Synthesis and Curing Properties of a Novel Curing Agent Based on *N*-(4-Hydroxyphenyl) Maleimide and Dicyclopentadiene Moieties

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ABSTRACT: A new type of epoxy resin curing agent, containing pendant phenol functions, was synthesized by the free-radical copolymerization of *N*-(4-hydroxyphenyl) maleimide with dicyclopentadiene (DCPD) monomer in the presence of a radical initiator. The chemical structure was characterized with Fourier transform infrared spectroscopy and nuclear magnetic resonance. The molecular weight of the new curing agent was determined by gel permeation chromatography. The activity and activation energy of this new curing agent with *o*-cresol formaldehyde novolac ep- oxy (CNE) was investigated with a nonisothermal differential scanning calorimetry technique at different heating rates. The thermal properties of the cured polymers were evaluated with thermogravimetric analysis, and the results exhibit good thermal stability. In addition, this new curing agent with CNE showed low moisture absorption because of the hydrophobic nature of the DCPD structure. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 56–61, 2011

Key words: resins; synthesis; thermal properties

INTRODUCTION

Epoxy resins have been widely used in advanced composite matrices, surface coatings, and semiconductor encapsulation applications because of their heat-, solvent-, moisture-, and chemical-resistance; good mechanical and electrical properties; and strong adherence to many substrates.[1–4] However, epoxy resins require high thermal-resistance properties and low moisture absorbance to satisfy the demands of advanced microelectronic packaging. Many approaches have been reported for enhancing their heat resistance and moisture resistance.[5–9]

The chemical structures of cured epoxy polymers constituted with imide groups are known for their good thermal stability.[10,11] There are three methodologies for introducing imide groups into epoxy resin networks: (1) the modification of the backbone of the epoxy with imide groups, (2) the use of a curing agent that contains imide groups, and (3) a combination of these two methods.[12] Sharma et al.[13] used the second methodology. They investigated the thermal stability using a mixture of imide–amine and diaminodiphenyl sulfone at various molar ratios as a cur- ing agent for epoxy resin. All of the cured epoxy resins showed good heat resistance. Abraham et al.[14] synthesized a new epoxy curing agent based on imide acid. They discovered that the cured epoxy resins had a high thermal stability; furthermore, the char residue and thermal stability of these products increased with increasing imide content. Gouri et al.[15] prepared a novel hydroxyl-terminated imide curing agent; the glass-transition temperatures of the cured epoxy resins were from 160 to 175°C. The char residue of the cured polymer was also substantially enhanced in the presence of the imide groups.

Dicyclopentadiene (DCPD), known as a byproduct of C_5 streams in oil refineries, is of interest because of its reactivity, low moisture absorption, and low cost.[16] Many experiments have focused on the reaction of DCPD with phenol and naphthol, and the experimental results show that DCPD-containing compounds exhibit a low dielectric constant and low moisture absorption.[17,18]

In this study, a novel copolymer containing both cycloaliphatic and imide groups was prepared through the free-radical copolymerization of *N*-(4-hydroxyphenyl) maleimide (HPM) and DCPD. The resulting compound was used as a curing agent for *o*-cresol formaldehyde novolac epoxy (CNE). The synthesis, characterization, curing reaction, thermal properties, and moisture absorption of the cured polymer were studied. The cured resins showed low water absorption and good thermal stability.

EXPERIMENTAL

Materials

p-Aminophenol (99.0%), maleic anhydride (99.5%), *p*-toluenesulfonic acid (p-TSA) (99.5%), imidazole (99.0%), azobisisobutyronitrile (AIBN) (98%), and dicyclopentadiene (98%) were purchased from Shanghai Chemicals (Shanghai, China). All solvents were used without further purification. A phenol formaldehyde novolac resin (PN) used as curing agent with a hydroxyl equivalent weight of about 126 g/equiv and a CNE (CTDCN-200, epoxy equivalent weight = 207 g/equiv) were kindly supplied by BaLing Petrochemical of China (Yuegang, China).

