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Improving Epoxy Resin Performance Using PPG and MDI by One-Step Modification

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Abstract: The toughening modification of epoxy resin by polyurethane prepolymer (PU) can effectively solve the disadvantage of high brittleness in its application. In this study, a convenient way to toughen epoxy resins was explored, and the monomers PPG and MDI for the synthesis of polyurethane prepolymers were used for a one-step modification of epoxy resins. The test results of viscosity and elongation at break showed that P-M reduced the viscosity of the epoxy resin and improved the toughness. Especially when the content of P-M was 25%, the elongation at the break of the modified EP reached 196.56%. From a thermogravimetric and pyrolysis kinetic analysis, the P-M modification had better thermal stability than the PU modification. These findings have particular implications for the toughening and engineering applications of epoxy resins.

Keywords: epoxy resin; modified; viscosity; thermal decomposition; kinetic

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1. Introduction

Epoxy resin (EP) has been widely used in coatings, adhesives, aviation, construction materials, composite materials, and photoelectric materials, due to its high bonding strength, mechanical strength, excellent chemical resistance, electrical insulation, and dimensional stability [1–5]. However, the shortcomings of epoxy resin such as high brittleness and easy cracking also greatly limit its application in the industrial field. The low toughness and poor crack resistance of EP caused by highly cross-linked structures has always been a problem and research direction for scholars to solve [6,7]. Consequently, many efforts have been focused on improving the toughness of EP in recent years.

In order to improve the toughness of EP, second components such as nanoparticles [8,9], fibers [10,11], and polymers [12,13] are used as toughening modifiers or even composite modification. Yang et al. [8] used the prepared regenerated cellulose and nano-carbon dioxide hybrid material as a modifier to increase the tensile strength and impact toughness of epoxy resin by 38% and 40%, respectively. Wang et al. [7] used liquid γ-aminopropyl triethoxysilane (APTES)-modified Sm2O3 nanoparticles to improve the mechanical properties of epoxy resins, and the peak elongation at break of the composite was only 0.68%. Although the modification of epoxy resin by nanomaterials can improve its flexibility to a certain extent, the problems of dispersion of nanoparticles in epoxy resin and interfacial incompatibility have not been solved. On the other hand, the uneconomical nature of nanoparticles also precludes them from being widely used in engineering.

Polymers are also often used to improve the toughness of epoxy resins, [14] of which polyurethanes have been widely studied due to their good flexibility [15]. Since Frisch first reported polyurethane (PU)-modified EP [16], many related works have been widely studied due to the superior flexibility and excellent mechanical properties of interpenetrating network polymers (IPNs) [17,18]. Bakar and Kostrzewa synthesized PUs with different isocyanates and polyols and discussed the effect of PU types on the toughness of

EP. Experiment results indicated that an IPN was formed through a graft reaction between the isocyanate-terminated PU and EP, greatly improving the toughness and reducing the glass transition temperature of the EP [19–23]. Li's research results showed that there was a graft reaction between the polymer network I formed by epoxy resin with a curing agent and polymer network II obtained via PUP reactions with a chain extender and cross-linker [24–26]. Dharmalingam Sivanesan et al. prepared polycaprolactone polyols with different molecular weights and chain lengths, and then prepared polyurethane-modified epoxy resins with hexamethylene diisocyanate. The results showed that the addition of polyurethanes and EP formed cross-linking bonds, thereby increasing the tensile strength from 63 MPa to 81 MPa [27]. Studies by many scholars have proved that due to the cross-linking effect of polyurethane and EP, the phenomenon of phase separation is avoided in the system, thereby improving the mechanical properties.

In previous studies, the modification of EP usually required two stages, namely the preparation of polyurethane and the blending with epoxy resin. In this paper, the steps of preparing the polymer were omitted. Moreover, the research on the toughening and modification of epoxy resin by PPG and MDI, the monomer for preparing the polyurethane prepolymer, has rarely been reported. In this study, epoxy resin was modified with MDI and PPG, compared with the traditional polyurethane prepolymer modification, and the effect of the modifier addition on the mechanical properties of epoxy resin was discussed. In addition, the viscosity, initial setting time, and thermal stability of the modified epoxy resin were also discussed in this study; the thermal decomposition kinetic parameters were analyzed by Kissinger and Flynn–Wall–Ozawa (F–W–O) methods, respectively.

