Polymer 51 (2010) 1563–1571

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Simultaneous cationic polymerization and esterification of epoxy/anhydride system in the presence of polyoxometalate catalyst

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ARTICLE INFO

Article history:
Received 24 October 2009
Received in revised form
31 December 2009
Accepted 3 February 2010
Available online 12 February 2010

Keywords:
Polyoxometalate
Cationic polymerization
Esterification

ABSTRACT

Polyoxometalate exhibits high catalytic performance for the simultaneous cationic polymerization and esterification of epoxy resin when anhydride is introduced as a co-hardener. The selective catalysis effect of polyoxometalate and the reaction mechanism was studied by differential scanning calorimetry (DSC), mid-infrared spectroscopy (MIR), near-infrared spectroscopy (NIR) and generalized two-dimensional correlation analysis. The cationic polymerization is the dominating reaction in neat epoxy systems. Increasing the amount of polyoxometalate and the polarity of the diluents fastens the curing rate of epoxy resin. Esterification was found to be the preferred reaction once anhydride was employed. When polyoxometalate was blocked by amine to form salt, it performs as an excellent catalyst for esterification in epoxy–anhydride systems. The epoxy materials catalyzed by polyoxometalate show quite good performance compared with ordinary epoxy resins. Moreover, thermal degradation analysis (TGA) shows that polyoxometalate could significantly decrease the thermal degradation temperatures of cured epoxy resins.

1. Introduction

The physical and chemical properties of cured epoxy resins are influenced by the separate chemistry and structure of epoxy monomers and curing agents [1]. Generally, epoxy curing agents can be divided into two major classes: alkaline and acidic, both have reactions as polyaddition and/or ionic polymerization with epoxy. Although the traditional alkaline class of epoxy curing agents is well studied, new functional class, especially Lewis acids type which always initiate a cationic polymerization of epoxy resins [2], is still in development.

After the pioneering work of Crivello et al. in photocationic initiators like aromatic sulfonium [3–5] and iodonium salts [6,7], numerous curing systems have been innovated. For example, Morio et al. [8], employed benzyl sulfonium salts as a latent hardener for thermo initiated cationic polymerization, and found that the epoxy systems have longer shelf-life and shorter gel time at high temperature. While combined sulfonium with benzylthiolanium salts, Stapp et al. [9], obtained dual cure systems with attractive properties of thermal and UV induced curing. Kobayashi et al. [10], prepared phosphonium ylides as thermally latent catalysts and suggested that a catalyst closer to an ylide structure would be more active than an ylene structure. Park et al. [11], found that phosphonium and pyrazinium salts are efficient latent cationic initiators, and Serra et al. [12], used rare earth metal triflates as high-efficient thermal initiators for DGEBA epoxy resins and other cyclic compounds.

While in another aspect, with the enormous development of microelectronic and material industries, to develop reworkable epoxy adhesive for electronic industry [13–15] and green decomposition process [16] instead of discarded epoxy resins has become a major challenge. Lewis acid can depolymerize cured epoxy resins, however, they also deteriorate the thermal and mechanical performance of materials when used as curing agents [1,2].

Compared with the above-mentioned toxic curing and decomposition agents, polyoxometalates (POMs) and related heteropolyacids compounds, with economical and environmental advantages, have been widely employed as applied catalysts and model systems for fundamental research [17–23]. On the one hand, POMs have a very strong, approaching the superacid region, Brönsted acidity; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions [21]. Since the pioneering work by Japanese and Russian research groups [20–23], the broad utility of POMs acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic

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doi:10.1016/j.polymer.2010.02.007

substances [17–23], and polymerization initiators for tetrahydrofuran [24,25]. However, there is few report on the POMs cured commercial epoxy resins and their thermal properties till now.

In the present work, we have found that polyoxometalate, tungstophosphoric acid ($H_3PW_{12}O_{40} \times H_2O$; HPW), is a kind of high-efficient curing agent for epoxy resins. POMs not only can be used to initiate cationic polymerizations of epoxy resins but also can be employed in formulations with anhydride which form a network with both ester and ether linkages. When complexes with amines, POMs epoxy systems exhibit quite good long-term room temperature stability, in addition to produce a cross-linked structure with good thermomechanical properties once cured.

2. Experimental section

2.1. Materials and samples preparation

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin DER 330 was provided by Dow Chemical Co. The epoxide equivalent of DER 330 is 177–188 g/eq. Methyl tetrahydrophthalic anhydride (MTHPA), Aradur. TM. HY 917 was provided by Huntsman Advanced Materials Americas. Inc.. Phosphotungstic acid ($H_3PW_{12}O_{40} \times H_2O$) was provided by Mallinckrodt Laboratory Chemicals (Phillipsburg, NJ). USA. Triethylene glycol monomethyl ether, poly(ethylene glycol) (PEG) with average M_n 1305–1595, Methoxyaceticacid, *N*,*N*-dimethylbenzylamine and other chemicals from Aldrich were used without further purification.

2.2. Synthesis of phosphotungstic acid-N,N-dimethylbenzylamine salt

The phosphotungstic acid (2.8 g, 1 mmol) was dissolved in 20 ml ethanol. *N*,*N*-Dimethylbenzylamine (2.7 g, 20 mmol) in10 ml ethanol alcohol was added dropwisely into the acid solution under magnetic stirring. The white precipitate $[C_6H_5CH_2N(CH_3)_2H]_3PW_{12}O_{40}$ was collected by centrifugal separator and washed with ethanol, then dried in vacuum at 60 °C for 12 h. Yield: 80%. ^{1}H NMR ([D6] DMSO): $d = 7.36–7.42$ (m, 5H; aromatic), 3.85 (s, 2H; CH_2), 2.45 ppm (s, 6H; CH_3).

The compositions studied are collected in Tables 1–3. In Table 1 the formulations containing 10 phr (per hundred weight percent of epoxy resin) of anhydride MTHPA, with different amount of POM are collected. In Table 2 the formulations with several ratios anhydride/DGEBA are specified. In Table 3 the formulations with several diluents/DGEBA are specified.

