure 4. The main peaks at 2.0−2.5 and 4.2−4.7 ppm correspond to the methylene (-CHCl-C$\underline{H}_2$-) and the methine (-C$\underline{H}$Cl-CH$_2$-) protons in PVC, respectively.[26] The peaks of methyl (-C$\underline{H}_3$) and methylene (-C$\underline{H}_2$-) are near 0.9 and 1.2 ppm, respectively,[27−29] which both are of the three carboxylic acid chains. These peaks indicate the successful grafting of the three carboxylic acids. At the same time, peaks 4, 5, and 6 indicate the presence of epoxy groups in the system.[30] So, 4-an-TG-X-PVC is a mixture of the grafting and some partial cross-linking structures. And the cross-linking degrees of 4-an-TG-R-PVC, 4-an-TG-P-PVC, and 4-an-TG-O-PVC are 12, 45.6, and 36.9%, respectively (S1). The grafting densities of 4-an-TG-R-PVC, 4-an-TG-P-PVC, and 4-an-TG-O-PVC are 27.75, 25.93, and 6.78%, respectively (S2).

3.1.2. Analyses of XPS, GPC, and Migration Stability.
Figure 5 shows the XPS spectra of PVC and 4-an-TG-X-PVC. Figures 6 and 7 show the XPS spectra of PVC and 4-an-TG-X-PVC with S and N elements, respectively. Comparing Figures 6 and 7, we can draw a conclusion that S and N elements were successfully introduced into 4-an-TG-X-PVC.

The existence of high-molecular-weight 4-an-TG-X-PVC was proved by GPC spectra (Figure 8a). The molecular weights (M_n) of PVC, 4-an-TG-R-PVC, 4-an-TG-P-PVC, and 4-an-TG-O-PVC were 43,700, 62,300, 64,000, and 66,700 g/mol, respectively. The GPC chromatograms of 4-an-TG-X-PVC shifted to higher molecular weights relative to PVC, suggesting that the reactants were covalently connected to the PVC chain.

Figure 8b demonstrates the migration degrees of 4-an-TG-X-PVC and DOP/PVC using a petroleum ether solvent. Clearly, the migration degree of DOP in petroleum ether was 48.2%. In comparison, nearly no migration occurred with the internal plasticizer (TG-X) in petroleum ether, indicating that 4-an-TG-X-PVC (X = R, P, or O) avoids migration.

The FTIR, ^{1}H NMR, XPS, and GPC results suggest that 4-an-TG-X-PVC (X = R, P, or O) was synthesized successfully (Table 1).

Table 1. GPC Data of 4-An-TG-X-PVC

sample	M_n	M_w	polydispersity
PVC	43,700	89,800	2.05
4-an-TG-R-PVC	62,300	108,000	1.73
4-an-TG-P-PVC	64,000	114,400	1.78
4-an-TG-O-PVC	66,700	142,800	2.14

3.2. Mechanical Property of 4-An-TG-X-PVC (X = R, P, or O). T_g, glass transition temperature, is the temperature at which a polymer changes from a glassy state to a rubbery state. As a result, materials with low T_g values are increasingly flexible. Many polar chlorine atoms in pure PVC make it rigid at room temperature with a high T_g and low thermal stability. Thus, pure PVC is of little or no value. This problem is solved through the use of plasticizers and thermal stabilizers. The DSC thermograms of PVC and 4-an-TG-X-PVC are displayed in Figure 9. The T_g values of PVC, 4-an-TG-R-PVC, 4-an-TG-
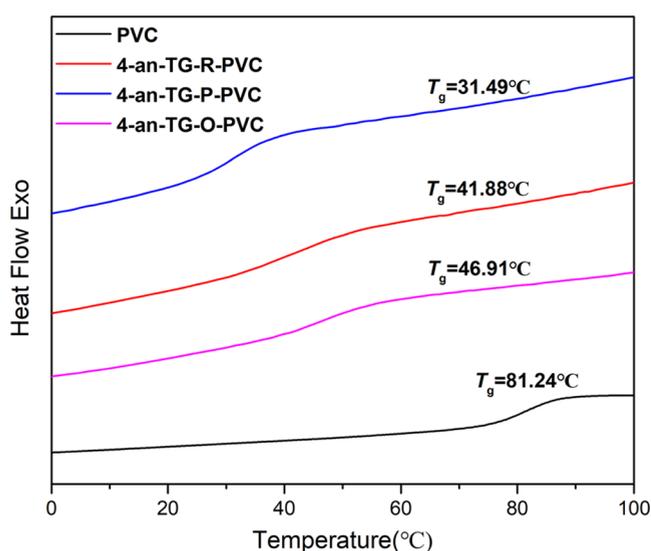
Figure 9. DSC thermograms of neat PVC and 4-an-TG-X-PVC.