2. Experimental Section

2.1. Materials

4,4′-Diphenylmethane diisocyanate (MDI) and polypropylene glycol (PPG Mw = 1000 g mol^{-1}) were supplied by Jining Baiyi Chemical Co. (Shandong, China). PPG was an industrial product that was dehydrated under a vacuum at 120 °C for 2 h before use. Epoxy resin (EP), with an epoxy value of 0.51 mol/100 g, was purchased from Guangzhou Qian Chemical Co., Ltd. (Guangzhou, China). The curing agent (model 421, amine value was 380 ± 20 mg KOH/g) was obtained from Boyu Biological Engineering Co., Ltd. (Shandong, China).

2.2. Preparation of Polyurethane Prepolymer

Under vacuum conditions, the PPG was added dropwise into the preweighed MDI using a peristaltic pump at a speed of 30 r/min (n (NCO): n (OH) = 1.5). Then, the reaction temperature was kept at 70 °C for 3.5 h and it yielded PUP. The viscosity of the PUP sample was 13,400 mPa·s, and the isocyanate content measured by the di-n-butylamine back drop method is 2.96%.

2.3. Preparation of Modified Epoxy Resin

EP, modified with different contents of PPG and MDI (n (NCO): n (OH) = 1.5), 0, 10, 20, 25, and 30 wt %, was prepared. First, PPG and MDI were added into EP and stirred at room temperature for 15 min. Then, the curing agent (33 wt % of EP) was added and stirred for 15 min. The mixture was poured into a mold coated with vacuum silicone grease and placed in a vacuum oven at 80 °C for 2 h to remove air bubbles. Next, it was demolded after curing for 24 h at room temperature, and the obtained materials were denoted as E-(P-M X%), where X was the amount of PPG and MDI.

For comparison, PPG and MDI in the above system were replaced with the as-synthesized PUP, and the other conditions were the same as the above procedure, leading to the PUP-modified EP with 0, 10, 20 25 and 30 wt %, which is designated as E-(PUP X%). The specific steps of sample preparation were shown in Figure 1.

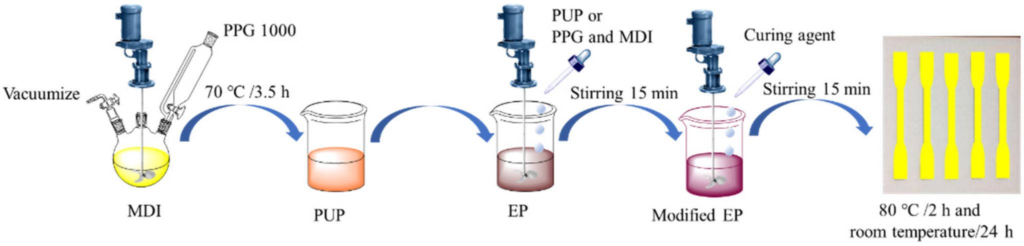


Figure 1. Preparation of samples.

2.4. Testing Methods

The VERTEX 70 (Brook, Germany) was used for the Fourier transform infrared spectroscopy (FT-IR) to test the sample structure with IR spectra from 400 to 4000 cm^{-1}.

The viscosity test of the sample was carried out according to GB/T 2974-2013, using the NDJ-1F rotational viscometer of Shanghai Changji Geological Instrument Co., Ltd., the rotor model was no. 29, and the speed was 10 r/min. The time from when the sample was measured to when the viscosity reached 60,000 mpa·s was selected as the initial setting time. We took the average value of three parallel experiments for each sample.

The tensile strength and elongation at break were tested on the FR-100C electronic universal testing machine (Farui, China) according to the GB/T 2567-2008 standard, and the tensile rate was 2 mm/min until the samples broke. The values of tensile strength and elongation at break were the average values of 3 samples. The tensile strength of the sample was calculated as Equation (1):

$$\sigma_t = \frac{F}{b \times h} \quad (1)$$

In the formula, σt is the tensile strength of the sample (MPa); F is the maximum load that the sample bears (N); b is the width of the sample (mm); h is the thickness of the sample (mm).

The elongation at break of the sample was calculated Equation (2):

$$e = \frac{\Delta L}{L_0} \times 100\% \quad (2)$$

where e is the elongation at break; L_0 is the gauge length of the sample (mm); ΔL is the gauge length elongation at break (mm).

Additionally, the tensile strength and elongation at break were tested on the FR-100C electronic universal testing machine (Farui, China) according to the GB/T 2567-2008 standard. Thermal stability was monitored on an STA 7300 (Hitachi, Japan) from room temperature to 600 °C, with heating rates of 5, 10, 15, 20 and 25 °C/min under a nitrogen atmosphere.