The mixtures were prepared by first dissolving POM into anhydride or other organic solvents, and then adding the POM solution to the DGEBA resin at room temperature and mixing until the solution became clear (around 1 min). After that, the samples were cooled down to −10 °C and maintained at this temperature until used. For isothermal curing, a multi-stage process was performed as 40 °C for 1 h, 100 °C for 2 h, and 150 °C for 2 h.

Table 1
Composition of the samples studied (epoxide, anhydride, POM) of the formulations with a 10 phr of MTHPA.

Sample[a]	POMs	MTHPA	DGEBA	Mole ratio[b]	T_g (°C)[c]
POM1-MTHPA10 phr	1	10	100	0.11	–
POM2-MTHPA10 phr	2	10	100	0.11	81.7
POM3-MTHPA10 phr	3	10	100	0.11	107.2
POM4-MTHPA10 phr	4	10	100	0.11	89.3
POM5-MTHPA10 phr	5	10	100	0.11	87.6

[a] phr: per hundred weight of epoxy resin.
[b] Mole ratio of anhydride to epoxy.
[c] T_g determined after curing in a dynamic scan registered at 10 °C/min.

Table 2
Composition of the samples studied (epoxide, anhydride, POM) of the formulations with a 3 phr of POM.

Sample[a]	POMs	MTHPA	DGEBA	Mole ratio[b]	T_g (°C)[c]
EP-MTHPA	–	90	100	1.0	–
POM3-MTHPA30 phr	3	30	100	0.33	91.5
POM3-MTHPA50 phr	3	50	100	0.55	86.3
POM3-MTHPA70 phr	3	70	100	0.77	86.7
POM3-MTHPA90 phr	3	90	100	1.0	89.2

[a] phr: per hundred weight of epoxy resin.
[b] Mole ratio of anhydride to epoxy.
[c] T_g determined after curing in a dynamic scan registered at 10 °C/min.

2.3. Differential scanning calorimetry (DSC)

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 5–10 mg. The kinetic studies were performed at heating rates of 2, 5, 10 and 20 °C/min. The glass transition temperature for each material (T_g) was calculated after complete curing, by means of a second scan, as the temperature of the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state.

2.4. Infrared spectroscopy

Near-infrared (NIR) and mid-infrared (MIR) spectroscopy experiments were performed using a Thermo Nicolet Nexus 440 Spectrometer. For NIR, 4 cm^{-1} resolution and 128 scans were used. The thickness of the sample cell was 2 mm. The time interval between each spectra collected was 70 s. For MIR, 4 cm^{-1} resolution and 32 scans were used. The thickness of the sample cell was about 0.03 mm. The time interval between each spectrum was 40 s.

2.5. Two-dimensional correlation analysis

Spectra at equal time intervals in certain wavenumber range were selected to 2D correlation analysis using the software “2D Pocha” which was composed by Daisuke Adachi (Kwansei Gakuin University).

2.6. Thermogravimetric analyses (TGA)

Thermal decompositions were performed from room temperature to 800 °C on powdered samples with masses between 8 and 15 mg using a Mettler–Toledo TGA-50 Thermogravimetric Analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere.

Table 3
Composition of the samples studied of the formulations with a 3 phr of POM and different solvents.

Sample[a]	MTHPA	PEO	Alcohol	Acid	POMs	DGEBA	Mole ratio
POM3-PEO10 phr	–	10	–	–	3	100	0.013[b]
POM3-Alcohol10 phr	–	–	10	–	3	100	0.10[c]
POM3-Acid10 phr	–	–	–	10	3	100	0.20[d]

[a] phr: per hundred weight of epoxy resin.
[b] Mole ratio of active hydrogen in hydroxyl-terminated PEO to epoxy.
[c] Mole ratio of active hydrogen in triethylene glycol monomethyl ether to epoxy.
[d] Mole ratio of active hydrogen in methoxyaceticacid to epoxy.

3. Results and discussion

3.1. Thermal cationic polymerization

Polyoxometalates, particularly tungstophosphoric acid ($H_3PW_{12}O_{40} \times H_2O$; HPW), were found to be efficient catalysts for several acid-catalyzed organic transformations and industrial applications. For example, Izumi et al. [26], found that POM is a more active cationic initiator than $HClO_4$ in the polymerization of THF. In the polymerization of 1,3,5-trioxane, the comparable reaction rates can be obtained with 25 times less of catalyst consumption than for conventional catalyst like $BF_3 \cdot OR_2$ [27].

However, POM can only be dissolved in polar solvents such as water, tetrahydrofuran (THF), lower alcohols, etc; they are insoluble in nonpolar solvents like hydrocarbons and most thermoset precursors like epoxy monomer (DGEBA). Therefore, we herein first choose liquid anhydride MTHPA as a reactive diluent with the anticipation that anhydride would react with epoxy groups in this system.

3.1.1. Effect of POM concentration

Fig. 1 shows the dynamic DSC curves obtained from DGEBA and POM/MTHPA at different catalyst percentages. Like most cationic systems, there is a great dependence of the onset and maximum crosslinking exotherm temperatures on the proportion of catalyst. Three peaks are observed for systems with POM from 1 to 3 phr, while only two peaks appeared when POM is above 4 phr.

On comparing the behaviors of crosslinking process with those obtained from the curing of a similar resin with a typical cationic initiator, BF_3 monoethylamine ($BF_3 \cdot MEA$) [28,29], it is noticeable that the crosslinking takes place with similar behaviors, and three exotherm peaks were also observed on the DSC thermograms of $BF_3 \cdot MEA$/DGEBA system. The first DSC peak appeared at low temperatures is related to the formation of active initiator species, the second, to the curing process and the third to an epoxy–OH reaction that takes place above 200 °C.

Unlike ordinary cationic initiators reported by other literature [12], the increase of POM percent only results in a faster reaction rate and low temperature curing. Glass transition temperatures after DSC scanning to 300 °C at a heating rate of 10 °C/min are displayed in Table 1. Except POM1-MTHPA10 phr system, which cannot be fully cured during this curing process, the other systems have similar T_g values (POM3-MTHPA10 phr system has the highest T_g). These T_g values are comparable to other thermal cationic polymerization systems. As isothermal curing could provide higher crosslink density, after the three-stage isothermal curing as mentioned in experimental parts, all the four systems can reach a T_g value of about 130 °C, which seems to show that POM does not have the negative effect of depolymerization during curing. A possible reason may come from the high-efficient of POM as effective and harmless catalyst used in organic synthesis.