Synthesis of HPM

HPM was synthesized by a two-step reaction procedure from *p*-aminophenol and maleic anhydride, as previously described.[19] The chemical structure was characterized by IR spectroscopy and elemental analysis.

IR (KBr, cm^{-1}): 3481 (Ph[bond]OH), 1705 (C=O symmetrical stretching), 1369 (C—N stretching), 714 (C=O bending), 688 (C=C bending). Anal. Calcd: C, 63.49%; H, 3.70%; N, 7.41%. Found: C, 63.51%; H, 3.68%; N, 7.44%.

Synthesis of poly[N-(4-hydroxyphenyl) maleimide-co-dicyclopentadiene] [poly(HPM-*co*-DCPD)]

HPM (18.9 g, 0.1 mol), DCPD (13.2 g, 0.1 mol), AIBN (0.642 g, 0.0039 mol), and toluene (70 mL) were charged under a nitrogen atmosphere in a 250-mL, three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The reaction mixture was maintained at 70°C for 12 h. After the reaction was completed, the mixture was diluted with 100 mL of tetrahydrofuran and precipitated in a water–methanol (50% methanol) mixture. The polymer was purified by repeated precipitation with the same solvent–no solvent system. The polymer was dried *in vacuo* at 70°C.

Hydroxyl equivalent weight = 323.6 g/mol. IR (KBr, cm^{-1}): 3410 (Ph—OH); 3039 (Ar—H); 2929 (—CH$_2$— for the DCPD ring); 1705 (C=O symmetrical stretching); 1516, 1450 (C=C for the benzene ring); 1388 (C—N stretching). ^{1}H-NMR (CD$_3$COCD$_3$, ppm): 8.70 (—OH of phenyl), 6.7–7.2 (aromatic proton), 1.0–3.0 (saturated protons of the DCPD ring).

Curing procedure

The cured epoxy resins were obtained via the thermal curing of poly(HPM-*co*-DCPD) with CNE. The CNE resin was mixed with poly(HPM-*co*-DCPD) or PN at various equivalent ratios of phenolic hydroxyl

to epoxy of 0.3:1, 0.7:1, and 1:1 with imidazole as a curing accelerator. Then, the epoxy–poly(HPM-*co*-DCPD) blend was cured in an oven at 130°C for 1 h (precuring) and at 150°C for 2 h (postcuring). The epoxy–PN blend was cured at 180°C for 2 h (precuring) and at 220°C for 3 h (postcuring). The CNE resins cured with poly(HPM-*co*-DCPD) at various equivalent ratios of phenolic hydroxyl to epoxy of 0.3:1, 0.7:1, and 1:1 were designated as H-*co*-D/CNE-1, H-*co*-D/CNE-2, and H-*co*-D/CNE-3, respectively. The CNE resins cured with PN with the same ratios were designated as PN/CNE-1, PN/CNE-2, and PN/CNE-3, respectively. The PN/CNEs were used as the control samples.

Instrumental analysis and measurements

Fourier transform infrared (FTIR) spectra was recorded with a WQF-410 spectrophotometer (Beijing Rayleigh Analytical Instrument Co., Ltd. Beijing, China) with KBr pellets. ^{1}H-NMR spectra were obtained with an INOVA-400 (Varian, Inc. Palo Alto, CA) with tetramethylsilane as an internal standard and CD$_3$COCD$_3$ as a solvent. Gel permeation chromatography (GPC) analysis was performed on a Waters 1525/2414 GPC instrument (Waters Corporation. Ashland, Massachusetts). Waters Styragel column sets were used with a 1.0 mL/min flow rate of tetrahydrofuran and calibrated by polystyrene standards. Differential scanning calorimetry (DSC) thermograms were recorded with thermal analysis in nitrogen. The dynamic scanning experiments ranged from 30 to 350°C at heating rates of 5, 10, 15, and 20°C. Thermogravimetric analysis (TGA) was done with an STA-449C (Netzsch Inc. Bavaria, Germany) at a heating rate of 10°C/min under a nitrogen atmosphere and at temperatures from room temperature to 800°C. The moisture absorption was tested as follows. Samples of the cured epoxy resins (1 × 1 × 0.1 cm^3) were dried *in vacuo* at 100°C for 24 h until traces of water were expelled; then, they were cooled to room temperature, weighed, placed in boiling water for 24 h, and reweighed, The moisture absorption was calculated as follows:
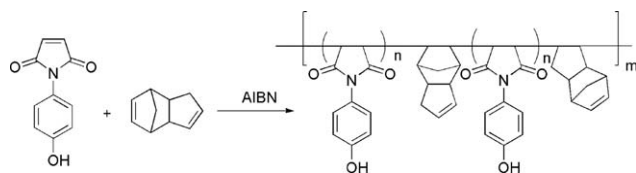
$$\text{Weightgain}(\%) = (W/W_0 - 1) \times 100\%$$