2.5. Kinetic Analysis of Thermal Decomposition

The thermal degradation process of EP can be expressed as Equation (3) when only considering whole chemical changes:

$$A(s) \rightarrow B(s) + C(g) \quad (3)$$

The conversion rate is defined as Equation (4):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_1} \quad (4)$$

where m_0 and m_1 are the initial mass of the sample and the final mass after reaction, respectively, and m_t represents the mass of the sample at time t.

The decomposition rate $d\alpha/dt$ is a function of the conversion rate α and temperature T, as Equation (5):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{5}$$

where k is the reaction rate constant. This term is a function of temperature T and can be expressed by the Arrhenius formula, as Equation (6):

$$k = A\exp(-\frac{E_a}{RT}) \tag{6}$$

where A is the frequency factor (s^{-1}), E_a is the activation energy of the decomposition reaction (KJ mol^{-1}), R is the general gas constant (R = 8.314 J mol^{-1} K^{-1}), and T is the reaction temperature (K).

Substituting Equations (6) and (5), we obtain Equation (7):

$$\frac{d\alpha}{dt} = A\exp(-\frac{E_a}{RT})f(\alpha) \tag{7}$$

For a constant heat rate $\beta = dT/dt$ thermal degradation system, the kinetic parameters can be obtained from the overall rate equation, as Equation (8):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-\frac{E_a}{RT})f(\alpha) \tag{8}$$

Several methods of calculating kinetic parameters can be obtained through various deductions of Equation (8). In this paper, we calculated the kinetic parameters of the modified EP by adopting the classic Kissinger (Equation (9)) and Flynn–Wall–Ozawa (Equation (10)) equations [28,29]. The advantage of the Kissinger method is that *Ea* can be obtained without understanding the thermal degradation reaction mechanism. Moreover, the Flynn–Wall–Ozawa (F–W–O) method is also known as the integral method, and it is very suitable for explaining the kinetic parameters under complex thermal degradation reactions.

$$\ln(\frac{\beta}{T_p^2}) = -\frac{E_a}{RT_p} + \ln\frac{AR}{E_a} \tag{9}$$

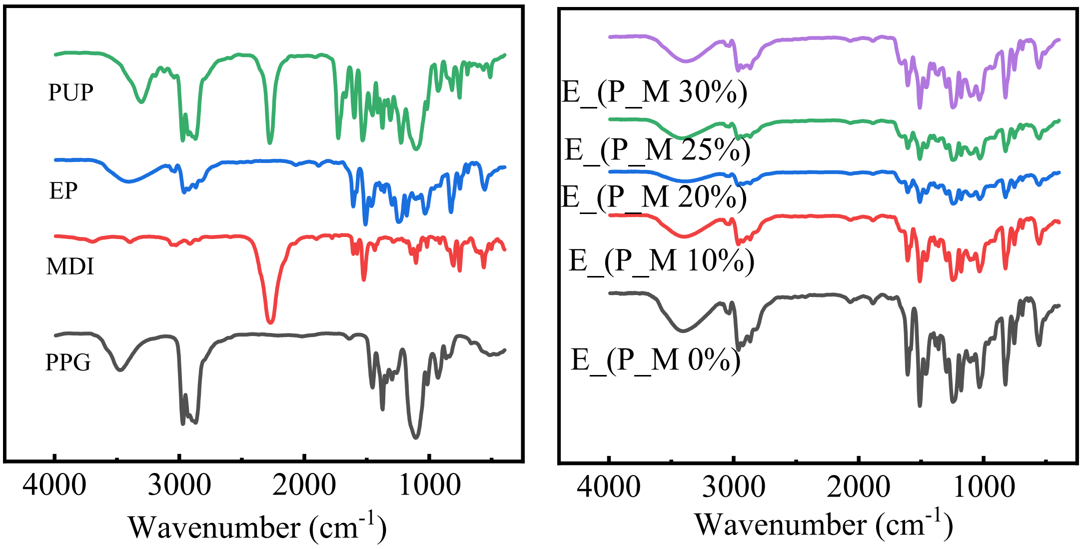
$$\ln(\beta) = \lg\frac{AE_a}{RG(\alpha)} - 2.315 - 0.4567\frac{E_a}{RT} \tag{10}$$