3.1.2. Effect of diluent polarity on the cationic polymerization

As POM needs to be dissolved into solvents (diluents) to initiate the cationic polymerization of epoxy, the polarity of diluents would be anticipated to affect the curing rate significantly.

To verify this point, several high boiling point liquids were chosen to study the polarity effect of diluents. In this experiment, the acid, methoxyaceticacid, has the highest proton mobility, then triethylene glycol monomethyl ether with one hydroxyl functional group each molecule, and the last one is the wax-like poly(ethylene glycol) with quite few free protons.

Fig. 2 shows the calorimetric curves for the curing of 3 phr POM systems with different diluents. Compared with the anhydride MTHPA, triethylene glycol monomethyl ether shifts the first peak to lower temperature while poly(ethylene glycol) to higher temperature. The curve of methoxyaceticacid does not show here because epoxy resin cures immediately when blended with the initiator.

The differences in curing can be explained by the acidity of POMs due to diluents. POMs have a very high solubility in polar solvents and exhibit an extremely high proton mobility and a "pseudoliquid phase" [22]. Solid POMs possess a discrete ionic structure, comprising fairly mobile basic structural units heteropolyanions and countercations (H^+, H_3O^+, $H_5O_2^+$, etc.). In aqueous or acid solution, POMs are strong fully dissociated acids. Thus, in strong polar solvents, like methoxyaceticacid, POMs behave as superacid, by virtue of the easy absorption, cationic polymerization occurs not only on the surface, but also in the bulk of the crystalline POMs, therefore, solid POMs behave like highly concentrated solutions, i.e., nearly all the POMs protons, not only the surface proton sites, participate in the catalytic reaction.

Unlike the acid, in low polar solvents (e.g., triethylene glycol monomethyl ether and PEG), POMs are partially dissociated. The cationic reaction occurs only on the surface of the catalyst. The pseudoliquid behavior apparently brings about high catalytic

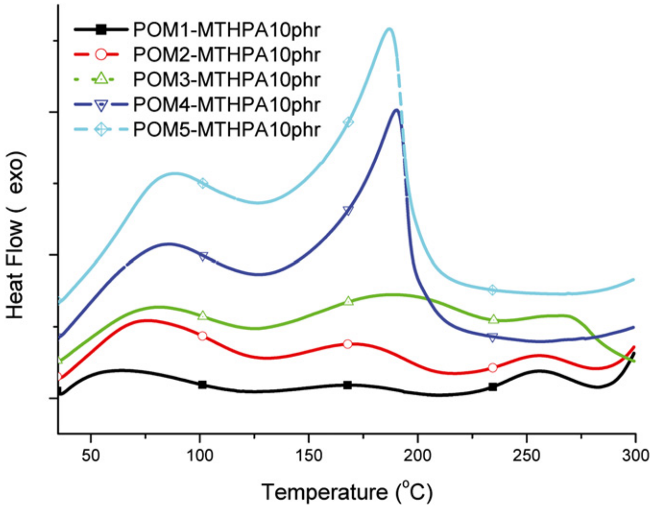


Fig. 1. Calorimetric curves for the curing of 10 phr MTHPA systems with different amount of POM at a heating rate of 10 °C/min.

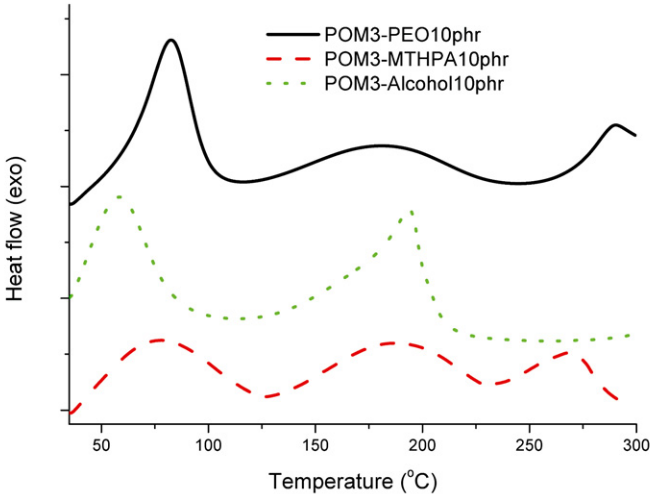


Fig. 2. Calorimetric curves for the curing of 3 phr POM systems with different solvents at a heating rate of 10 °C/min. PEO and alcohol stand for poly(ethylene glycol) and triethylene glycol monoethyl ether respectively.

activities in high polar diluents at relatively low temperatures, i.e., the cationic polymerization takes place most quickly in methoxyaceticacid at first, then triethylene glycol monomethyl ether, then MTHPA which also has few acid molecules, and then PEG the last due to the low density of hydroxyl groups.

3.2. *Simultaneous catalysis of etherification and esterification*

The cationic polymerization is the dominant reaction in the above studied systems; however, there rises another issue: the esterification of anhydride with epoxy would be a competitive process, which may not be fully performed during curing. While the T_g values in Table 1 do not show this effect.

In literatures, reactive diluents have been used in cationic curing process, but mostly can be initiated by catalyst to have copolymerization. For example, Pascault et al. [30], had studied the BF_3-4-methoxyaniline (MA) complex with a reactive diluent gamma-butyrolactone, which can be initiated to have a ring-opening copolymerization with DGEBA.

3.2.1. *IR analysis of the mechanism*

To study the epoxy curing mechanism and the effect of anhydride, in-situ real time near-infrared spectroscopy (NIR) monitoring is employed due to its ability to differentiate OH, NH and CH vibrations. Furthermore, generalized two-dimensional (2D) correlation analysis [31–33], which can handle spectral fluctuations as an arbitrary function of time or any other physical variables, is of the most significant method in the dynamic analysis [34,35].

