Preparation of 2-ethyl-4-methylimidazole derivatives as latent curing agents and their application in curing epoxy resin

Dingfeng Lei, Wenshi Ma, Linfeng Wang, Dongqiao Zhang
College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China
Correspondence to: W. Ma (E-mail: mcwshma@scut.edu.cn)

ABSTRACT: Three kinds of 2-ethyl-4-methylimidazole (EMI) derivatives (*N*-acetyl EMI, *N*-benzoyl EMI, and *N*-benzenesulfonyl EMI) were synthesized through the reaction of EMI with acetyl chloride, benzoyl chloride, and benzenesulfonyl chloride, respectively. And the structure was confirmed by Fourier transform infrared spectroscopy (FTIR) and [1]H-nuclear magnetic resonance spectroscopy (^{1}H NMR) spectra. Furthermore, the synthesized EMI derivatives were applied in diglycidyl ether of bisphenol A epoxy resin (DGEBA) as latent curing agent. Differential scanning calorimeter (DSC) was used to analyze the curing behavior of DGEBA/EMI derivative systems, indicating DGEBA could be efficiently cured by the EMI derivatives at 110~160°C, and the corresponding curing activation energy ranged from 71 to 86 kJ/mol. Viscosity data proves that the storage life of DGEBA with *N*-acetyl EMI (NAEMI), *N*-benzoyl EMI (NBEMI), and *N*-benzenesulfonyl EMI (NBSEMI) at room temperature was 38 d, 50 d, and 80 d, and that at 10°C was 90 d, 115 d, and 170 d, respectively. Besides, thermogravimetry (TG), izod impact strength (IIS), and tensile shear strength (TSS) were tested to characterize the thermal stability and mechanical properties of DGEBA cured by EMI derivatives. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42563.
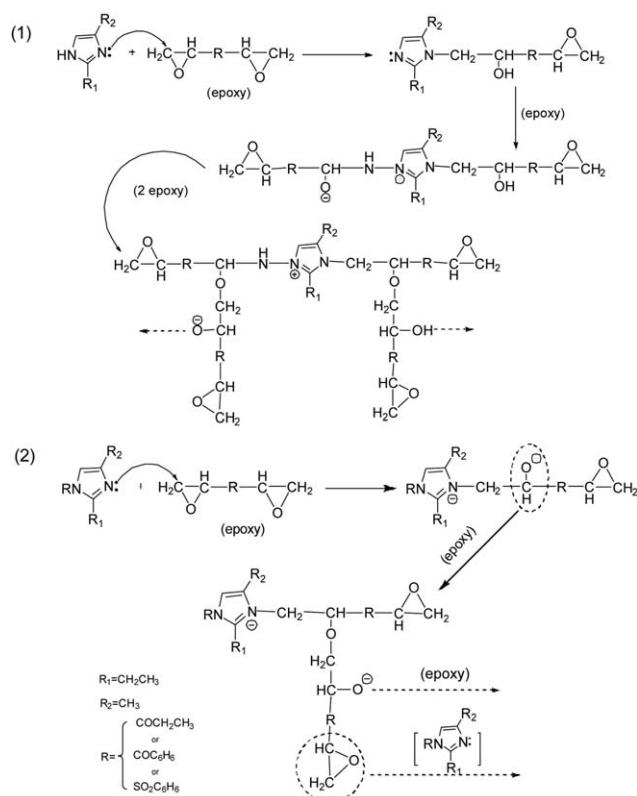
INTRODUCTION

Imidazoles, which are penta cyclic compounds containing both secondary amine and imine, have been widely used as curing agent in a variety of epoxy resins, due to the high curing efficiency, intermediate curing temperature of imidazole/epoxy resin system and the excellent mechanical properties of the curing product.[1,2] It is previously reported that the curing mechanism of imidazoles/epoxy resins system is different from other amine curing systems.[3–5] The attack of the imino nitrogen on the terminal carbon atom of epoxy group unfolded the ring structure and generated adduct between imidazole and epoxy resin at the same time. Then the adduct reacted with another epoxy group to form ionic compound, which served as the initiator of the curing reaction,[6] as shown in Scheme 1 (1). This distinctive curing mechanism makes imidazoles more efficient than other curing agents when applied to epoxy resin.[7]

However, the storage stability of imidazoles/epoxy system is not satisfactory at room temperature, which restricts its application to one-pot curing system.[8,9] Considerable researches have been conducted on improving the storage stability of imidazoles as curing agent. *N*-substituted imidazole derivatives as curing agents were synthesized by some researchers, and the inductive effect and steric hindrance of substituent group could prevent the imi-
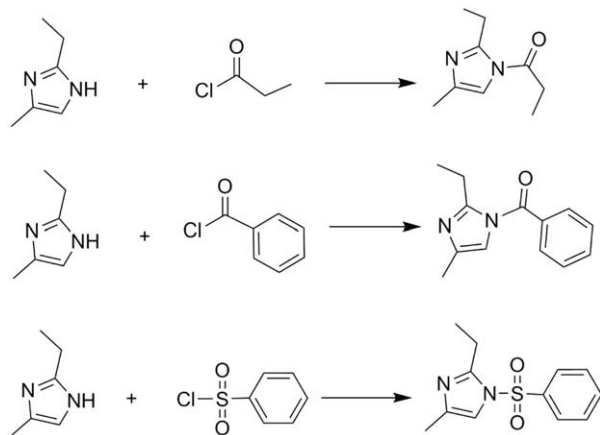
dazoles from reacting with epoxy resin at room temperature.[8–10] Other researchers restricted the activity of imidazoles by interacting with metal salts to form the metal-imidazole complexes.[11–13] The metal could be Mn, Co, Ni, Cu, Zn, Ag, and lanthanide elements. When on heating, the imidazole molecule could be released from complex and regain the curing capacity. Encapsulation is another method to modify the storage stability of imidazoles, by which a wall was built around the imidazole molecules, which would not react with epoxy group until be heated. The material of wall could be polycaprolactone, urea-formaldehyde, and ethylene glycol.[14–17] Unfortunately, the study have not obtained a perfect latent curing agent yet, for the *N*-substitution and encapsulation did not improve the latency of imidazole curing agent to a satisfactory level, and the compatibility between metal-imidazole complexes and epoxy resins was poor.