3. Results and Discussion

3.1. FT-IR of P-M-Modified Epoxy Resin

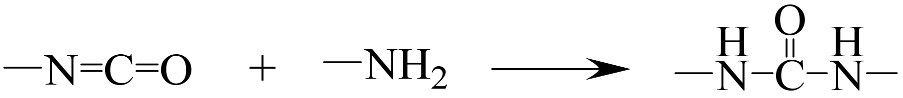
Figure 2 presents the FT-IR spectra of modifying agents and E-(P-M X%). The characteristic peaks at 3400 and 913 cm^{-1} are stretching vibrations of the hydroxyl and epoxy groups in the EP, respectively, and peaks at 2271 and 1523 cm^{-1} are stretching vibrations of the N=C=O groups and the benzene rings in the MDI. The vibrational peaks of C–O–C and –OH in the PPG are at 1108 and 3475 cm^{-1}, respectively. In the PUP, the characteristic peaks at 2271 and 1735 cm^{-1} are NCO and urethane groups, respectively.

In the infrared spectra of E-(P-M X%), it can be clearly seen that the N=C=O characteristic peak near 2270 cm^{-1} in the MDI disappears, and a new characteristic peak that belongs to C=O in carbamate appears near 1730 cm^{-1}. The disappearance of the N=C=O groups may be due to the reaction with a curing agent containing more reactive amino groups (Equation (11)). The IR results prove that during the E-(P-M X%), PPG and MDI reacted to form carbamate, and a part of the MDI was consumed by the curing agent.



(**a**) (**b**)

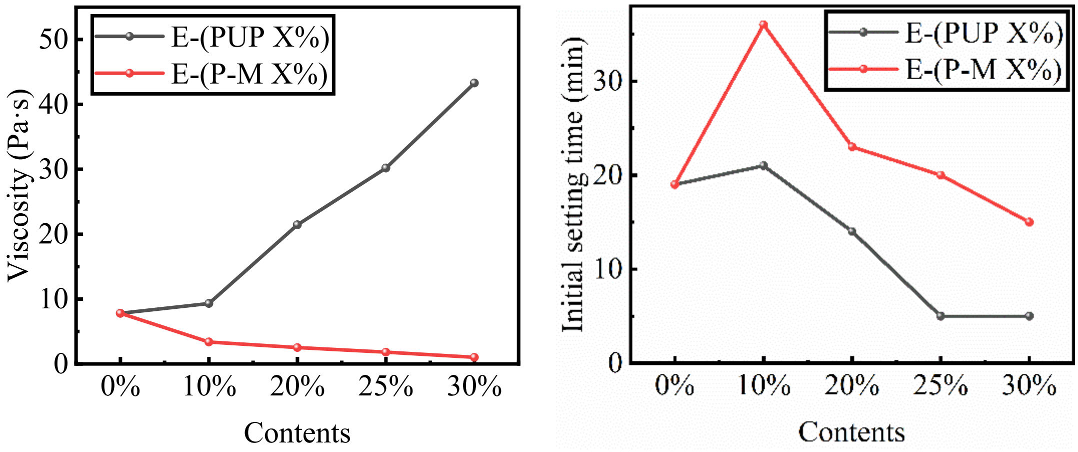
Figure 2. FT-IR spectra of modifying agents and E-(P-M X%). (**a**) Modifiers and pure EP, (**b**) Modified Epoxy Resin.



$$-N{=}C{=}O \quad + \quad -NH_2 \longrightarrow -\overset{H}{N}-\overset{\overset{O}{\|}}{C}-\overset{H}{N}- \qquad (11)$$

3.2. Properties of Modified Epoxy Resin

The viscosity of EP has a significant effect on its processing ability and the properties of cured samples. The lower viscosity facilitates operability during later construction [30]. Figure 3 shows the viscosity and initial setting time results for the PUP-M and P-M samples. In the viscosity test, two extremes can be seen, the viscosity of the PUP-M sample increases sharply with the increase of the amount of this modifier, because the prepared PUP itself has a higher viscosity due to its larger molecular weight. The epoxy resin itself has a large viscosity base, so it shows a viscosity trend, while the PPG and MDI monomers as modifiers are just the opposite, because PPG and MDI as monomers have a very low viscosity. Adding it to the epoxy resin acts as a diluent to a certain extent, so the higher the amount of monomer added, the lower the viscosity of the system.



(**a**) (**b**)

Figure 3. Viscosity and initial setting time of the modified EP. (**a**) Viscosity, (**b**) initial setting time.