P-PVC, and 4-an-TG-O-PVC are 81.24, 41.88, 31.49, and 46.91 °C respectively. Hence, the T_g of 4-an-TG-X-PVC is significantly lower than that of neat PVC, which may be because the covalent connection of long fatty chain segments shows higher free volume and promotes the movement between PVC chains, contributing to the internal plasticization of PVC.

The tensile properties of neat PVC and 4-an-TG-X-PVC are summarized in Table 2. Tensile strengths of PVC, 4-an-TG-R-PVC, 4-an-TG-P-PVC, and 4-an-TG-O-PVC are 30.56, 10.6, 17.1, and 13.5 MPa, respectively, and their elongations at break are 46.81, 249.7, 250.4, and 269.8%, respectively. Clearly, 4-an-TG-X-PVC has larger elongation at break and lower tensile strength than PVC. The reason is that the replacement of the

Table 2. Tensile Data of Neat PVC and 4-An-TG-X-PVC

sample	tensile strength (MPa)	elongation at break (%)
PVC	33.97 ± 2.52	48.00 ± 1.19
4-an-TG-R-PVC	10.60 ± 3.47	249.70 ± 6.02
4-an-TG-P-PVC	17.10 ± 3.31	250.40 ± 31.16
4-an-TG-O-PVC	13.50 ± 2.79	269.80 ± 30.82

chlorine atom with the internal plasticizer prolongs the separation distance of PVC chains to the chains and plays a lubricating role of PVC chains. The results provide a feasible alternative strategy for the use of DOP to improve the plasticizing performance of PVC.

3.3. Thermal Properties of 4-An-TG-X-PVC (X = R, P, or O). *3.3.1. TGA-FTIR Analysis.* The gas products formed during the thermal degradation of neat PVC or 4-an-TG-X-PVC were studied via TGA-IR (Figure 10) and TGA-MS (Figure 11). The gas products of thermal degradation of neat PVC or 4-an-TG-X-PVC are mainly H_2O (3500−4000 and 1500−1600 cm^{-1}), C_6H_6 (3029 and 1460 cm^{-1}), CO_2 (2372 cm^{-1}), HCl (2865 cm^{-1}), and ester group (1746, 1267, and 1103 cm^{-1}). Because IR only offers qualitative data about the functional groups of various pyrolysis products, we also conducted MS to clarify the pyrolysis mechanism in PVC and identify the exact compositions of the products. The MS spectra from the decomposition products of PVC and 4-an-TG-X-PVC are shown in Figure 11a−d, where the intense ion signals at m/z = 18, 36, 44, and 78 are ascribed to gases H_2O, HCl, CO_2, and C_6H_6, respectively. The integrated areas under the peaks of HCl and C_6H_6 in PVC are much larger than those of 4-an-TG-X-PVC (Figure 11b,d), indicating more HCl and C_6H_6 gases were emitted from the thermal decomposition of PVC than 4-an-TG-X-PVC. Meanwhile, the signal of 4-an-TG-X-PVC is higher (Figure 11c), indicating that 4-an-TG-X-PVC produces more CO_2, which is attributed to the grease chain segment on 4-an-TG-X-PVC.

3.3.2. Thermal Stability Evaluated by Discoloration Test and TGA Analysis. Basically, the PVC-heated degradation mainly involves a gradual unzipping of nearby labile Cl atoms, with the emission of HCl. The colors after the thermal aging test are listed in Table 3. Results show that 4-an-TG-P-PVC has a better heat stabilization and better color than 4-an-TG-R-PVC and 4-an-TG-O-PVC.