2-ethyl-4-methylimidazole (EMI) is one of the most common imidazole-based curing agents. Here, we report an approach to enhance the storage stability of EMI in epoxy resin. Both Heise and Dearlove proved that 1-substituted imidazoles initiated curing reaction through the nucleophilic attack on epoxy group, which led to the etherification reaction,[4,5] as shown in Scheme 1, therefore nucleophilicity plays a key role in the curing process, and the storage stability of EMI may be improved

Scheme 1. Proposed curing mechanism of epoxy cured by EMI and EMI derivatives.
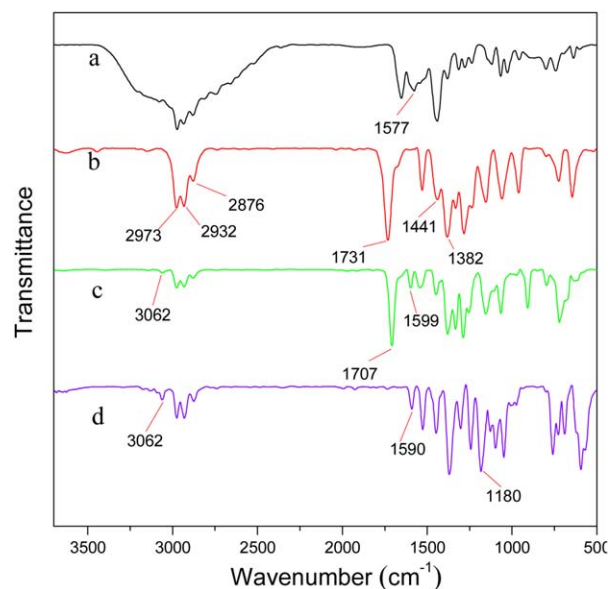

Figure 1. FTIR spectra of (a) EMI, (b) NAEMI, (c) NBEMI, and (d) NBSEMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

if the nucleophilicity is weakened. In this article, 1-substituted EMI derivatives were synthesized through the reaction between EMI and corresponding acyl chloride compounds, including N-acetyl EMI (NAEMI), N-benzoyl EMI (NBEMI), and N-benzenesulfonyl EMI (NBSEMI), as shown in Scheme 2. Acetyl chloride, benzoyl chloride, and benzenesulfonyl chloride were chose as reactants to synthesize 1-substituted EMI, for the electron withdrawing property of acyl may weaken the nucleophilicity of EMI, and then deprive the reactivity of EMI at room temperature. Besides, the reaction between acyl chloride and EMI is easy to perform and the by-products are easy to remove. Then the curing behavior, storage stability, thermal, and mechanical properties of the DGEBA/EMI derivative systems was studied.

EXPERMENTAL

Materials

EMI (viscosity: 4∼8 Pa s), benzenesulfonyl chloride, and diglycidyl ether of bisphenol A epoxy resin (DGEBA) were purchased from Tianjin Chemicals, Tianjin Fuchen Chemicals, and China Petroleum Chemicals, respectively. Both acetyl chloride and benzoyl chloride were purchased from Chinasun Specialty Chemicals. Triethylamine, tetrahydrofuran (THF), and dichloromethane were
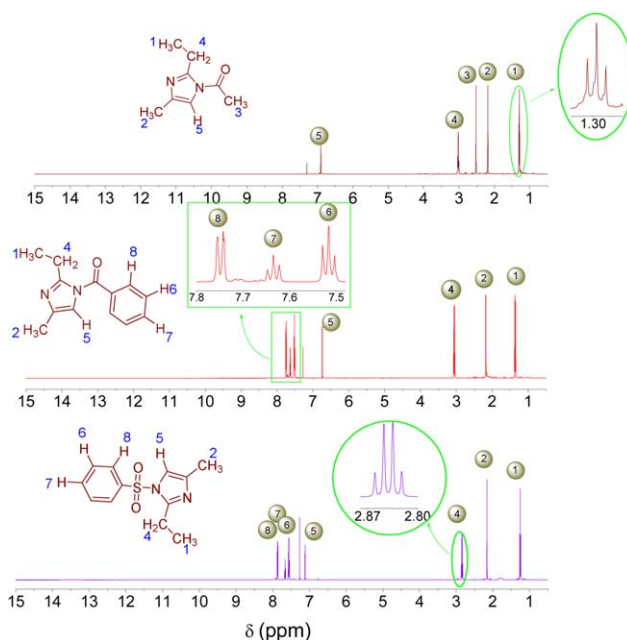

Scheme 2. Synthesis routes of EMI derivatives.

Figure 2. ^{1}H NMR spectra of NAEMI, NBEMI, and NBSEMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Chemical Shifts (PPM) of ^{1}H NMR Spectra of EMI Derivatives

EMI derivatives	H1	H2	H3	H4	H5	H6	H7	H8
NAEMI	1.30/t	2.18/s	2.52/s	3.03/q	6.91/s	–	–	–
NBEMI	1.35/t	2.18/s	–	3.07/q	6.74/s	7.52/t	7.632/t	7.75/d
NBSEMI	1.26/t	2.16/s	–	2.85/q	7.12/s	7.562/t	7.662/t	7.87/d

supplied by Rich Joint Chemicals. All chemicals used in these experiments were used as received without further purification except THF and dichloromethane dried by molecular sieve.

Synthesis

Synthesis of NAEMI. EMI (5.02 g, 0.05 mol) and triethylamine (6.07 g, 0.06 mol) were dissolved in THF (100 mL), and another solution of acetyl chloride (3.93 g, 0.05 mol) in THF (50 mL) was added dropwise under N_2 at 6~8°C in 1 h, then the solution was stirred at room temperature for 8 h. The precipitated amine hydrochloride and solvent were removed by vacuum filtration and rotary evaporation, respectively. 6.54 g of viscous liquid product was obtained.

Synthesis of NBEMI. EMI (6.61 g, 0.06 mol) and triethylamine (7.28 g, 0.072 mol) were dissolved in dichloromethane (100 mL), and another solution of benzoyl chloride (8.43 g, 0.06 mol) in dichloromethane (50 mL) was added dropwise under N_2 at 6~8°C in 1 h, then the solution was stirred at room temperature for 12 h. The reaction mixture was washed by water for several times and the organic solvent was removed by rotary evaporation. 10.5 g of viscous liquid product was obtained.