Notably, the initial setting time of the two modified EPs first increases and then decreases, but the reason for this trend is different. With the increase in P-M content, the active NCO group increases, the reaction becomes more intense, and the viscosity rises faster, so the initial setting time is short, while the initial viscosity of the PUP modification system increases with the rise in PUP content. When the PUP content is 30%, the initial viscosity of the system is 43,274 mPa·s, which dramatically shortens the time for the system's viscosity to reach 60,000 mPa·s (i.e., the initial setting time). At the same dosage, the initial setting time of the P-M modification is always slightly higher than that of the PUP. In practice, this means that the P-M modification provides a longer operational time.

In conclusion, the viscosity of the system can be greatly reduced during the modification of P-M, and the operating time estimated from the initial setting time can also be adjusted by the amount of P-M added.

Figure 4 represents the tensile strength and elongation at break of the PUP-M and P-M samples. The tensile strength showed a decreasing trend in both modified samples, but the mechanism was different. In the process of the P-M modification, an infrared analysis revealed that the MDI also consumed part of the curing agent 421 when the PPG reacted to generate PUP, which resulted in the incomplete curing of the EP itself when the amount of modifier was too high. However, a decrease in tensile strength of the PUP-M samples has been reported in the literature due to the formation of alkanone structures by the epoxy groups in PUP and EP with NCO end groups, [31] which led to the decrease in tensile strength.

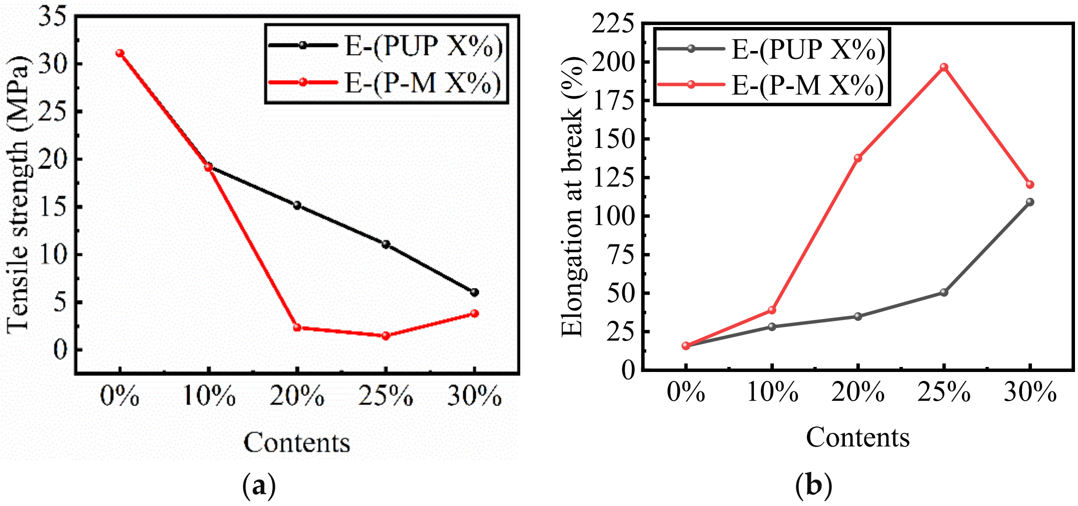


Figure 4. Tensile strength and elongation at break of the modified EP. (**a**) Tensile strength, (**b**) elongation at break.

The P-M modification showed a larger elongation at break, and for (EP-P-M 25%), the elongation at break achieved a maximum of 196.56%. It can be clearly seen that both modification methods can improve the elongation at the break of EP to a certain extent. This is because both modifiers contain the generated PUP, and PPG as a flexible segment in PUP can improve the sample's flexibility, which has been reported in many papers [32].

The elongation at the break of P-M was higher than that of PUP. During the modification process of P-M, the curing agent 421 consumed a part of the MDI, which caused free PPG to form a continuous collision polymer due to the dehydration and condensation of a gunshot during the curing process of EP. The result of the infrared analysis confirmed this conjecture. Obviously, the chain polymer of free PPG dehydration–condensation in the system is beneficial to the flexibility of the system. With the increase of P-M content, the late resin hardly has any strength, so the elongation at break shows a decreasing trend at that time.