where W is the weight of the sample after its placement in boiling water for 24 h and W_0 is the weight of the sample before its placement in water.

RESULTS AND DISCUSSION

Synthesis and characterization

The copolymer of HPM and DCPD was obtained by free-radical copolymerization with AIBN as the
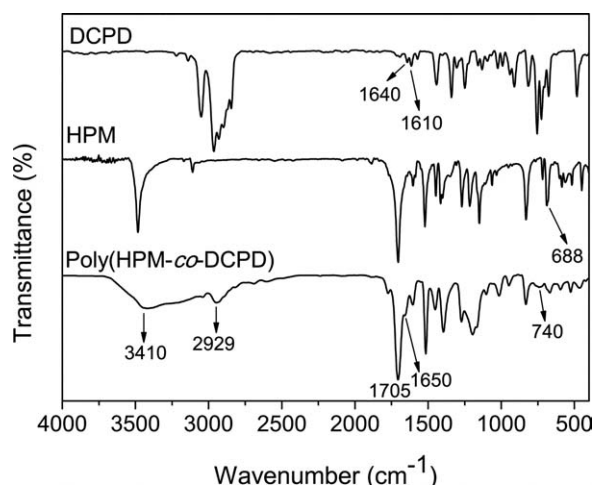
Scheme 1   Synthesis of poly(HPM-co-DCPD).

initiator. The HPM monomer was electron-deficient, which made it more reactive toward the electron-rich DCPD monomer. DCPD did not form a homopolymer under the conditions of the reaction.[20] Thus, Scheme 1 is proposed to depict the copolymerization reaction scheme.

The chemical structure of the obtained poly(HPM-co-DCPD) was characterized with FTIR. Figure 1 shows that the FTIR spectra of poly(HPM-co-DCPD) displayed characteristic absorption peaks at 3410 cm^{-1} (Ph—OH), 1705 cm^{-1} (C=O, symmetrical stretching), and 1388 cm^{-1} (C—N stretching) that characterized the structure of the HPM unit. The FTIR spectra also had bands with a frequency of 2929 cm^{-1} (—CH$_2$—), assigned to the DCPD unit. The frequency of 740 cm^{-1} characterized the DCPD segment. The distinctive absorption at 688 cm^{-1} for C=C in HPM disappeared. The absorption signals for double bonds in DCPD were observed at 1650 and 1604 cm^{-1}; accordingly, it became obvious that both double bonds were conserved in the linear copolymer compared to the starting materials of DCPD.

The chemical structure of the new compound was further confirmed with ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectrum of poly(HPM-co-DCPD) (Fig. 2), all signals corresponding to the proposed structure were observed. The protons adjacent to the cyclopentene ring in DCPD and the norbornene ring in DCPD were present but compressed within the

range 5.34–5.90 pm. This spectrum also proved the persistence of both types of double bonds in the copolymer. The characteristic peaks of the aromatic ring at 6.7–7.2 ppm and the —OH absorption peaks at 8.7 ppm were all observed. The signals in the range 3.35–4.0 ppm corresponded to protons from imide, but their overlapping with the signals of the end bridge protons prevented a sharp integration. The ^{1}H-NMR spectrum exhibited broad peaks at 1.0–3.0 ppm, which were attributed to the presence of saturated protons in the DCPD ring. This demonstrated the success of the poly(HPM-co-DCPD) synthesis.