Synthesis of NBSEMI. The preparation of NBSEMI was in the same way as that of NBEMI except that the benzenesulfonyl chloride was added at room temperature. And buff crystal product was obtained.

Preparation of DGEBA/EMI Derivative Systems

For the liquid curing agents, EMI, NAEMI, and NBEMI were added into DGEBA at different concentration, respectively. Sub-sequently, the systems were stirred by magnetic stirrer for 30 min and homogeneous systems were obtained. For the crystal curing agent, NBSEMI was dispersed in DGEBA at different concentration by milling, and the crystal particles dissolved in DGEBA slowly at room temperature after 24 h.

Characterization

FTIR spectra were obtained with Analect RFX-65 Fourier Transform infrared spectrometer, scanning from 4000 to 400 cm^{-1}. ^{1}H-NMR spectra were carried out with AVANCE Digital 400MHz spectrometer in deuterated chloroform solvent. DSC was performed on NETZSCH DSC 204 F1 device heating from 20 to 350°C at different heating rates under N_2. Viscosity was acquired on NDJ-1 rotary viscometer to analyze the storage stability at room temperature. TG analysis was performed on NETZSCH TG 209 F1 instrument at a heating rate of 20°C/min from 30 to 700°C under N_2. Impact tester (XJW-2.25) was used to test the unnotched impact strength of the curing specimen. Adhesive property of the DGEBA/EMI derivative systems to aluminum, steel, and copper was measured on UT-2080 electronic universal material testing machine according to ISO 4587:2003.

RESULTS AND DISCUSSION

Structure of the EMI Derivatives

The FTIR spectra of EMI and the corresponding derivatives are shown in Figure 1. The absorption in 3420~2430 cm^{-1} and 1577 cm^{-1} attributed to N–H linkages[18,19] appears in the spectrum of EMI rather than that of the EMI derivatives, suggesting N–H bond from EMI reacted with the acyl chloride from the modifier. NAEMI and NBEMI show characteristic absorption of
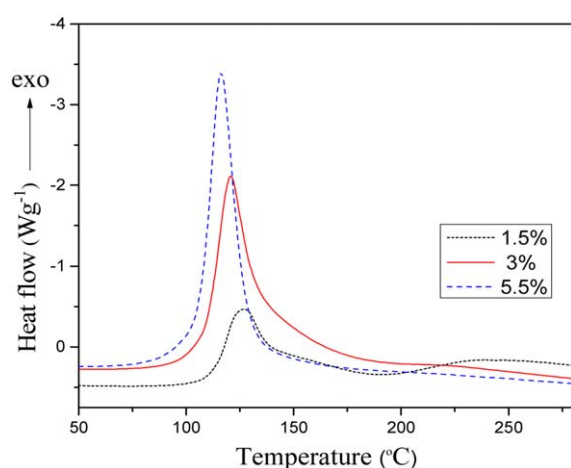

Figure 3. Dynamic DSC curves of the DGEBA/EMI system with the concentration of EMI at 1.5%, 3.0%, and 5.5%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
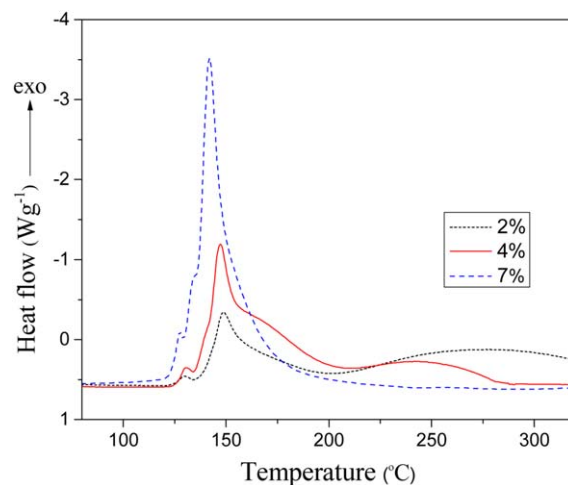

Figure 4. Dynamic DSC curves of the DGEBA/NAEMI system with the concentration of NAEMI at 2 wt %, 4 wt %, and 7 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
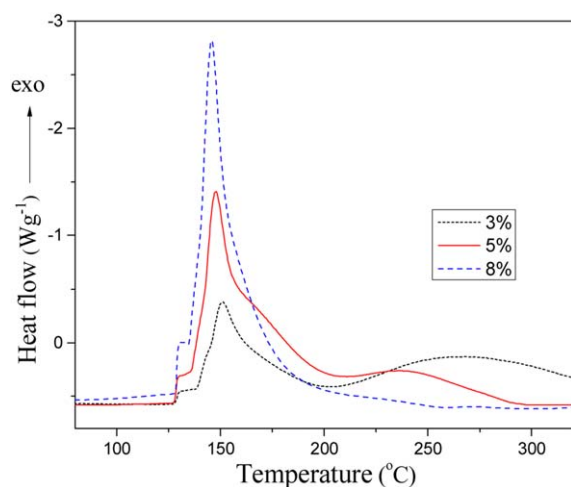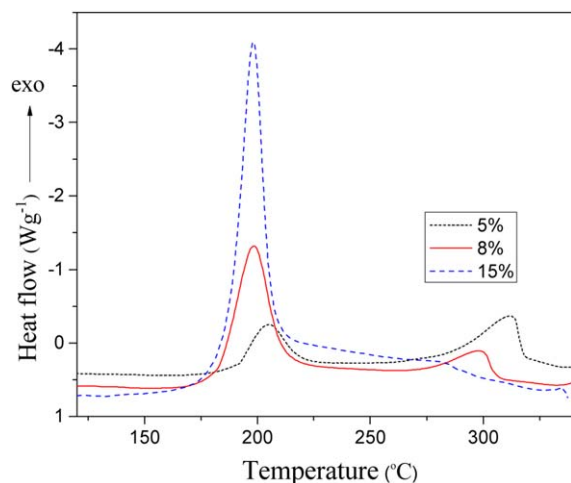
Figure 5. Dynamic DSC curves of the DGEBA/NBEMI system with the concentration of NBEMI at 3%, 5%, and 8%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

C=O at 1731 cm^{-1} and 1707 cm^{-1}, respectively. The peaks at 1600∼1590 cm^{-1} and 3062 cm^{-1} for NBEMI and NBSEMI are responsible for the vibration of benzene skeleton and Ph–H. The NBSEMI also exhibits an absorption peak at 1180 cm^{-1} corresponding to the vibration of S–N. The absorption at about 1440 cm^{-1} and 1380 cm^{-1} of the four spectrograms are attributed to C–N bond.[20] Peaks at 2980∼2840 cm^{-1} are attributed to the C–H stretching of the imidazole ring and the aliphatic chain.[21] These peaks confirm the reaction between the secondary amine of EMI and the acyl chloride groups of N-acetyl chloride, N-benzoyl chloride, and N-benzenesulfonyl chloride as shown in Scheme 2.