3.3. Thermal Properties

Figure 5 displays the TG (weight loss) and DTG (weight derivative) curves of EP-(P-M X%) and EP-(PUP X%). The initial decomposition temperature (Ti) of unmodified EP is 325.96 °C, and the weight loss reached a maximum at 368.83 °C. EP-(PUP X%) slightly reduces the initial decomposition temperature of EP, while EP-(P-M X%) obviously has a higher Ti than EP-(PUP X%), which indicates that EP-(P-M X%) modification makes the polymer have higher crosslinking density, which is attributed to the MDI in the modification process not only reacted with PPG to form PUP but also grafted into EP through the reaction with curing agent. EP-(PUP X%) exhibits lower thermal stability mainly due to the presence of more relatively weak urethane linkages in the system [33]. However, this phenomenon of reduced thermal stability was not found in the P-M modification process, because in addition to the grafting of PUP to EP, there was also a part of MDI to EP to form oxazolidinones.

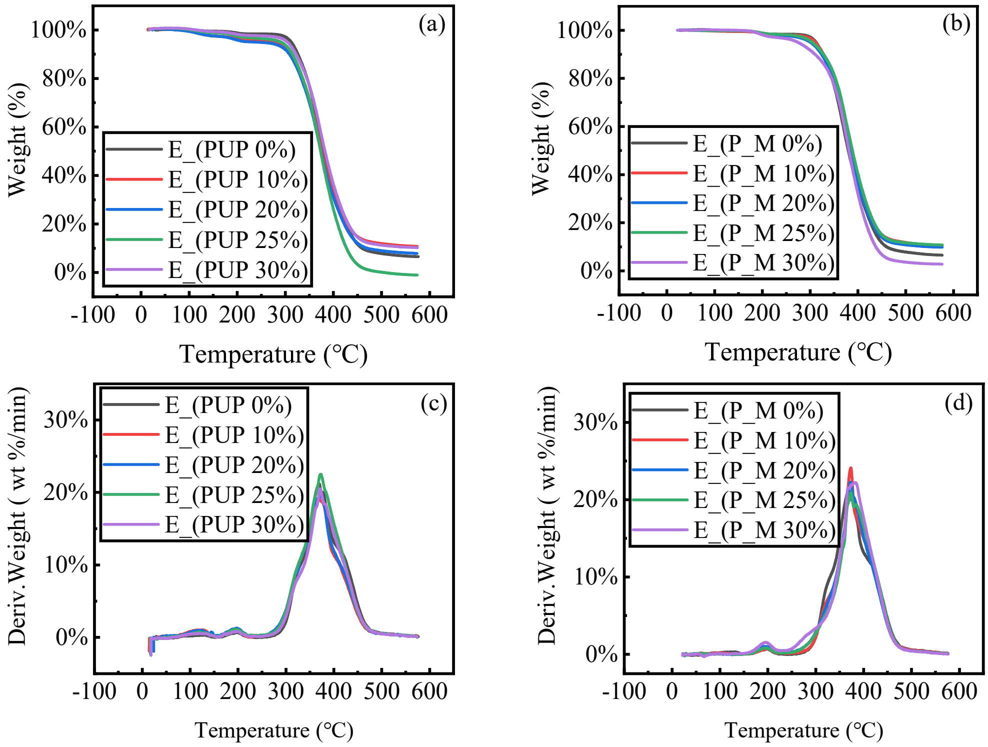


Figure 5. TG and DTG of the modified EP. (**a**) TG of PUP modified EP, (**b**) TG of P-M modified EP, (**c**) DTG of PUP modified EP, (**d**) DTG of P-M modified EP.

3.4. Thermal Decomposition Kinetic

Kissinger Method

For the Kissinger method, Ea was determined by the slope of the linear fit of ln (β/Tp2) to 1/Tp with varying P-M contents (Figure 6). The thermal degradation kinetic parameters are listed in Table 1. Consequently, there was a linear relationship for different P-M contents, signifying the reliability of the Kissinger method under this system. The Ea value of the unmodified EP was 58.97 KJ·mol^{-1}; E-(P-M 20%) and E-(P-M 25%) increased by 11.32 KJ·mol^{-1} and 6.47 KJ·mol^{-1}, respectively, compared to the unmodified EP, suggesting that the material needs to absorb more heat during thermal degradation, i.e., it has a higher thermal stability. The Ea value calculated by Kissinger method was basically consistent with the Ti results shown by thermal stability, which both proved that the EP-(P-M X%) had a higher thermal stability. When Ea/RT < 10, the value of Ea calculated by the Kissinger method is highly reliable (i.e., the error is less than 5%) [34].