Generally, the thermal degradation of PVC is a two-step process. The first step (185−375 °C) is dehydrochlorination, which includes the formation of conjugated polyene segments after the release of HCl. The second step (375−500 °C) is mainly the cyclization of the conjugated polyene structure to form an aromatic mixture and is the main cause of color change. Weight loss of the 4-an-TG-X-PVC was evaluated using TGA. The TGA curves of the PVC specimens heated in nitrogen at 20 °C/min are shown in Figure 12. The thermal data for 4-an-TG-X-PVC (X = R, P, or O) with 30 and 50% mass loss temperatures (T_{30} and T_{50}), the temperature at the maximum weight loss rate of the degradation (T_p), and char yield at 600 °C can be found in Table 4. Compared with 4-an-TG-P-PVC and 4-an-TG-O-PVC, the T_{30}, T_{50}, and char yield of 4-an-TG-R-PVC were higher. The thermogravimetric results and found PVC thermal stabilities of 4-an-TG-P-PVC and 4-an-TG-O-PVC are better than 4-an-TG-R-PVC. These TGA results agree well with the discoloration test results. Meanwhile, the discoloration test results showed that the 4-an-TG-P-PVC has better long-term thermal stability than 4-an-TG-O-PVC. Figure 13 shows the plasticization and thermal stability mechanism. During the thermal decomposition of 4-an-TG-X-PVC (X = R, P, or O), it seems that the degradation starts from the side chain (fatty acids). In addition, epoxy group structures can improve PVC thermal stability.
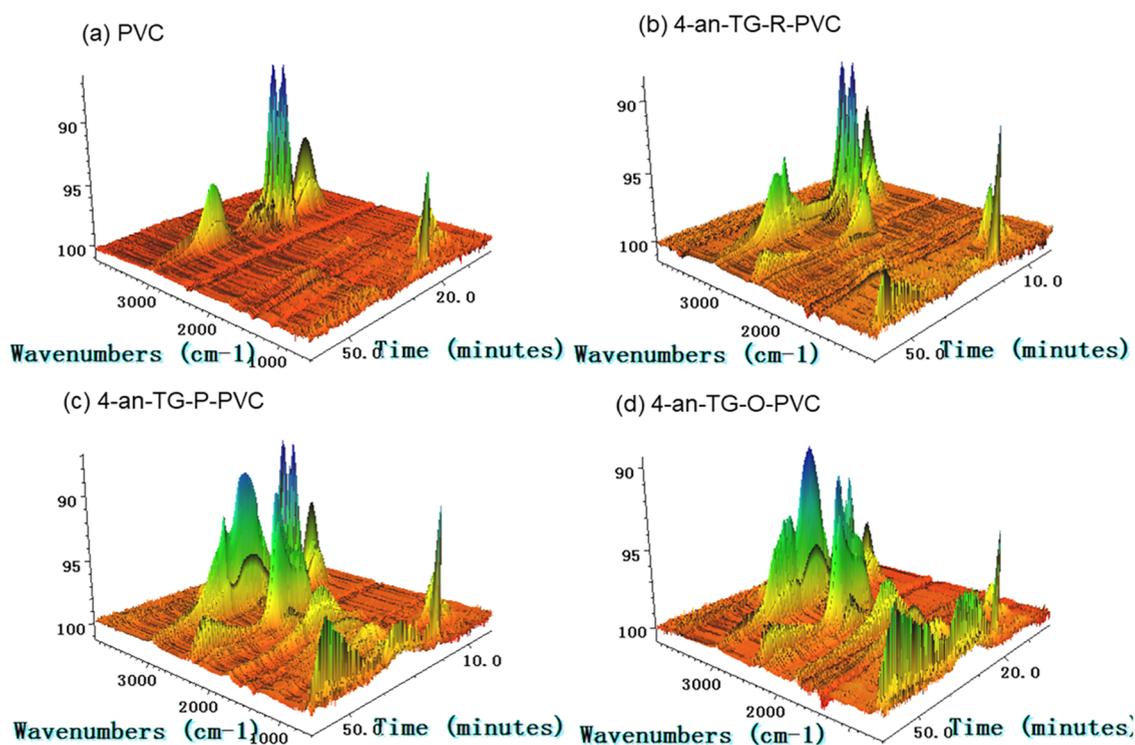
Figure 10. 3D TG-IR spectra (a–d) of gases from PVC and 4-an-TG-X-PVC.
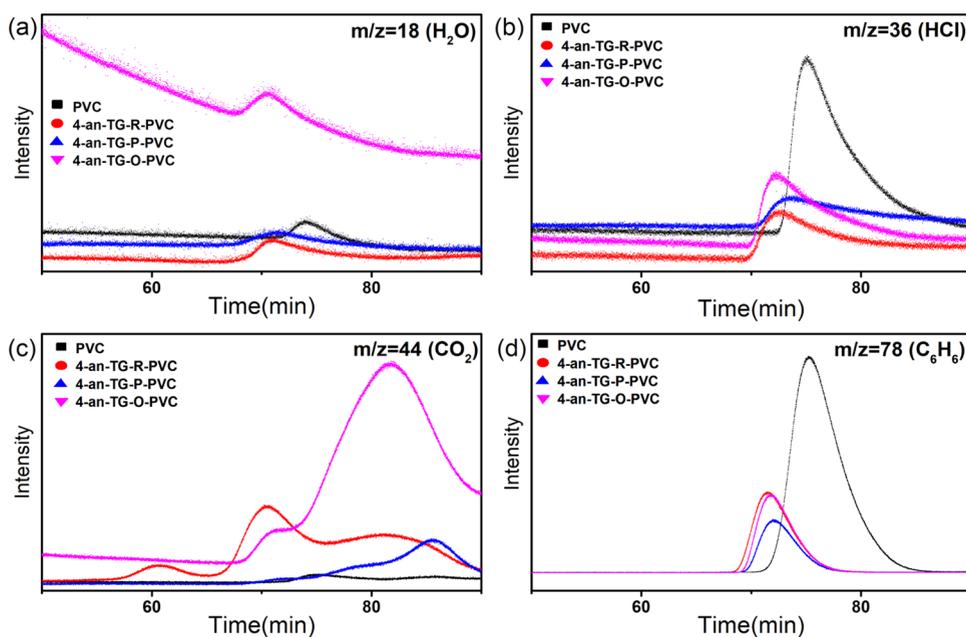