^{1}H NMR spectra shown in Figure 2 further confirm the structure of the EMI derivatives, and the corresponding data is listed in Table I,[22–25] in which the unit of chemical shifts (δ) is part per million (ppm), and the letter s, d, t, and q in Table I refer to singlet, doublet, triplet, and quartet. NAEMI shows an extra peak of –CO–CH compared with EMI, and N-benzoyl EMI and

NBSEMI show extra peaks of aromatic hydrogen at 7.5∼7.9. The signal at about 13.6 corresponding to the N–H on imidazole[26] does not appear in the three spectra. The peak at 7.26 is attributed to the absorption of deuterated chloroform solvent.

Analysis of Curing Behavior

The dynamic DSC curves of DGEBA with EMI, NAEMI, NBEMI, and NBSEMI at various concentrations heated at 10°C/min are given in Figures 3–6, respectively. And the corresponding exothermic parameters are shown in Table II. Considering the difference among the curing efficiency of each EMI derivatives, the DSC of the four systems was characterized at different concentration to present the exothermic properties more efficiently. A sharp exothermic peak attributed to curing reaction can be observed in DSC curves of each system, and there is a small shoulder at the start of the main peak for the DGEBA cured by NAEMI and NBEMI. Heise et al.[27–30] owed this small exothermic peak to the formation of adducts between imidazoles and epoxy resin, which is the initial step of curing process.[3–5] However, this small shoulder peak does not appear on the curves of DGEBA/EMI system in Figure 3 and DGEBA/NBSEMI in Figure 6.

The concentration of curing agents affected the shape of the DSC curves obviously. As shown in Figures 3–5, a broad exothermic peak appears at the temperature higher than 200°C when the concentration is relatively low, and the extra exothermic peak of DGEBA/NBSEMI system in Figure 6 is sharper and appears at higher temperature. Omrani et al.[6] attributed this extra peak to the reason that epoxy groups were not exhausted when the concentration of curing agent was small, and the remaining epoxy groups were available for further reaction. The relative area of the extra peak at high temperature decreases with the increasing of the curing agent concentration, and the extra peak does not appear when the concentration of NAEMI reaches to a certain extent, for the more epoxy groups consumed by curing agent, the less reaction occurring at high temperature.

Table II. Exothermic Properties of DGEBA Cured by EMI Derivatives at Different Concentration

Curing agents	Concentration (wt %)	Onset temperature (°C)	Peak temperature (°C)	ΔH_{tot} (J/g)
EMI	1.5	102.5	126.7	155.5
	3	84.8	120.6	297.3
	5.5	74.9	116.3	325
NAEMI	2	125.4	148.9	117
	4	124.1	146.0	256
	7	121.5	142.0	385
NBEMI	3	127.5	150.9	136
	5	127.2	147.8	298
	8	127.8	145.8	409
NBSEMI	5	174.6	204.8	78
	8	168.3	198.2	196
	15	156.4	197.9	316

Figure 6. Dynamic DSC curves of the DGEBA/NBSEMI system with the concentration of NBSEMI at 5%, 8%, and 15%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
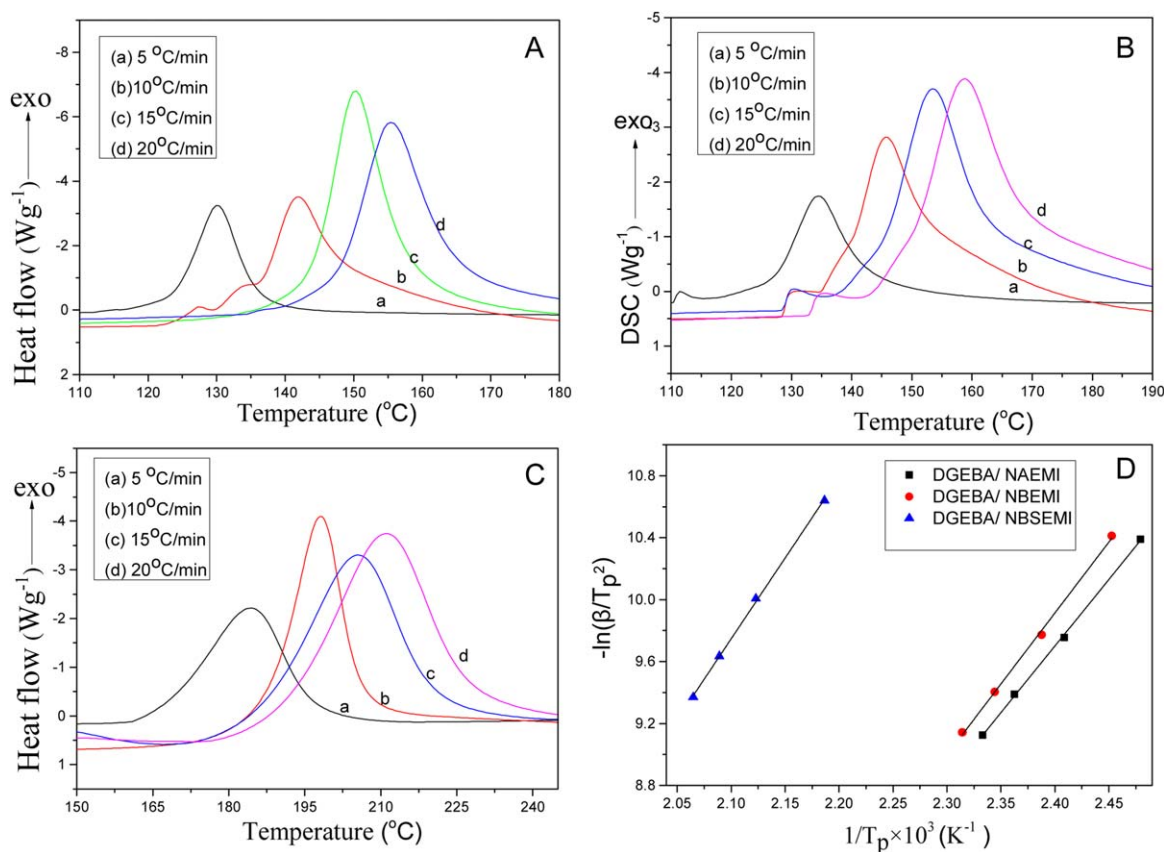
Figure 7. Dynamic DSC curves of the DGEBA/EMI derivatives system at heating rates of 5, 10, 15, and 20°C/min, (A) DGEBA/NAEMI, (B) DGEBA/NBEMI, (C) DGEBA/NBSEMI; (D) Plot for determination of the E_k and the A by Kissinger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Table II, with increasing the concentration of EMI derivatives, the curing systems release more heat and the exothermic peaks shift to lower temperature, because higher ratio of curing agent might leads to faster reaction.[31] The curing temperature of the DGEBA with EMI derivatives is higher than that with EMI, especially for DGEBA/NBSEMI system. Since the electron-withdrawing ability of sulfonyl is stronger than that of carbonyl, which was proved through comparing the dissociation constants of acetic acids with different substituent groups,[32] the EMI substituted by phenylsulfonyl owned weaker nucleophilicity than that substituted by acetyl and benzoyl, so more heat was needed to stimulate the curing reaction.

