Toughening Epoxy Resin with Blocked Isocyanate Containing Soft Chain

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ABSTRACT: A series of imidazole (MI) blocked 2,4-toluene diisocyanate (TDI) with polyethylene glycol (PEG-400) as soft segment (PEG-MI-*b*-TDI) were synthesized for toughening and curing the bisphenol A type epoxy resin (E-44). Fourier transform infrared (FTIR) spectrum indicates that the NCO groups of the isocyanate molecule are blocked with MI. For curing epoxy systems, elimination of epoxy group and the formation of urethane bonds were studied by FTIR spectroscopy. The results of mechanical property were shown that the tensile shear and impact strengths of neat MI and MI-*b*-TDI cured E-44 are lower than those of PEG-MI-*b*-TDI cured E-44. Based on the scanning electron microscope studies, microstructure evolutions of the E-44 cured by different curing agents were imaged. The mechanical, thermal, and dynamic mechanical properties were measured by universal testing machine, differential scanning calorimeter and dynamic mechanical analyzer (DMA). The toughness of E-44 cured by PEG-MI-*b*-TDI was effectively improved without sacrificing the tensile shear strength. Based on the DMA studies, the long soft chain of PEG brought in a noticeable lowering in the glass transition temperature (T_g). The glass transition temperature is near 165°C for the neat MI cured E-44, which is higher than the T_gs of the other curing agents cured epoxy. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41345.

INTRODUCTION

Epoxy resins are widely used as matrix resins for fiber-reinforced composites due to high-mechanical strength and modulus, good adhesion property, and dimensional stability.[1–3] However, as a consequence of their highly cross-linked structure, these materials tend to suffer from brittleness, poor crack resistance, and low fracture toughness, which limit their applications in certain areas.[4–6] Therefore, much research has been carried out to enhance the toughness of the cured epoxy resins without any significant loss in other properties.[7,8]

Several methods have been proposed for increasing the toughness of epoxy resins and one of the most effective approaches is the introduction of a second component which is capable of phase separation as reactive liquid rubber,[9–11] thermoplastic,[12,13] or core-shell particles.[14–16] Considerable attention has been paid to the use of functionalized curing agents for epoxy resins. The toughness of the epoxy resins could be improved by designing molecule structure of curing agents or synthesizing flexible curing agents,[17] what is an increasingly popular option now.

For epoxy resins, the curing agent having polyfunctionality is the most ideal product due to its excellent curing property. It is well known that isocyanates react with compounds containing active hydrogen atoms easily, which can also react with epoxy. However, the high reactivity of isocyanates do not allow their storage and use in one-component systems,[18,19] which would have been, satisfactorily, overcome by blocking them with a compound containing an active hydrogen atom, blocking agent, through the formation of carbamate having a labile bond which can dissociate at a higher temperature to regenerate isocyanate and blocking agent functionality.[20,21] The imidazole (MI) is not only the blocking agent of isocyanates but also the most widely used curing agent in the epoxy resins. Hence, in this article, isocyanate was blocked by MI, after isocyanate reacted with soft segment of flexible molecules to form isocyanate prepolymer, what the functional curing agent was obtained. A rapid reaction between a multifunctional isocyanate and a hydroxyl terminated oligomer leaded to form of urethane bond (—NH—CO—O—). The polyethylene glycol (PEG) is a kind of macromolecule with long soft chain structure. When PEG reacted with

Table I. Raw Materials List

Designation	Chemical description	Suppliers
E-44	Bisphenol A type epoxy resin	Wuxi Guangming Huagong Equipment Co., (China)
TDI	2,4-Toluene diisocyanate	ICI company (Britain)
PEG-400	Polyethylene glycol	Tianjin Kermel Chemical Reagent Co. (China)
DMF	N,N-dimethylformamide	Tianjin Kermel Chemical Reagent Co. (China)
MI	Imidazole	Tianjin Kermel Chemical Reagent Co. (China)

polyisocyanate as soft segment, the isocyanate prepolymer with long soft chain structure would be prepared. During the process of curing epoxy resins, this functional curing agent could release MI and free ─NCO groups which would react with epoxy groups. So, the soft chain would be introduced in the epoxy matrix. Thus, the epoxy resin could be toughened by the blocked isocyanate having long soft chain (PEG-MI-*b*─2,4-toluene diisocyanate (TDI)).