The obtained poly(HPM-co-DCPD) was also characterized by GPC. The GPC spectra showed that the number-average molecular weight of poly(HPM-co-DCPD) was 1945 g/mol, and the average molecular weight was 2619 g/mol. The molecular weight distribution was 1.27.

All of these characterization confirmed that poly(HPM-co-DCPD) was successfully synthesized.

Curing reaction of poly(HPM-co-DCPD) on the epoxies

The mixture of poly(HPM-co-DCPD) and CNE [Fig. 3(a)] and the cured product H-co-D/CNE-1 [Fig. 3(b)] are shown in Figure 3. In the spectrum of H-co-D/CNE-1, prepared with a hydroxyl equivalent to epoxy equivalent ratio of 0.3, the epoxide group absorption at 910 cm^{-1} was absent, which indicated that the epoxy was completely cured.

The curing reactions of CNE with poly(HPM-co-DCPD) were studied with DSC for the composition with a 0.3:1 hydroxyl equivalent to epoxy equivalent ratio. Figure 4 shows the dynamic heating curves at various heating rates of 5, 10, 15, and 20°C/min. The characteristic curing temperatures for the novel curing agent poly(HPM-co-DCPD) in the presence of

Figure 1   FTIR spectra of DCPD, HPM, and poly(HPM-co-DCPD).
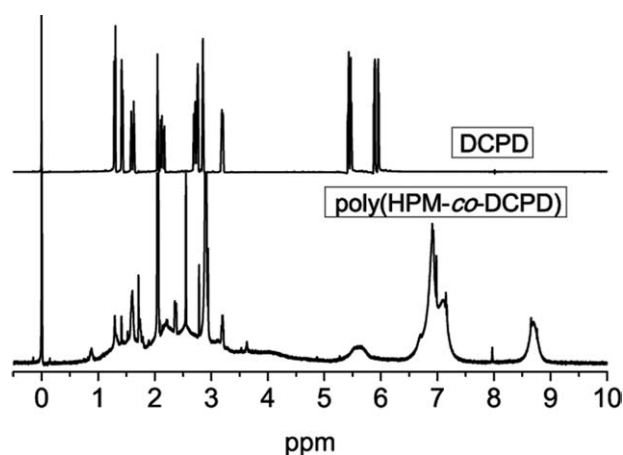
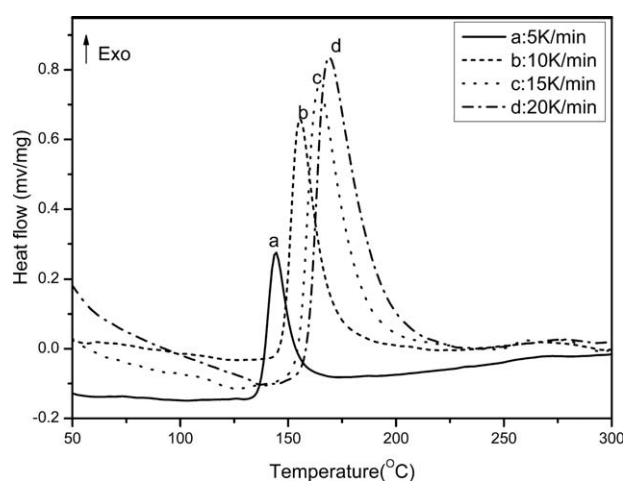Figure 2 ^{1}H-NMR spectra of DCPD and poly(HPM-co-DCPD).
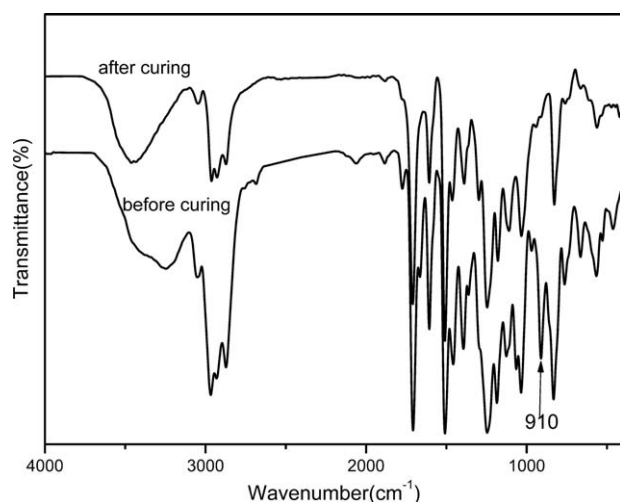
Figure 3 FTIR spectra of (before curing, a) a mixture of poly(HPM-*co*-DCPD) and CNE and (after curing, b) the cured product (H-*co*-D/CNE-1).