Fig. 3 shows the NIR spectra of POM3-MTHPA30 phr system isothermal curing at 130 °C. The band at 7000 cm^{-1} can be assigned to the overtones of OH related groups. The overlapped bands from 6100 to 5500 cm^{-1} are assigned to the H–C overtones of epoxy groups, phenylene groups and backbone [36–39]. The band at 4530 cm^{-1} can be assigned to the combination vibrations of epoxy groups.

During the polymerization process, bands at 6069, 5885 and 4530 cm^{-1} (epoxy vibrations) decrease, which results from the consumption of epoxy groups; while bands at 5780–5500 cm^{-1} (backbone CH_2/CH vibrations) increase, which is attributed to the transfer from epoxide CH_2/CH to backbone's CH_2/CH. Additionally, bands at 4890–4786 and 7000 cm^{-1} (OH related vibrations) also increase because of the chain termination of the polymerization.

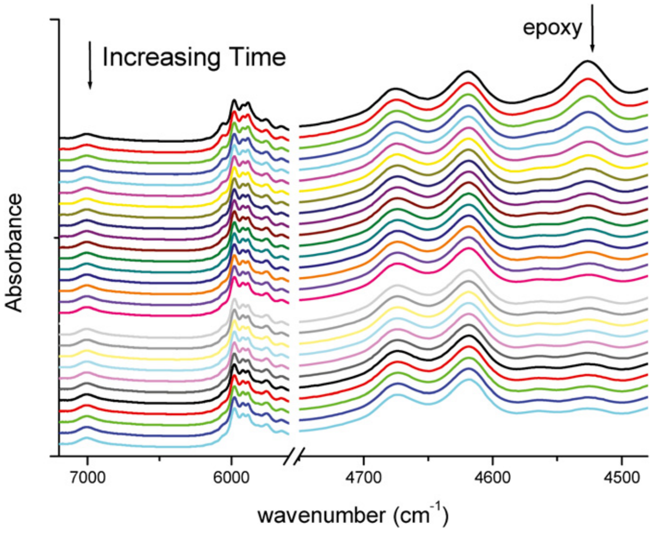


Fig. 3. NIR Spectra of a POM3-MTHPA30 phr system isothermal curing at 130 °C.

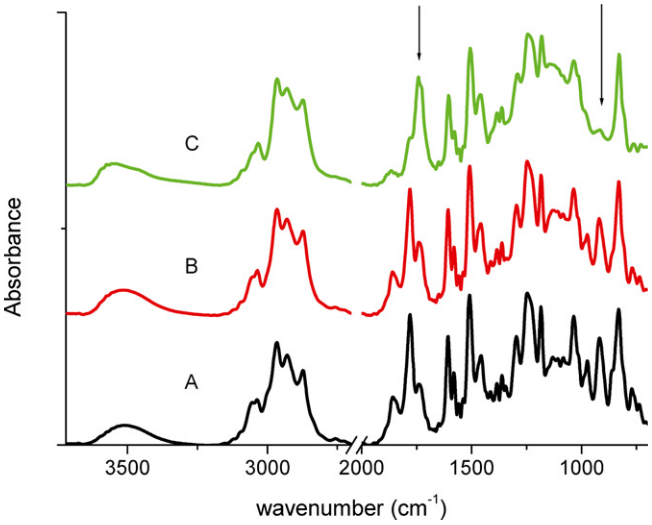


Fig. 4. Mid-IR Spectra of a POM3-MTHPA30 phr system at various curing conditions; curve A: before curing; curve B: cured at 40 °C for 20 min; curve C: cured at 130 °C for 60 min.

Moreover, the completion of polymerization could be confirmed by the intensity decrease of epoxy characteristic absorption band at 4530 cm^{-1}, which is always used to analyze curing conversion. Normalized absorbance of this band suggests the curing conversion is above 90% within 30 min at 130 °C.

To future investigate what happens with the anhydride MTHPA, NIR spectra is not a suitable tool in this case as it only provides information of epoxy groups. Therefore, mid-IR was employed. First, the system was cured at 40 °C, at which temperature it was assumed that MTHPA would have little reaction with epoxy. Then the temperature was quickly increased to 130 °C to enable the reaction between MTHPA and epoxy. During this process, we focused on the characteristic absorbance of epoxy groups (centered at 3056, 2998 and 916 cm^{-1}) and carbonyl group of MTHPA (centered at 1783 cm^{-1}).

As shown in Fig. 4, the band at 916 cm^{-1} and the band at 1783 cm^{-1} decrease due to the consumption of epoxy and carbonyl group of MTHPA, respectively. While the band around 1730 cm^{-1} (assigned to the carbonyl group of ester) increase indicating the

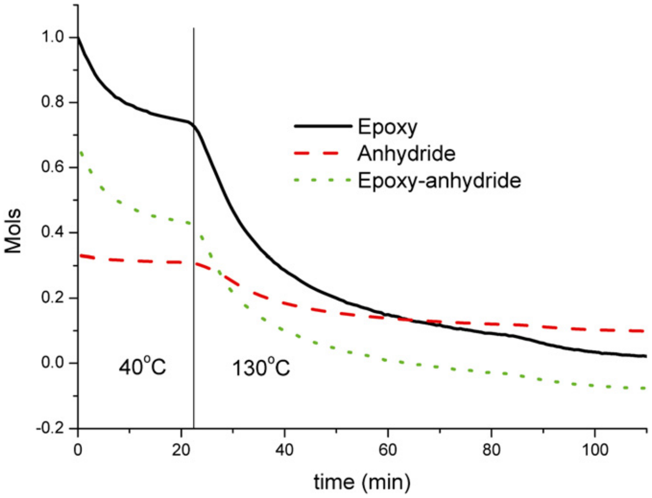


Fig. 5. Evolution of the anhydride and the epoxide mols during the isothermal curing at 40 °C and 130 °C of a POM3-MTHPA30 phr system followed by FTIR/ATR.