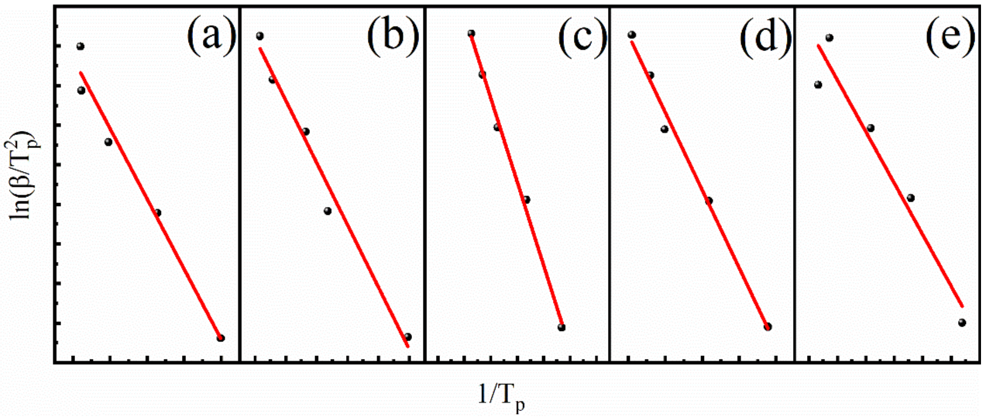


Figure 6. Relationship between ln (β/Tp) and 1/Tp in thermal degradation. (**a**) EP-(P-M 0%), (**b**) EP-(P-M 10%), (**c**) EP-(P-M 20%), (**d**) EP-(P-M 25%), (**e**) EP-(P-M 30%).

Table 1. The thermal degradation kinetic parameters for the Kissinger method.

P-M Contents	R^2	Slope	Intercept	E_a (KJ·mol^{-1})
EP-(P-M 0%)	0.9765	−7093.42	10.49	58.97
EP-(P-M 10%)	0.9822	−5933.12	7.07	49.33
EP-(P-M 20%)	0.9960	−8454.20	13.86	70.29
EP-(P-M 25%)	0.9920	−7870.63	12.21	65.44
EP-(P-M 30%)	0.9392	−5211.02	4.94	43.32

For the F–W–O method, Ea was determined by the slope of the linear fit of lg β to $1/T_p$ with different P-M contents (Figure 7). Unlike the Kissinger method, E_a of the thermal degradation system at each moment can be calculated directly. In this paper, E_a was calculated with a 10 to 80% conversion rate (increments of 10%), and the results are shown in Table 2. E_a was highly dependent on the conversion rate due to the multistage reactivity of the modified EP during thermal degradation [26]. Moreover, Ea gradually increased from low to high conversion because the degradation reactions occurred at various stages in the thermal degradation process. The initial stage was primarily involved in the evaporation of water, so Ea was low.

Table 2. F–W–O method to calculate the thermal degradation kinetic parameters.

α	Ea (KJ·mol^{-1})				
	EP-(P-M 0%)	**EP-(P-M 10%)**	**EP-(P-M 20%)**	**EP-(P-M 25%)**	**EP-(P-M 30%)**
10%	42.92	49.09	50.81	41.90	34.44
20%	51.34	51.43	57.83	56.73	52.05
30%	56.03	52.45	57.85	59.37	55.58
40%	57.58	53.84	58.06	61.46	57.11
50%	58.48	55.79	58.64	58.58	57.38
60%	59.97	56.61	58.89	58.01	57.81
70%	62.54	59.51	62.06	60.08	59.93
80%	67.34	63.51	66.21	63.24	63.32
Average	57.03	55.28	58.79	57.42	54.70

The Ea obtained by the F–W–O method did not differ much from that of the Kissinger method because the Kissinger method does not involve the conversion rate during the degradation process. The thermal degradation kinetic parameters obtained by the two methods proved that the P-M modification did not significantly reduce the material's thermal stability like the PUP modification.