CNE are summarized in Table I; these included the kickoff temperature (T_i), where the curing started; the temperature of the peak position of the exotherm (T_p); and the temperature of the end of the curing exotherm (T_f), obtained by the extrapolation of the end of the exothermic transition. As expected in the sample, the peak at curing temperature increased with increasing heating rate.

The activation energy of the poly(HPM-*co*-DCPD)/CNE was determined from DSC studies. It was simulated by the method of Kissinger.[21] The governing equation is shown as follows:

$$-\ln(\beta/Tp^2) = E_k/RTp - \ln AR/E_k \qquad (1)$$

where E_k is the activation energy, β is the heating rate, R is the ideal gas constant, and T_p is the peak

TABLE I
DSC Thermograms of Epoxy Curing at Various Heating Rates for Poly(HPM-*co*-DCPD)/CNE with a Hydroxyl/ Epoxy Equivalent Ratio of 0.3

Entry	Heating rate (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)
1	5	137.4	144.1	153.6
2	10	148.0	155.4	168.6
3	15	155.2	164.1	183.7
4	20	159.1	168.9	192.5

temperature of the DSC thermogram. Hence, the activation energy of the H-*co*-D/CNE-1 was obtained from the slopes of the plots of ln(Heating rate/T_p^2) versus $1/T_p$ [eq. (1)]. The plot is shown in Figure 5. The activation energy of H-*co*-D/CNE-1 (77.75 kJ/mol) was much higher than the activation energy the of diamino diphenyl methane system/CNE (54.3 kJ/mol) with the same analysis method.[22] This implied that poly(HPM-*co*-DCPD) had a lower reactivity toward epoxy groups than the amino agent. Further investigation should be carried out to study curing kinetic models in the future.

Thermal properties of the cured epoxy resins

The thermal properties of the cured resins were evaluated by TGA under nitrogen. Figure 6 shows the TGA thermograms of the cured epoxy resins. The 10% degradation temperature ($T_{10\%}$), the temperature of maximum rate of weight loss (T_{max}), and the char yield percentage at 800°C are shown in Table II. The $T_{10\%}$ values for H-*co*-D/CNE-1, H-*co*-D/CNE-2, and H-*co*-D/CNE-3 were 362, 361, and 357°C, respectively. It exhibited a little lower thermal stability than those of the PN/CNEs (where $T_{10\%}$ under nitrogen was around 375°C). These

Figure 4 DSC thermograms of epoxy curing at various heating rates for poly(HPM-*co*-DCPD)/CNE with a hydroxyl/epoxy equivalent ratio of 0.3.
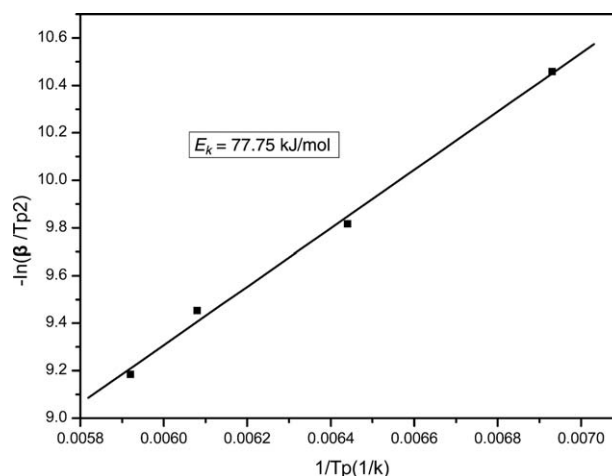