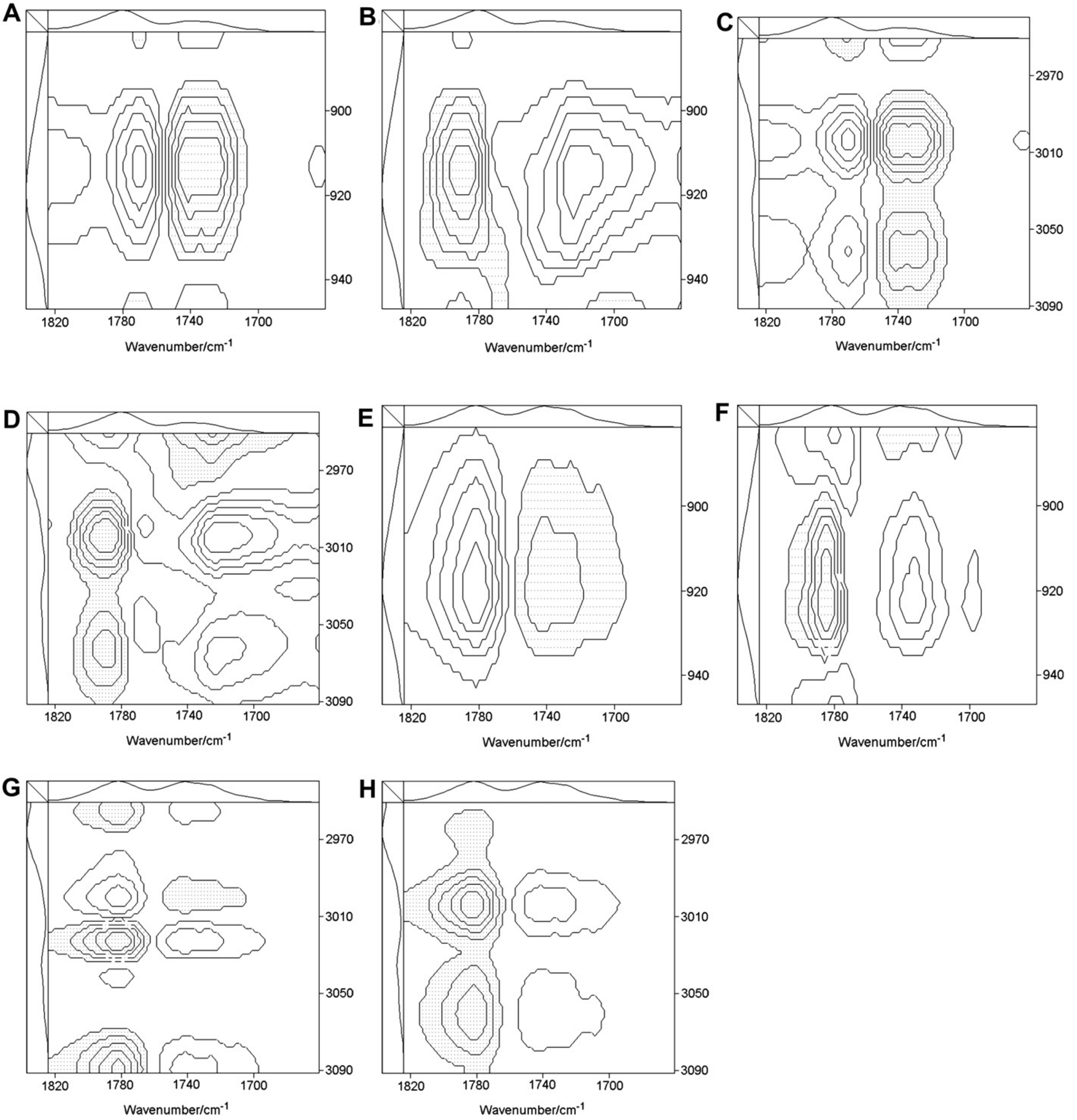


Fig. 6. Generalized 2D correlation spectra of a POM3-MTHPA30 phr system isothermal cured at 40 °C (A, B, C, D) and 130 °C (E, F, G, H). Synchronous: A, C, E, G; Asynchronous: B, D, F, H.

formation of esters. When the vibration of CH_3 groups (at 2965 cm^{-1}) was used as internal standard, the intensity changes of bands assigned to epoxy (centered at 916 cm^{-1}), carbonyl group of MTHPA (centered at 1783 cm^{-1}) and the mol differences between epoxy and anhydride are shown in Fig. 5. However, there is still a small intensity decrease of carbonyl group of MTHPA at 40 °C.

From Figs. 4 and 5, it can be found clearly that cationic polymerization of epoxy group and esterification of epoxy and anhydride occur simultaneously in the presence of POM. To further analyze this phenomenon, generalized 2D correlation spectroscopy on the evolution of mid-IR spectra of the curing process was presented.

3.2.2. 2D correlation spectroscopy analysis

According to the publications of Noda [31], cross band $\Phi(\nu_1, \nu_2)$ located at the off-diagonal positions $(\nu_1 \neq \nu_2)$ of a synchronous spectrum represents the simultaneous changes of spectral signals at ν_1 and ν_2. If the sign of a cross band is positive (unshaded area), it means that spectral intensities at corresponding wavenumbers are either increasing or decreasing together. If the sign is negative

Table 4
2D results summarized from Fig. 6.

Temperature	2D results from Fig. 6 (cm^{-1})					
40 °C	2998 > 1783[a]	3056 > 1783	2998 > 1727	3056 > 1727	916 > 1783	916 > 1727
130 °C	2998 > 1783	3056 > 1783	2998 > 1731	3056 > 1731	916 > 1783	916 > 1731

"$>$" means "change prior to".

(shaded area), it is indicated that one spectral intensity is increasing while the other is decreasing.

Asynchronous spectrum is the complementarity of synchronous spectrum. In the asynchronous spectrum a cross band between two dynamic spectral features can develop only if their intensities vary out of phase with each other, and the intensity of asynchronous correlation band $\Psi(\nu_1,\nu_2)$ is able to give information about the sequential order of intensity changes between band ν_1 and band ν_2. If $\Psi(\nu_1,\nu_2)$ is positive, band ν_1 varies prior to band ν_2, and if $\Psi(\nu_1,\nu_2)$ is negative, band ν_2 varies prior to band ν_1. But the above rules are reversed if the sign of a synchronous band at the same coordinate $\Phi(\nu_1,\nu_2)$ is negative. It is noteworthy that "prior to" used here does not mean two band vary one after another in absolute sequences. It indicates the intensity change at one band takes place predominantly but still simultaneously with the other band.