Weaker nucleophilicity means weaker activity and lower curing efficiency, so the total exothermic heat (ΔH_{tot}) of DGEBA/ NBSEMI system is less than that of other two systems,[10] and the ΔH_{tot} of DGEBA cured by EMI derivatives is obviously less than that cured by EMI when the concentration of curing agent is relatively low. When it comes to the increasing trend of ΔH_{tot} with the increasing of curing agent concentration, the amplification of DGEBA/EMI is much less than that of DGEBA/EMI derivative systems. That may be caused by the difference between the curing mechanisms of DGEBA/EMI and DGEBA/ EMI derivatives system, as shown in Scheme 1.

The dynamic DSC heating at 5, 10, 15, and 20°C/min was also measured to discuss the curing kinetic parameters of the DGEBA/EMI derivative systems, as shown in Figure 7(A–C), and the adopted concentration of NAEMI, NBEMI, and NBSEMI were 7 wt %, 8 wt %, and 15 wt %, respectively. Kissinger method[33] was adopted to calculate the activation energy

Table III. Curing Kinetic Parameters for the DGEBA/EMI Derivative Systems Derived from Kissinger Method

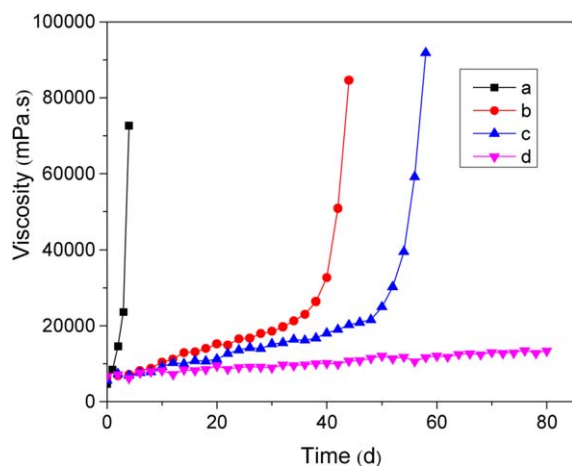| Curing agent	T_m (°C) of DSC curves at different β (°C/min)				Slope	Y-intercept	E_k (kJ/mol)	A (s^{-1})
	5	10	15	20				
NAEMI	130.2	142	150.2	155.5	8.60	−10.95	71.53	4.89×10^5
NBEMI	134.6	145.7	153.4	158.9	9.17	−12.08	76.20	1.62×10^6
NBSEMI	184.2	197.9	205.5	211.1	10.44	−12.17	86.77	2.63×10^6

Figure 8. Viscosity evolution of DGEBA with different curing agents at room temperature, (a) 2 wt % of EMI, (b) 3 wt % of NAEMI, (c) 3 wt % of NBEMI, and (d) 8 wt % of NBSEMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
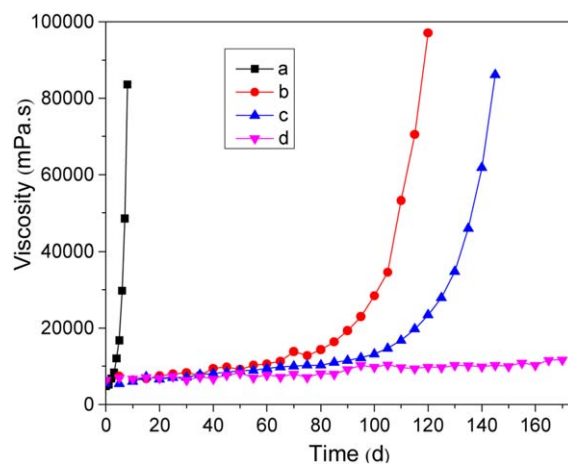
Figure 9. Viscosity evolution of DGEBA with different curing agents at 10°C, (a) 2 wt % of EMI, (b) 3 wt % of NAEMI, (c) 3 wt % of NBEMI, and (d) 8 wt % of NBSEMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(E_k) and frequency factor (A), which was based on the following equation:

$$-\ln\left(\frac{\beta}{T_m^2}\right) = \frac{Ek}{RTm} - \ln\frac{AR}{Ek} \tag{1}$$

where β is the heating rate (°C/min); T_m is the maximum exothermic peak temperature; A and R are Arrhenius constant and