Figure 5 Plot for the determination of E_k by the Kissinger method in different curing reactions for poly(HPM-co-DCPD)/CNE with a hydroxyl/epoxy equivalent ratio of 0.3.
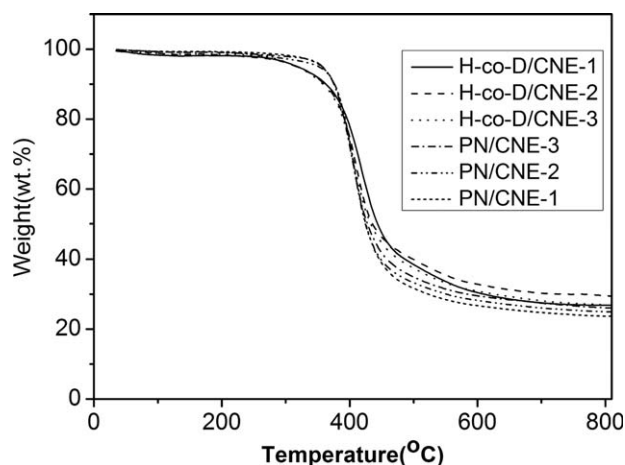
Figure 6 TGA thermograms of the cured epoxy resins.

differences were attributed to the aliphatic structure of DCPD, which reduced the thermostability.[23,24] Then, the T_{max} values for H-co-D/CNE-1, H-co-D/CNE-2, and H-co-D/CNE-3 were 419, 409, and 407°C, respectively. It showed a bit higher thermal stability than those of the PN/CNEs (where T_{max} under nitrogen was around 405°C). Also, the final char yields of poly(HPM-co-DCPD)/CNEs were higher than those of the PN/CNEs at 800°C. The good thermal stability and higher char yields of poly(HPM-co-DCPD)/CNEs could have been due to the incorporation of imide groups into the epoxy resins, which provided better thermal stability.

Moisture absorption

Moisture absorption increased the dielectric constant of the cured polymer and had a detrimental effect on the mechanical properties.[18] Thus, it was important for decreasing the moisture absorption to obtain a higher performance epoxy polymer. Table III summarizes the water absorption of the cured epoxy resins. Because of the hydrophobic nature of the aliphatic DCPD structure, the cured polymers of the poly(HPM-co-DCPD)/CNEs showed a relatively low moisture absorption in the range 1.02–1.51% compared to those of PN/CNEs in the range 1.90–2.59%.

TABLE II
Thermal Properties of the Cured Epoxy Resins at a Heating Rate of 10°C/min

Resin sample	$T_{10\%}$ (°C)	T_{max} (°C)	Char yield at 800°C (%)
H-co-D/CNE-1	362	419	26.9
H-co-D/CNE-2	361	409	29.5
H-co-D/CNE-3	357	407	26.9
PN/CNE-1	375	403	23.7
PN/CNE-2	376	405	24.9
PN/CNE-3	375	405	26.1

TABLE III
Moisture Absorption of the Cured Polymers

Resin sample	Moisture absorption (%)
H-co-D/CNE-1	1.51
H-co-D/CNE-2	1.23
H-co-D/CNE-3	1.02
PN/CNE-1	2.59
PN/CNE-2	2.13
PN/CNE-3	1.90

In addition, the results in Table III show that the moisture absorptions for H-co-D/CNE-1, H-co-D/CNE-2, and H-co-D/CNE-3 were 1.51, 1.23, and 1.02%, respectively. The moisture absorption decreased from 1.51 to 1.02% when the stoichiometric ratio for poly(HPM-co-DCPD) to epoxy increased from 0.3 to 1. This might have been mainly due to the effect of the crosslinking density. The moisture absorption decreased with decreasing crosslink density of the resins, which was consistent with the results reported in other references.[25,26]