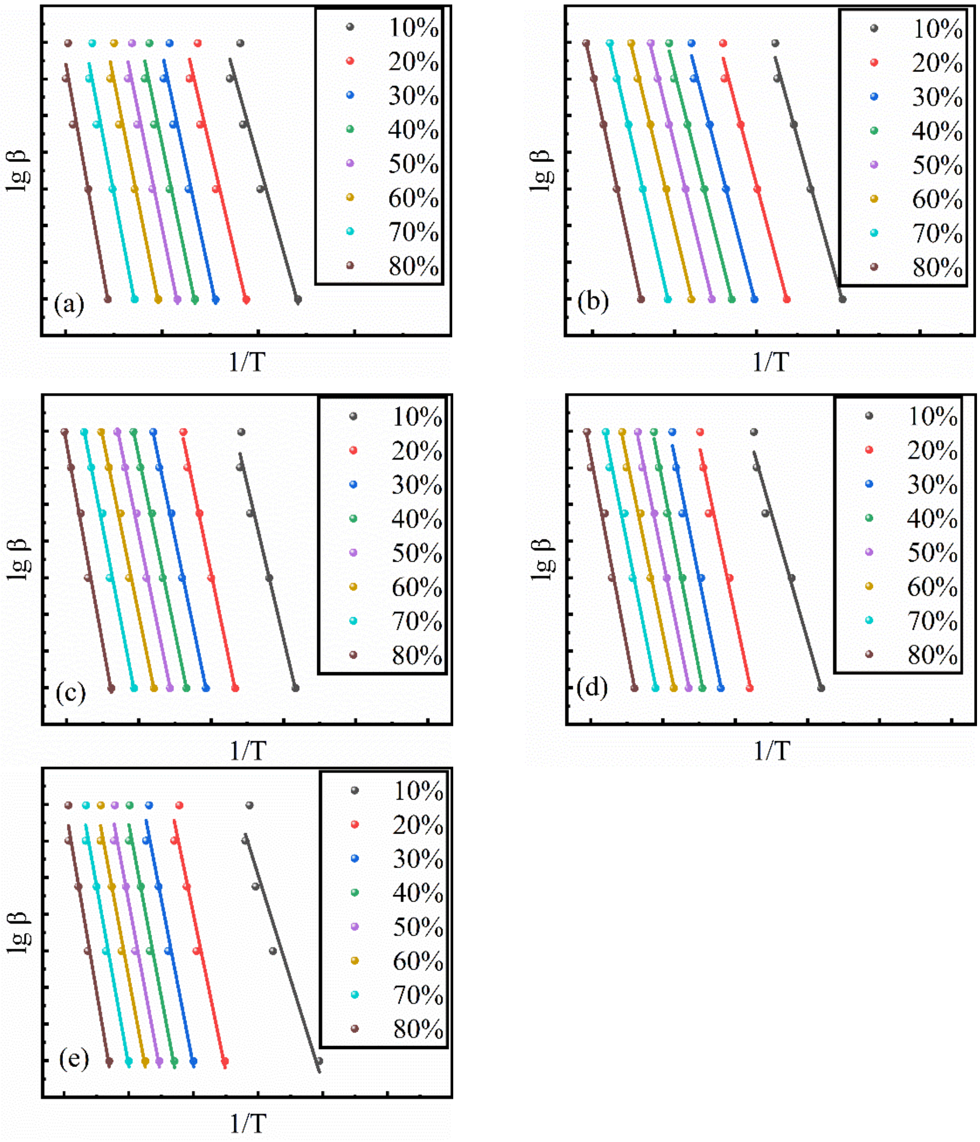


Figure 7. Relationship between lgβ and 1/Tp in thermal degradation. (**a**) EP-(P-M 0%), (**b**) EP-(P-M 10%), (**c**) EP-(P-M 20%), (**d**) EP-(P-M 25%), (**e**) EP-(P-M 30%).

4. Conclusions and Future Work

This study laid a theoretical foundation for the facile preparation of EP with good flexibility. The modification of EP with MDI and PPG was used to compare with conventional PUP modification. Due to the low viscosity of the added monomer, which acts as a diluent in the system, the viscosity was obviously reduced from 7820 mPa·S to 1034 mPa·S. Interestingly, as the monomer content increased, the highly reactive NCO group increased. The increase of the group made the viscosity of the system rise sharply in the later stage. The one-step modification of EP by MDI and PPG greatly improved the flexibility, and a maximum value of 196.56% was obtained when the dosage was 25%. This indicated that both modification methods reduced the tensile strength. In addition, the thermogravimetric test and thermal degradation kinetics results both proved that the one-step modified EP had better thermal stability.

This kind of P-M-EP with a good flexibility has great application prospects in industry, such as road repair materials and concrete crack repair. Of course, the application performance in practical engineering, such as the ability to repair cracks, will be systematically reported in follow-up studies.

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