The aim of this study was to investigate the morphology and properties of epoxy resins toughened by blocked isocyanate having long soft chain structure. By studying the effect of curing agent structure and blocking and deblocking on the toughness of the epoxy resin, a novel flexible curing agent was developed which would offer new insight to the mechanism for epoxy toughness improvement.
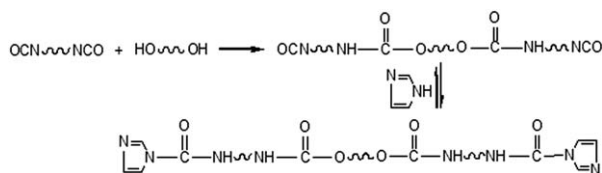
EXPERIMENTAL

Materials
The raw materials used in this study are listed in Table I. All these materials except epoxy resin were laboratory grade chemicals and were used without further purification. *N,N*-dimethylformamide (DMF) was dried by a 4 Å molecular sieve for 24 h followed by distillation before use.

Preparation of Blocked Isocyanate
A 250-mL four-necked flask equipped with mechanical stirrer, nitrogen inlet, condenser, and thermometer was charged with PEG-400, and TDI, which molar ratio of NCO/OH was 100 : (1–4). Then, DMF was directly mixed in. The reactants were heated at 50°C in a constant temperature bath. The reaction time was 1 h. Then, the blocking agent, NCO: (H + OH) was 1 : 1.1, was added in one-time fashion. The reactants were heated at 60°C for 2 h. Thus, the functional curing agent, MI blocked isocyanate, was prepared.

Curing Conditions
The prepared specimens, which MI content was 4 wt % of E-44, were placed in an air-circulating oven at 100°C for 2 h.

In the next step, the specimens were removed from the oven and allowed to cool to room temperature.

Characterizations and Measurements
FTIR Analysis. Fourier transform infrared (FTIR) spectra for the samples were recorded using Spectrum 100 FTIR (PerkinElmer Corporation, USA) analyzer in the range of 4000–400 cm^{-1}; the samples were dissolved in acetone and evaporated on potassium bromide disk under infrared lamp.

Differential Scanning Calorimetric Analysis. A differential scanning calorimeter (DSC 204F1, Netzsch, Germany) was used to examine the thermal behavior of epoxy matrix. Samples of ~10 mg were sealed in aluminum pans and ramped from 30 to 300°C under nitrogen gas at 10°C/min.

Scanning Electron Microscopy Analysis. The fracture surface of fractured specimens from charpy impact test was analyzed using S-3400 (Hitachi, Japan) scanning electron microscope (SEM). All the specimens were sputter coated with gold before taking the micrographs in order to reduce the charging effect.

Dynamic Mechanical Analysis. Thermodynamic properties of specimens were measured using a dynamic mechanical analyzer (DMA) Q800 (TA company, USA). DMA over a temperature range from 40 to 180°C at a heating rate of 4°C/min at 11 Hz. The samples were rectangular bars (40 mm × 10 mm × 4 mm).

Tensile Shear and Impact Strength Tests. Tensile shear tests were put into practice on a NLW-20 shear tester of adhesive at
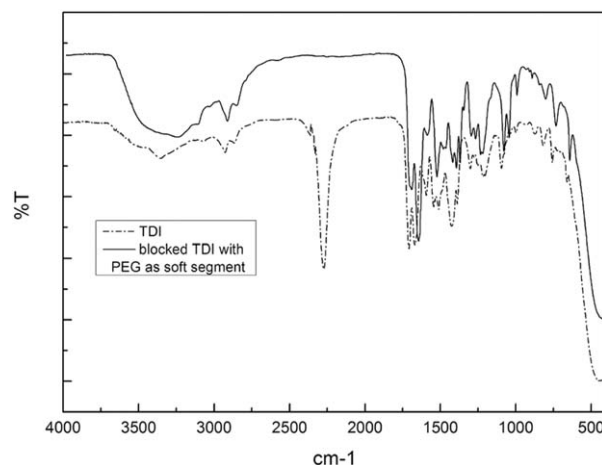

Scheme 1. Synthesis of functional curing agents.