CONCLUSIONS

In this article, a novel imide ring and DCPD-containing epoxy curing agent, poly(HPM-co-DCPD), was successfully synthesized through free-radical copolymerization; this compound was used as a curing agent with CNE. The curing kinetics of poly(HPM-co-DCPD)/CNE were studied by the Kissinger method. The results of the curing kinetics investigation show that poly(HPM-co-DCPD) had a lower reactivity toward the epoxy groups than the amino agent. As compared with the PN/CNEs, the poly(HPM-co-DCPD)/CNEs exhibited higher char yields of 26.9–29.5%, good thermal stability ($T_{10\%}$ under nitrogen was around 360°C), and lower moisture absorptions of 1.02–1.51%. The combination of the aforementioned good properties was considered to depend on the introduction of both imide and DCPD moieties into the skeleton. These good overall properties make the resulting epoxy curing agent an alternative method for obtaining a packaging material.

References

1. Zuo, C. W.; Han, J. L.; Si, Z. H.; Xue, G. J Appl Polym Sci 2009, 114, 3889.
2. Hwang, H. J.; Hsu, S. W.; Chung, C. L.; Wang, C. S. React Funct Polym 2008, 68, 1185.
3. Liu, R.; Wang, X. D. Polym Degrad Stab 2009, 94, 617.
4. Yang, Y.; Chen, G.; Liew, K. M. J Appl Polym Sci 2009, 114, 2706.
5. Kim, W. G.; Lee, J. Y. J Appl Polym Sci 2002, 86, 1942.
6. Ren, H.; Sun, J. Z.; Zhao, Q. Polymer 2008, 49, 5249.
7. Dai, Z.; Li, Y. F.; Yang, S. G.; Zhao, N.; Zhang, X. L.; Xu, J. Eur Polym J 2009, 45, 1941.

8. Tao, Z. Q.; Yang, S. Y.; Chen, J. S.; Fan, L. Eur Polym J 2007, 43, 1470.

9. Ahmad, S.; Gupta, A. P.; Sharmin, E.; Alam, M.; Pandey, S. K. Prog Org Coat 2005, 54, 248.

10. Levchik, S. V.; Weil, E. D. Polym Int 2004, 53, 1901.

11. Wu, W. L.; Hsu, K. C.; Cheng, W. H. J Appl Polym Sci 2008, 108, 2052.

12. Shau, M. D.; Chin, W. K. J Polym Sci Part A: Polym Chem 1993, 31, 1653.

13. Sharma, P.; Choudhary, V.; Narula, A. K. J Appl Polym Sci 2006, 101, 3503.

14. Abraham, G.; Packirisamy, S.; Vijayan, T. M.; Ramaswamy, R. J Appl Polym Sci 2003, 88, 1734.

15. Gouri, C.; Reghunadhan Nair, C. P.; Ramaswamy, R. J Appl Polym Sci 1993, 73, 695.

16. Shieh, J. Y.; Lin, C. Y.; Huang, C. L.; Wang, C. S. J Appl Polym Sci 2006, 101, 342.

17. Hwang, H. J.; Shieh, J. Y.; Li, C. H.; Wang, C. S. J Appl Polym Sci 2007, 103, 1942.

18. Ren, H.; Sun, J. Z.; Wu, B. J.; Zhou, Q. Y. Polymer 2006, 47, 8309.

19. Liu, Y. L.; Chen, Y. J.; Wei, W. L. Polymer 2003, 44, 6465.

20. Akhmedov, A. I.; Isakov, É. Chem Technol Fuels Oils 1989, 25, 156.

21. Kissinger, H. E. Anal Chem 1957, 29, 1072.

22. Rwei, S. P.; Cheng, C. Y.; Liou, G. S.; Cheng, K. C. Polym Eng Sci 2005, 45, 478.

23. Lin, C. H.; Chiang, J. C.; Wang, C. S. J Appl Polym Sci 2003, 88, 2607.

24. Hsiue, G. H.; Wei, H. F.; Shiao, S. J.; Kuo, W. J.; Sha, Y. A. Polym Degrad Stab 2001, 73, 309.

25. Karad, S. K.; Attwood, D.; Jones, F. R. Compos A 2005, 36, 764.

26. Jeffrey, K.; Pethric, R. A. Eur Polym J 1994, 30, 153.