Figure 11. MS signals (a–d) of main degradation gases from PVC and 4-an-TG-X-PVC.

4. CONCLUSIONS

The self-plasticization of 4-an-TG-R-PVC, 4-an-TG-P-PVC, and 4-an-TG-O-PVC was conducted by covalently linking ricinoleic acid, palmitic acid, and oleic acid as internal plasticizers to PVC, respectively. DSC shows that the T_g of internal PVC materials decreased from 81.24 to 41.88 °C, 31.49 and 46.91 °C, respectively. FTIR and ^{1}H NMR spectra verify the successful connection of these molecules to PVC chains. GPC shows that the M_n of 4-an-TG-X-PVC (X = R, P, or O) increased from 43,700 to 62,300, 64,000, and 66,700 g/mol, respectively. The migration stability test reveals no migration of 4-an-TG-X-PVC in petroleum ether. Hence, this strategy proves the covalent connection of internal plasticizers of PVC and inhibited migration of the plasticizer molecules. Furthermore, the activation energy under different heating rates based on TGA was obtained by the Doyle equation. TGA-IR and TGA-MS reveals that the resulting HCl concentration from 4-an-TG-X-PVC is less than PVC. 4-An-TG-X-PVC shows better color than the neat PVC as a whole in the discoloration tests.