Fig. 6A shows that synchronous band $\Phi(1783, 916\ cm^{-1})$ is positive, and $\Phi(1727, 916\ cm^{-1})$ is negative. This information indicates that consumption of epoxy and carbonyl group of MTHPA takes place simultaneously. So we come to the conclusion that cationic polymerization of epoxy group and esterification of epoxy and anhydride occur simultaneously in the presence of POM. Information from other synchronous spectrum also supports this point.

In the asynchronous 2D spectrum (Fig. 6B), one negative crosspeak, $\Psi(1783, 916\ cm^{-1})$ and one positive crosspeak $\Psi(1727, 916\ cm^{-1})$ are evidenced. While in the corresponding synchronous 2D spectrum (Fig. 6A), $\Phi(1783, 916\ cm^{-1})$ is positive and $\Phi(1727, 916\ cm^{-1})$is negative. On the basis of Noda's rule [31], the intensity of bands in Fig. 6 changes in the following sequence: band at 916 changes prior to bands at 1783 and 1727 cm^{-1}, which suggests that the intensity change of epoxy takes place prior to that of carbonyl group of MTHPA.

In summary, the results obtained from generalized 2D correlation analysis were presented in Table 4. The intensity change of epoxy groups (centered at 2998, 3056 and 916 cm^{-1}) takes place prior to that of carbonyl group of MTHPA (centered at 1783 cm^{-1}) regardless of the temperature, which indicates that the reactions in the system are nearly the same no matter at 40 or 130 °C.

In generally, $H_3PW_{12}O_{40}$ not only initiates cationic polymerization, but also catalyzes the reaction between epoxy and MTHPA at the same time, i.e., both of the reactions take place simultaneously. This phenomenon is similar with the anhydride/epoxy/tertiary amine system, in which amine-catalyzed epoxide isomerization occurs along with the reaction between anhydride and epoxy [40]. Cationic polymerization takes place at first, while catalyzed esterification seems to be the dominant reaction at the presence of anhydride, which we will demonstrate in the next paragraphs.

3.3. *Preferential esterification in the presence of anhydride*

From the above analysis, it seems the simultaneous esterification and cationic polymerization would affect the cured epoxy resin. Then like the anhydride/epoxy/tertiary amine system, one would wonder which reaction would be preferred with the increase of anhydride amount.

3.3.1. *Effect of anhydride content*

Fig. 7 shows the DSC curves of different amount of anhydride cured epoxy systems. The calorimetric curves show great dependence on the amount of MTHPA. Without POM, the neat DGEBA/MTHPA system can hardly be cured. With the increase of MTHPA content in POM catalyzed systems, the first peak at low temperature shifts to high temperature and peak area decreases at the same time, while the second peak moves to low temperature with the increase of peak area, moreover, the third peak at high temperature disappears.

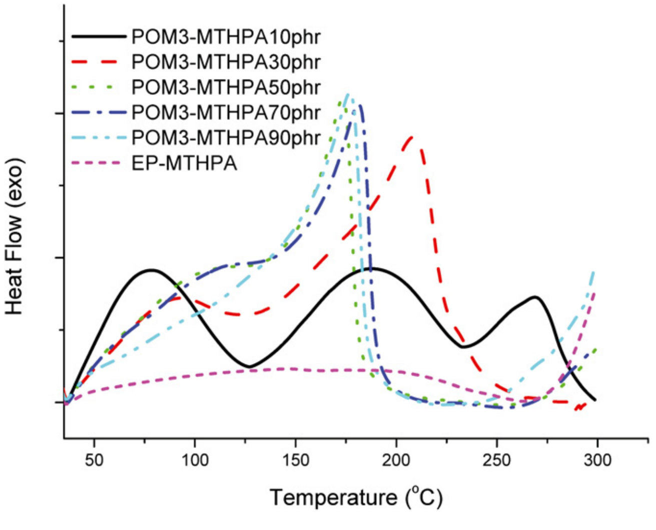
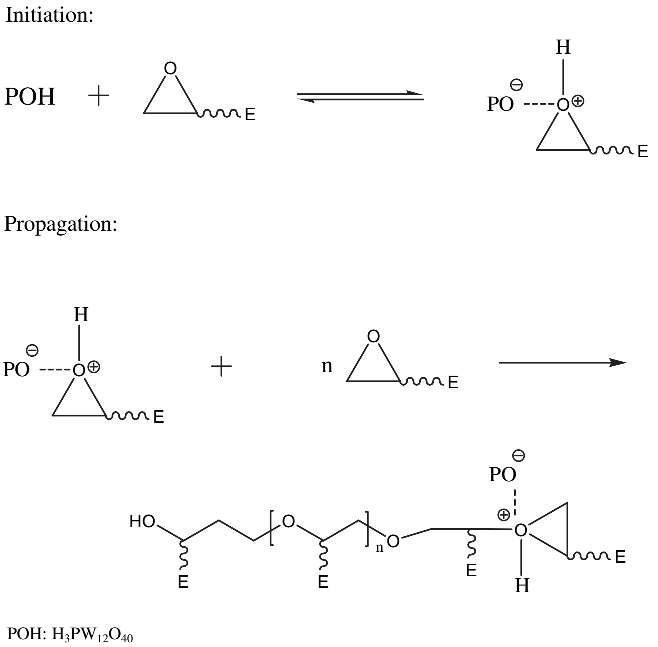
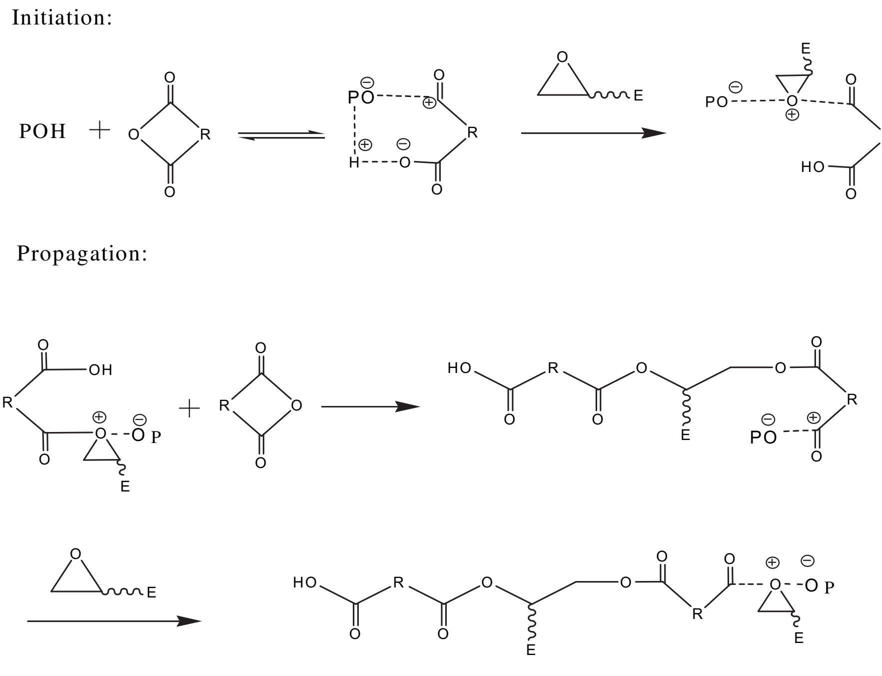