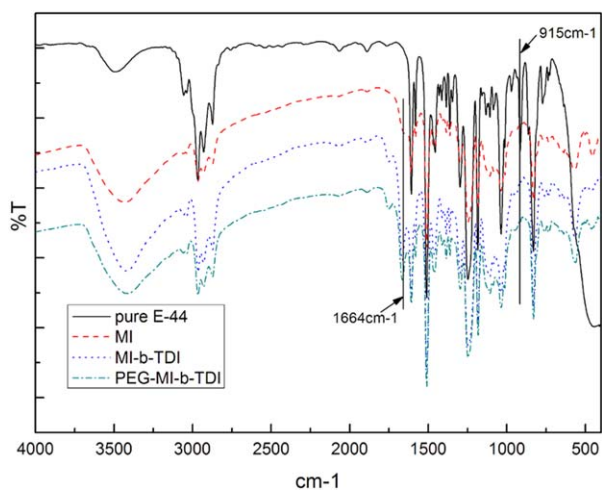**Figure 1.** FTIR spectra of blocked isocyanates with PEG as soft segments.

Figure 2. FTIR spectra of cured epoxy resin systems with different curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

room temperature. Joint areas of aluminum alloy specimen were 15×15 mm^2.

Impact tests were carried out on a JJ-20 memorable impact tester at room temperature. Specimens were molded with dimension of 80 mm length, 10 mm width, and 4 mm thickness.

RESULTS AND DISCUSSION

Synthesis of Functional Curing Agents
The functional curing agents (PEG-MI-*b*-TDI) were synthesized from TDI, PEG-400, and MI, as shown in Scheme 1.

FTIR Analysis
FTIR Analysis of Blocked Isocyanates with PEG as Soft Segments. The FTIR spectra of blocked isocyanates with PEG as soft segments were depicted in Figure 1.

The NCO group had characteristic absorption peak at around 2250–2270 cm^{-1} which was due to the antisymmetric stretching. From Figure 1, the NCO absorption peak at 2270 cm^{-1} was seen to decrease sharply when PEG-400 was 1%. This indicated that the NCO groups of the isocyanate molecule were blocked with the H of MI and the OH of PEG.[22]

FTIR Analysis of Cured Epoxy Resin Systems. The FTIR spectra of cured epoxy resin systems were shown in Figure 2.

From Figure 2, the absorption characteristic of epoxy group was at 915 cm^{-1}. The strong absorptions at 3400 cm^{-1} (OH forms hydrogen bend) increased gradually. There was a strong absorption at 1664 cm^{-1} (stretching vibration of —NH—C(=O)—) when the curing agent was MI-*b*-TDI or PEG-*b*-TDI. These all
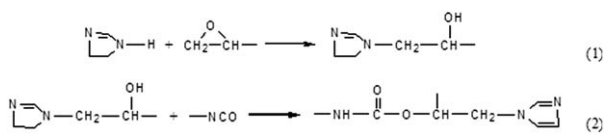
Table II. Tensile Shear Strength of Epoxy Resins Cured by Different Curing Agents

| Curing agents | MI | $n_{-OH} : n_{-NCO}$ (PEG-400 as soft segment) | | | | |
		0	1	2	3	4
Tensile shear strength (MPa)	7.528	8.957	10.510	8.476	8.390	6.543

conclude that the scheme which epoxy resins react with amine curing agents was as Scheme 2.