ideal gas constant, respectively. Based on this equation, the curing activation energy (E_k) could be obtained from the slope of $-\ln (\beta/T_m^2)$ versus $1/T_m$ plot in Figure 7(D),[34] and A could be calculated from the y-intercept (I) by the following equation:[35]
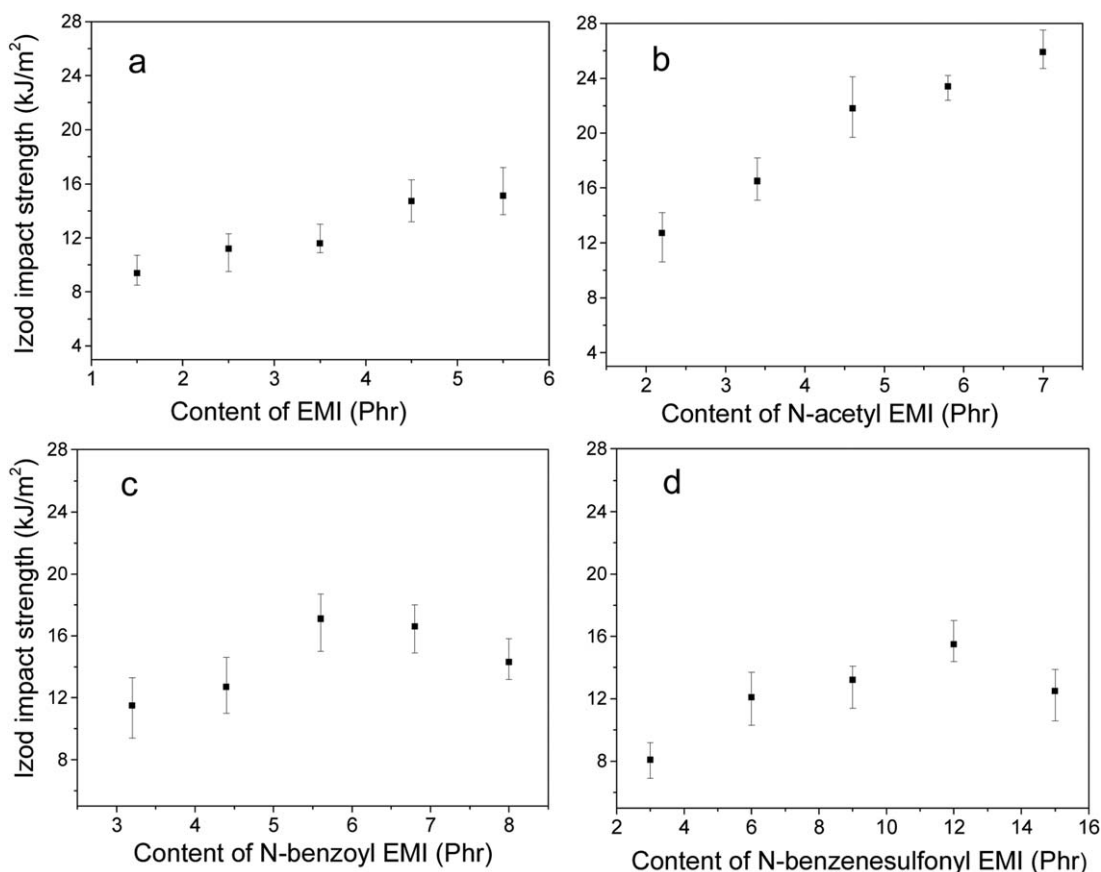
$$A = \frac{Ek}{Rexp(I)} \tag{2}$$

Figure 10. Izod impact strength of the epoxy resin cured by (c) EMI, (b) NAEMI, (c) NBEMI, and (d) NBSEMI.

Table IV. Tensile Shear Strength of the DGEBA/EMI Derivative Systems on Metals

Curing agent	Concentration (wt %)	Tensile shear strength/Mpa		
		Aluminum	Steel	Copper
EMI	1.5	6.7	12.3	13.2
	3	9.9	10.2	9.1
	5.5	7.6	15.8	10.8
DGEBA/NAEMI	2	6.3	10.1	8.8
	4	10.3	9.5	12.4
	7	8.6	14.1	16.4
DGEBA/NBEMI	3	7.7	11.9	9.2
	5	8.2	10.7	12.4
	8	10.3	15.4	12.1
DGEBA/NBSEMI	5	7.9	15.9	9.8
	8	11.2	12.7	11.3
	15	9.6	16.6	15.2

As shown in Figure 7(A–C), the exothermic peak temperatures of the DSC curves for the three systems shift to higher value with increasing heating rate (β). The peak temperatures and the corresponding kinetic parameters calculated with eq. (1) are shown in Table III. The modification dramatically weakened the reactivity of EMI and raised the energy barrier of curing reaction, thus the E_k for DGEBA/EMI derivative systems is at 71.5~86.8 kJ/mol, which is higher than the 63.6 kJ/mol of DGEBA/EMI system reported by Zhang,[36] and the Arrhenius constant ranges from 4.89×10^5 to 2.63×10^6 s^{-1}. The order of E_k for the three systems is DGEBA/NBSEMI >DGEBA/NBEMI >DGEBA/NAEMI, which is coincide with that of exothermic onset and peak temperature in Table II. NBSEMI owned the highest E_k of curing reaction for its stronger electron-withdrawing capacity than the other two EMI derivatives, and that the E_k of NBEMI is higher than that of NAEMI due to the larger steric hindrance of benzoyl than acetyl.

Storage Stability of Curing System

DGEBA with imidazole derivatives as curing agent was stored at room temperature (25~35°C) and in refrigerator (10°C), respectively. And the viscosity of curing system was measured regularly to investigate the storage stability.

For the curing system stored at room temperature, as shown in Figure 8, the viscosity of DGEBA/EMI system going from 4700 up to 72600 mPa s in just 3 days (d) demonstrates poor storage stability, while the viscosity of DGEBA/NAEMI and DGEBA/NBEMI systems changes slowly until the curves reach a turning point, after which the viscosity increases rapidly. The turning point of DGEBA/NAEMI and DGEBA/NBEMI systems is 38 and 50 d, respectively. The electron-withdrawing effect of the substituent groups and the elimination of N–H bond in the substitution reaction may contribute to the better storage stability.[10,32] That the DGEBA/NBEMI system possessed better storage stability than the DGEBA/NAEMI system may be attributed to larger steric hindrance of phenyl group. The strongest electron-inducing ability of benzenesulfonyl may explain the phenomenon that almost no viscosity change of DGEBA/NBSEMI system was found after 80 d.