Fig. 7. Calorimetric curves for the curing of 3 phr POM systems with different amount of MTHPA at a heating rate of 10 °C/min.



Scheme 1. Schematic mechanism of the cationic curing reaction.



POH: $H_3PW_{12}O_{40}$

Scheme 2. Schematic mechanism of the POM catalyzed esterification.

Surprisingly, the glass transition temperatures of the materials after dynamic scanning displayed in Table 2 almost keep constant whatever the amount of anhydride. Furthermore, after isothermal curing process, all the systems can reach a T_g value above 110 °C. In other words, the addition of anhydride would clearly favorite the esterification reaction instead of cationic polymerization of epoxy, i.e., POM prefers to catalyze the esterification of epoxy and anhydride in the competition of cationic polymerization with esterification, and thus result in the completion of reaction of anhydride with epoxy even though epoxy and anhydride are in stoichiometric proportion.

Combined with the above experimental results, the whole curing process can be concluded into Schemes 1 and 2. In Scheme 1, POM initiates the cationic polymerization of epoxy without anhydride; while in Scheme 2, POM prefers to catalyze esterification in the presence of anhydride, at the same time it also initiates the polymerization of epoxy left, thus results in a fully cured system. In other words, the major reaction is cationic polymerization of epoxy (etherification) at low concentration of anhydride; while the esterification would become the dominant reaction with the increase of anhydride percentage.

3.3.2. *POM-amine complexes catalyst for esterification*

POM acts as both superacid and catalyst for the cationic polymerization and esterification, as POM prefers esterification reaction, then what would happen if the cationic polymerization were blocked?

To stop the cationic polymerization at low temperature, amines and trialkylphosphine etc. are always added as polymerization inhibitor. In our experiments, amines added show effective results as the cationic polymerization at low temperature were stopped completely. However, it is well known that most Lewis acids can be blocked with selected amines to provide latent catalysts with extended shelf stability in thermal curing stable one-can systems. Moreover, POM-amine complexes have been widely used as effective catalysts for esterification and other reactions [17–23], which render a great possible for the application of these complexes into epoxy systems. Although the initiation mechanism for BF_3-amine complexes is controversial [41], it has been postulated that the complex dissociates in the presence of protic compounds (trace water, hydroxyls, or alcohols present in the resins) to give the tetrafluoroborate ammonium salt ($RNH_3^+BF_3^-$) with the labile hydrogen acting as the actual initiating species [42].

In our case, the amine-added systems can be cured quickly at high temperature. To study the storage stability and cure reaction of the POM-amine complex added systems, phosphotungstic acid-*N*,*N*-dimethylbenzylamine was synthesized.

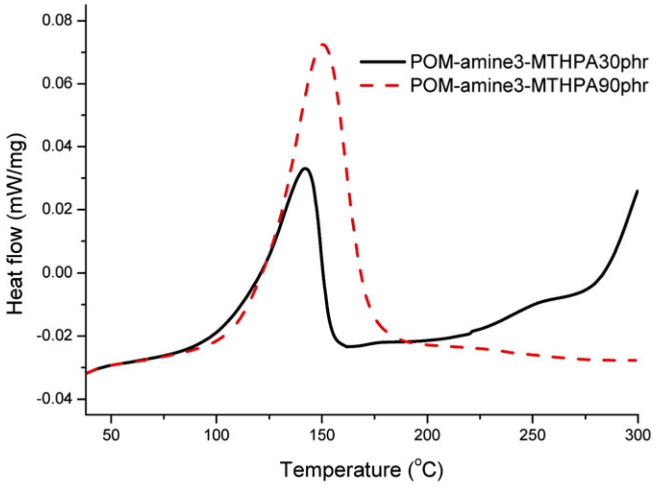


Fig. 8. Calorimetric curves for the curing of 3 phr POM-amine complex systems with different amount of MTHPA at a heating rate of 10 °C/min.

The storage stability of the mixture at low concentrations of POM-amine complex was determined by monitoring the consumption of the epoxy groups using near-infrared spectroscopy (4530 cm^{-1}, epoxide group). At a concentration of 3 phr complex content and 30 phr MTHPA, no apparent conversion of the epoxide group was observed over a period of 3 h at 50 °C. A step increase of the cure temperature to 150 °C caused the reaction to proceed toward gelation quickly. This behavior demonstrates that the formulation shows good storage stability at low temperature.