Table 3. Discoloration of 4-An-TG-X-PVC at 180 °C

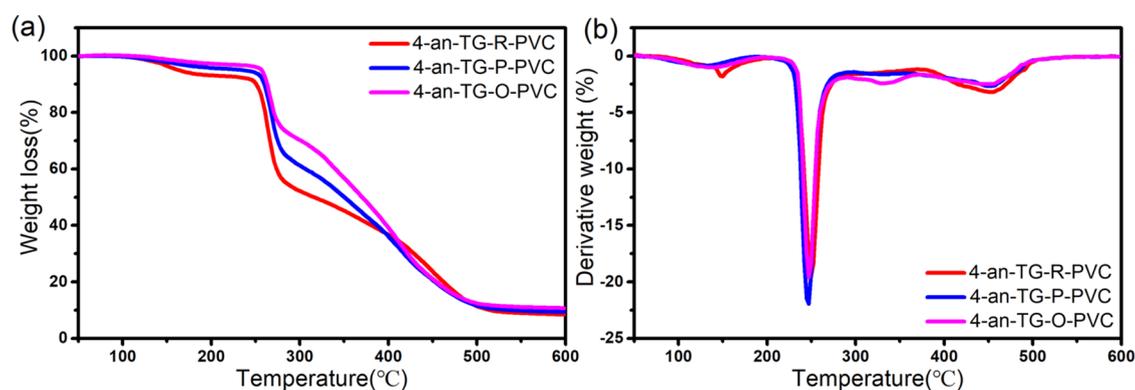| Sample	Thermal degradation time (min)							
	0	5	10	15	20	25	30	35
4-an-TG-R-PVC								
4-an-TG-P-PVC								
4-an-TG-O-PVC								

Figure 12. (a) TGA thermograms of 4-an-TG-X-PVC and (b) DTGA thermograms of 4-an-TG-X-PVC.

Table 4. TGA Data of 4-An-TG-X-PVC

sample	$T_{30}{}^{a}$ (°C)	$T_{50}{}^{a}$ (°C)	$T_p{}^{b}$ (°C)	char yield (%)
4-an-TG-R-PVC	266	316	264.7	8.4
4-an-TG-P-PVC	276	351	267.9	9.4
4-an-TG-O-PVC	301	371	266.7	10.7

[a]T_{30} and T_{50} are the temperatures at weight loss of 30 and 50%, respectively. [b]T_p is the temperature at the maximum weight loss rate of the degradation.
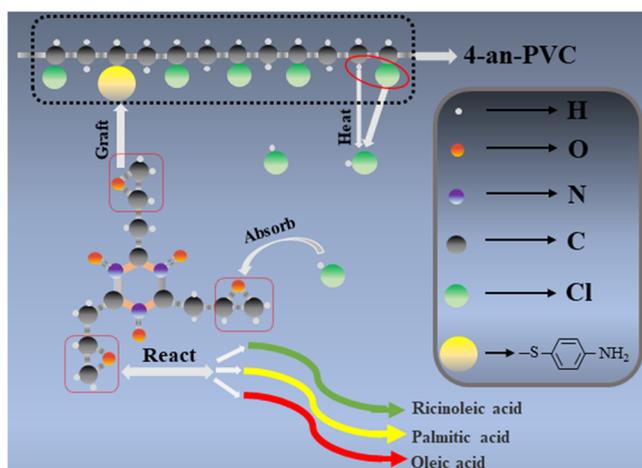
Figure 13. Internal plasticizing mechanism and thermal mechanism of 4-an-TG-X-PVC.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03655.

Cross-linking degree of 4-an-TG-X-PVC and m:h ratio of 4-an-TG-X-PVC (PDF)

AUTHOR INFORMATION

Corresponding Author

Mei Li − CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China; orcid.org/0000-0002-8684-0590; Email: lm@icifp.com

Authors

Tianxiang Deng − CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China

Shouhai Li − CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China

Puyou Jia − CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest

Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China

Na Yao − *CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China*

Haiyang Ding − *CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China*

Lina Xu − *CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China*

Yan Zhang − *CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China*

Xiaohua Yang − *CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Institute of Chemical Industry of Forest Products, Nanjing 210042, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c03655

Author Contributions

T.D. contributed for conceptualization, methodology, writing original draft, and project administration. S.L. performed formal analysis. S.L., P.J., and L.X. reviewed and edited the manuscript. N.Y. contributed for visualization. H.D., Y.Z., and X.Y. performed investigation. M.L. contributed for funding acquisition, resources, and supervision.

Notes

The authors declare no competing financial interest.

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