For the curing system stored at 10°C, as shown in Figure 9, the trend of viscosity evolution likes that of the curing system stored at room temperature, while the storage time is much longer. The viscosity of DGEBA/EMI system reaches 83600 mPa s in 8 d, and the turning point of DGEBA/NAEMI and DGEBA/NBEMI systems is 90 and 115 d, respectively. For DGEBA/NBSEMI system, the viscosity shows little augment after 170 d.

Mechanical Properties

The specimens for impact test were cured by EMI (80°C, 1 h), NBEMI (120°C, 1.5 h), NAEMI (120°C, 1.5 h), and NBSEMI (165°C, 3 h) in rectangular mold. The dimension of the Izod impact specimens was $80 \times 10 \times 4$ mm, and five samples for each formula were tested for an average value. As shown in Figure 10, Izod impact strength (IIS) of the samples cured by EMI, NAEMI, NBEMI, and NBSEMI is at 9.4~15.1, 12.7~25.9,
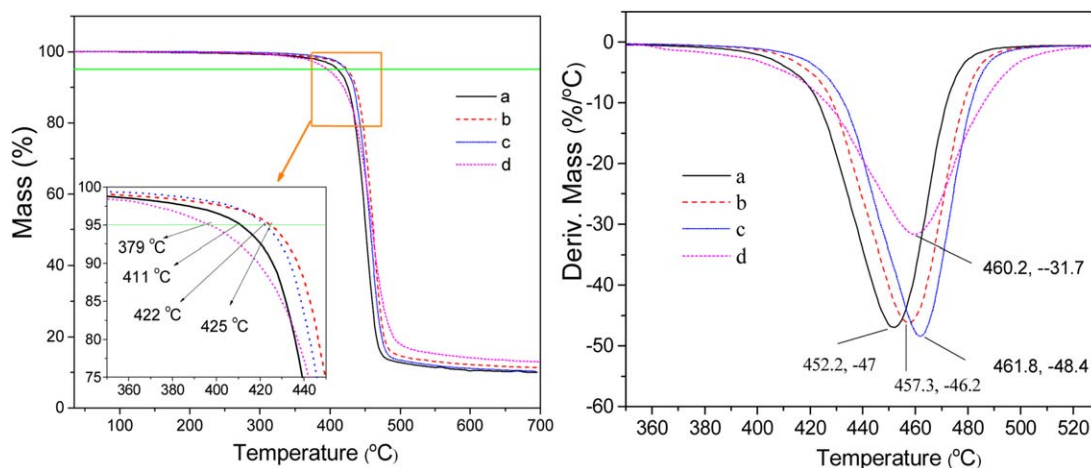

Figure 11. TG and DTG curves of the DGEBA cured by (a) 7 wt % of EMI, (b) 8 wt % of NBEMI, (c) 7 wt % of NAEMI, and (d) 15 wt % of NBSEMI, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

11.5∼17.1, and 8.1∼15.5 kJ/mol, respectively. It is obvious that the IIS of the systems cured by EMI and NAEMI increases with the content of curing agent, for higher concentration of curing agent led to denser cross-linked structure and enhanced the strength of the curing product. While the IIS of the samples cured by NBEMI and NBSEMI reaches the maximum value when the content of curing agent is 5.6 wt % and 12 wt %, respectively, and further increase of EMI derivatives weaken the IIS. That may be contributed to the rigid benzene ring on molecule of NBEMI and NBSEMI, which might block the movement of the molecular chain, the toughness of the material was weakened when the content of NBEMI and NBSEMI exceed a certain threshold. The IIS of DGEBA cured by NBEMI and NBSEMI is similar to that of DGEBA/EMI, and that of DGEBA cured by NAEMI is superior to other three systems, for the flexibility of ethyl is much better than that of benzene ring, which may help to toughen the material. Tensile shear strength (TSS) was measured to evaluate the adhesive property of the DGEBA/EMI derivative systems on aluminum, steel, and copper. Three specimens for each formula were tested for an average value, as shown in Table IV. It can be seen that the modification of EMI does not affect the adhesive property obviously, the TSS of specimens based on aluminum, steel, and copper is 6∼11, 9∼17, and 9∼16 MPa/m^2, respectively. The TSS of steel and copper are higher than that of aluminum, since the low surface energy of epoxy resin makes it more likely to infiltrate into the material that with high surface energy, and the surface energy of steel and copper is much higher than that of aluminum,[37] so more epoxy resin permeated into the micropore or gap on steel and copper and more excellent adhesive strength was obtained. The adhesive strength is controlled by the concentration of curing agent to some extent, even though the influence of the concentration in different systems does not follow any certain rule.

Thermal Stability of Curing Systems

The curing products of DGEBA used for TG analysis were cured by EMI (80°C, 1 h), NBEMI (120°C, 1.5 h), NAEMI (120°C, 1.5 h), and NBSEMI (165°C, 3 h), respectively. The TG and DTG curves are shown in Figure 11. All samples are degraded at 370∼500°C, and the resin cured by NBEMI and NAEMI present better thermal stability than that cured by EMI. The products of DGEBA/NAEMI and DGEBA/NBEMI lose 5% of weight at 422°C and 425°C, which is 11°C and 14°C higher than that of the DGEBA/EMI product, respectively, and these two products maintain thermal stable superiority in the whole degradation process. The DGEBA/NBSEMI product begins to degrade at a lower temperature than that of the DGEBA/EMI product and lose 5% of weight at 397°C, while the degradation rate is smaller than that of other systems. The curing behavior analysis indicates that the curing efficiency of NBSEMI is relatively low and a higher concentration of NBSEMI is needed to cure DGEBA, and higher concentration of curing agent means more crosslink center, which may led to the smaller degradation rate. Compared with the DGEBA cured by Cu(PGE-EMI)$_4$Cl in previous work,[38] which reached 5% of weight loss below 390°C,

the products of DGEBA/EMI derivatives in this study show great advantage in thermal stability.

The products of DGEBA/EMI, DGEBA/NAEMI, DGEBA/NBEMI, and DGEBA/NBSEMI reach the highest degradation rate at 452.2, 457.3, 461.8, and 460.2°C, respectively, as indicated in the DTG curves [Figure 11(B)]. The maximum value of the weight loss per centigrade of DGEBA/NBSEMI system is 31.7%/°C, which is much less than that of other three systems, and the corresponding degradation peak is relatively wide, which means a smaller rate and a larger temperature range for degradation.