DSC study gives interesting results of the curing behaviors of POM-amine complex catalyzed epoxy/MTHPA systems. Fig. 8 shows the curing process of 30 phr and 90 phr MTHPA added systems. For the stoichiometric anhydride/epoxy system, 90 phr MTHPA, the curing reaction initiates at about 100 °C with the maximum exotherm temperature of 150 °C, the cured resin has a T_g of about 123 °C. If compared these results with the amine (*N*,*N*-dimethylbenzylamine) catalyzed anhydride/DGEBA systems, one would find that the reaction enthalpy is a little higher, 311 J/g, while T_g increases about 20 °C (the T_g of the amine-catalyzed system is about 98 °C). Clearly, POM-amine complex catalyzes a more complete esterification reaction of epoxy with anhydride.

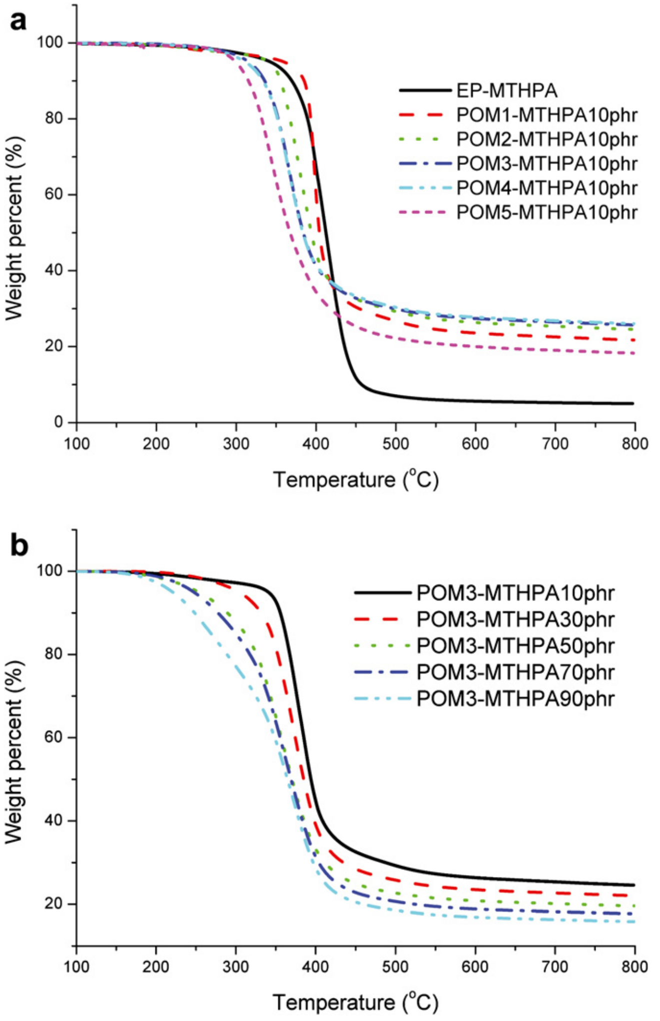


Fig. 9. Effect of POM and anhydride amount on the thermal degradation behavior of epoxy systems. (a) TGA curves of systems with different amount of POM in nitrogen environment at 10 °C/min; (b) TGA curves of systems with different amount of anhydride in nitrogen environment at 10 °C/min.

While for the system with 30 phr MTHPA, both of the curing behavior and glass transition temperature show that the system is not fully cured. The esterification reaction takes place at about the same temperature range in Fig. 8, however, the enthalpy of this peak is only about one third of the 90 phr MTHPA system, and another peak at high temperature appears due to cationic polymerization. The T_g of this system is only about 71 °C. In other words, all the MTHPA has reacted with epoxy while epoxy groups are not fully polymerized.

From the above results, it can be concluded that the POM-amine complex is a highly effective catalyst for esterification reaction (with good storage stability at low temperature) while shows lower ability as cationic initiator.

3.4. Thermal stability

As POMs are efficient chemical decomposers and oxidants, it will be quite interesting to investigate their effects in epoxy systems. Misono et al. [43], have studied a series of homogeneous reactions such as decomposition of isobutyl propionate, and found that POMs are 60–100 times more active than ordinary acid like H_2SO_4 and *p*-toluenesulfonic acid.

Fig. 9(a) shows the thermal degradation behaviors of fully cured epoxy systems with different amount of the POM. With the increase of POM content, both of the thermal decomposition temperatures and char yield drop down.

However, when the anhydride content changes while POM keeps constant as shown in Fig. 9(b), the decomposition temperature decreases quickly with the increase of anhydride content. The kind of thermal decomposition can also be observed in Fig. 7, in which another exotherm peak at about 250 °C appears after fully cured. In these systems, the content of ester linkages increases with the anhydride, while thermal decomposition temperature drops down at the same time.

It can be deduced from the above results that POMs are efficient chemical decomposers for the ester groups. Taking POM3-MTHPA90 phr system as an example, the initial decomposition temperature is only about 220 °C at a scanning rate of 10 °C/min, i.e., it is a quite good material with high glass transition temperature and mechanical performances, which can also be decomposed at low temperature.

Although the properties of POMs and their amine complexes still need further study, the primary study of mechanical properties shows that the fully cured DGEBA epoxy resin with POM are comparable to those cured with hardeners such as amines and anhydrides, which needs further investigation in our future works. In general, POMs have shown quite good performances as both cationic polymerization initiators and efficient catalysts for esterification and decomposition.

4. Conclusions

Polyoxometalate, tungstophosphoric acid ($H_3PW_{12}O_{40}\ \times H_2O$; HPW), is a kind of high-efficient curing agent for epoxy resins. The generalized two-dimensional correlation analysis and DSC investigation showed that cationic polymerization and esterification occur at the same time when anhydride is added into the epoxy systems, however, esterification would be the preferred reaction with high portion of anhydride. When complexes with amines, POM-epoxy systems exhibit quite good long-term room temperature stability, and can be used as high-efficient catalyst for esterification. Furthermore, POM could significantly decrease the thermal degradation temperature of cured epoxy resins with ester linkages.

Acknowledgement

This research work was supported by the National Nature Science Foundation of China (Grant 20704008, 20974027), and the Specialized Research Fund for the Doctoral Program of Higher Education of China (SRFDP; No. 20070246001). Y.Y. acknowledges the Juan de la Cierva Program of MICINN.

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