CONCLUSIONS

FTIR and ^{1}H NMR spectra prove that the three kinds of curing agents (NAEMI, NBEMI, and NBSEMI) are successfully synthesized. The DGEBA can be efficiently cured by the EMI derivatives at 110∼160°C, and the corresponding curing activation energy range from 71 to 86 kJ/mol. The modification of EMI enhanced the storage ability of curing system based on DGEBA. Besides, TG and DTG curves indicate that the thermal stability of DGEBA cured by NAEMI or NBEMI is better than that cured by EMI. The curing products of DGEBA/EMI derivatives do not show obvious compromise in impact strength and adhesive property compared with that of DGEBA/EMI. Our research is useful for the preparation of latent epoxy resin system.

AUTHOR CONTRIBUTION

Dingfeng Lei: Designing research, conducting experiment, analyzing data, and drafting article. Wenshi Ma: Designing research, analyzing data, and revising article. Linfeng Wang: Designing research, interpreting data, and revising article. Dongqiao Zhang: Designing research, analyzing data, and revising article.

REFERENCES

1. Mitsukazu, O.; Kenchi, Y. *J. Mater. Sci.* **1989**, *24*, 3189.

2. Holbery, J. D.; Bordia, R. K. *J. Mater. Sci.* **2001**, *36*, 5301.

3. Farkas, A.; Strohm, P. F. *J. Appl. Polym. Sci.* **1968**, *12*, 159.

4. Dearlove, T. J. *J. Appl. Polym. Sci.* **1970**, *14*, 1615.

5. Heise, M. S.; Martin, G. C. *Macromolecules* **1989**, *122*, 99.

6. Omrani, A.; Leonardo, C. S.; Abbas, A. R.; Mousa, G. *Thermochim. Acta* **2008**, *468*, 39.

7. Wu, C. S. *J. Mater. Sci.* **1992**, *2*, 2952.

8. Wang, F.; Xiao, J.; Wang, J. W.; Li, S. Q. *J. Appl. Polym. Sci.* **2008**, *107*, 223.

9. Ricciardi, F.; Romanchick, W. A.; Joullie, M. M. *J. Poly. Sci. Polym. Lett. Ed.* **1983**, *21*, 633.

10. Wong, F. F.; Chen, K. L.; Lin, C. M.; Yeh, M. Y. *J. Appl. Polym. Sci.* **2007**, *104*, 3292.

11. Barton, J. M.; Buist, G. J.; Hamerton, I.; Howlin, B. J.; Jones, J. R. *J. Mater. Chem.* **1994**, *4*, 379.

12. Hamerton, I.; Howlin, B. J.; Jones, J. R. *J. Mater. Chem.* **1996**, *6*, 305.

13. Kaplan, M. L.; Wayda, A. L.; Lyons, A. M. *J. Polym. Sci. Part A Polym. Chem.* **1990**, *28*, 731.

14. Ham, Y. R.; Lee, D. H.; Kim, S. H.; Shin, Y. J. *J. Ind. Eng. Chem.* **2010**, *16*, 728.

15. Yin, T.; Rong, M. Z.; Zhang, M. Q.; Yang, G. C. *Compos. Sci. Technol.* **2007**, *67*, 201.

16. Chen, K. L.; Shen, Y. H.; Ye, M. Y. *J. Taiwan. Inst. Chem. E* **2012**, *43*, 306.

17. Lee, D. H.; Yang, M.; Sun, H. K.; Min, J. S.; Jae, S. S. *J. Appl. Polym. Sci.* **2011**, *122*, 782.

18. Brown, J.; Hamerton, I.; Howlin, B. J. *J. Appl. Poly. Sci.* **2000**, *75*, 201.

19. Bilge, E.; Reyhan, A.; Erdal, E. *J. Mater. Sci.* **2013**, *48*,7456.

20. Subramani, S.; Nasar, A. S.; Gnanarajan, T. P.; Iyer, N. P. *Polym. Int.* **2000**, *14*, 546.

21. Frederick, P. E.; Ishida, H. *J. Mater. Sci.* **1986**, *21*, 1561.

22. Park, S. J.; Heo, G. Y. *Macromol. Chem. Phys.* **2005**, *206*, 1134.

23. Goh, Y.; Ijima, T.; Tomoi, M. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 2689.

24. Jang, E. S.; Sher, B. K.; Seo, J.; Akhtar, K. *Macromol. Res.* **2011**, *19*, 989.

25. Li, W.; Guo, X. X.; Fang, J. H. *J. Mater. Sci.* **2014**, *49*, 2745.

26. Yang, C. L.; Xu, J.; Chen, W. *J. Mater. Sci.* **2014**, *49*, 7040.

27. Heise, M. S.; Martin, G. C. *J. Appl. Polym. Sci.* **1990**, *39*, 721.

28. Vogt, J. *J. Adhesion* **1987**, *22*, 139.

29. Ghaemy, M.; Sadjady, S. *J. Appl. Polym. Sci.* **2006**, *100*, 2634.

30. Ooi, S. K.; Cook, W. D.; Simon, G. P.; Such, C. H. *Polymer* **2000**, *41*, 3639.

31. Berger, O.; Lohse, F. *J. Appl. Polym. Sci.* **1985**, *30*, 531.

32. Gao, H. B. Organic Chemistry; Higher Education Press: Beijing, **2004**; Vol. *4*, Chapter 12, p 433.

33. Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.

34. Liu, W. B.; Qiu, Q. H.; Wang, J. *Polymer* **2008**, *49*, 4399.

35. Lee, J. Y.; Shim, M. J.; Kim, S. W. *J. Appl. Polym. Sci.* **2001**, *81*, 479.

36. Zhang, X. Y: Analysis and Test Techniques for Adhesives, Chemical industry Press: Beijing, 2004; Chapter 10, p 390.

37. Meng, S. Hand Book of Adhesives and Sealants; Chemical Industry Press: Beijing, **2005**; Chapter 2, p 40.

38. Barton, J. M.; Hamerton, I.; Howlin, B. *J. Polymer* **1998**, *39*, 1929.