The epoxy groups reacted with the primary amine to secondary hydroxyl group. Thus, the epoxy groups disappeared and the hydroxyl groups increased. Then, the secondary hydroxyl groups reacted continuous with NCO group.[23]

Mechanical Properties
The effects of curing agents with various PEG-400 contents on tensile shear strength and impact strength were presented in Tables II and III, respectively. In Table II, compared with neat MI curing agent, the tensile shear strength of TDI blocked by MI (MI-*b*-TDI) as curing agent initially increased from 7.528 to 8.957 MPa by about 19%. It was found that the tensile shear strengths of neat MI and MI-*b*-TDI cured E-44 were lower than those of PEG-MI-*b*-TDI cured E-44, which could be attributed to the presence of long soft chains within the epoxy matrix. There was an increase in the tensile shear strength with PEG-400 content up to 1%, and then a gradual decreased with increasing the PEG-400 content. Beyond 1%, the reduction in the values of curing system might be ascribed to the finite NCO of TDI occupying the reaction centers of the PEG during blocking reaction. That is to say, some OH of PEG-400 reacted with NCO which would offer mechanical strength of the cured epoxy system, others which did not react would be as lubricant or impurity.

Table III illustrated the Charpy impact strengths of the epoxy samples. It was evident from Table III that the impact strengths increased with an increase in PEG content. As PEG content was 1%, the impact strengths attained a maximum, and then decreased. In order to explain the phenomenon, the structures of curing agents should be taken into account. The impact strength of MI-*b*-TDI cured E-44 was low and toughening became less effective which was due to the limit of soft structure —NH—CO—O—. However, it was long soft chain of PEG that made impact strength of PEG-MI-*b*-TDI cured E-44 higher and toughening more effective. There was a decrease in impact

Table III. Impact Strength of Epoxy Resins Cured by Different Curing Agents

| Curing agents | MI | $n_{-OH} : n_{-NCO}$ (PEG-400 as soft segment) | | | | |
		0	1	2	3	4
Impact strength (kJ/m^2)	2.995	4.414	22.364	6.975	6.795	4.549

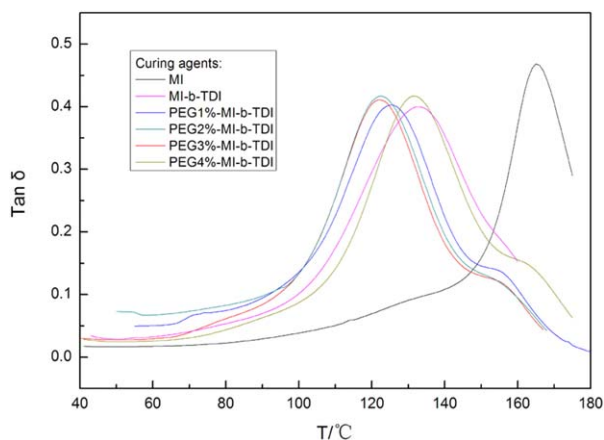**Scheme 2.** Scheme of imidazole blocked isocyanate curing epoxy resin.

Figure 3. Effect of different curing agents on tan δ. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strength above 1% of PEG content.[6] That might be because the PEG unreacted in time would play a lubricant role in the system. So the more PEG contents were there in system, the lower was impact strength. This would be explained in terms of the result of SEM and thermodynamic properties.

Dynamic Mechanical Thermal Analysis
Dynamic mechanical loss factor (tan δ) and storage modulus (E') of different curing agents cured epoxy as a function of temperature were depicted in Figures 3 and 4, respectively. The glass transition temperature was near 165°C for the neat MI cured E-44, which was higher than the T_gs of the other curing agent cured epoxy. In other words, the blocked isocyanate in epoxy system caused a significant decrease in the glass transition temperature. The glass transition temperatures were list in Table IV. With the increase in PEG content, there were unreacted PEG and uncompleted deblocking reaction which made E-44 uncompleted reaction. It was for this reason that there was a small second tan δ peak at around 160°C for each PEG-MI-b-TDI sample.

Figure 4 showed that the neat MI cured epoxy had higher initial storage modulus. In all samples, the values of E' decreased with increase in temperature. A significant drop in epoxy at about

Table IV. DMA and DSC Results for Epoxy Resins

Curing agents	T_g (°C)	T_c (°C)
MI	165	117.4
MI-b-TDI	133	120.0
PEG1%-MI-b-TDI	125	127.0
PEG2%-MI-b-TDI	122	125.0
PEG3%-MI-b-TDI	122.5	127.6
PEG4%-MI-b-TDI	132	125.0

T_c, curing temperature.

120°C might be attributed to the T_gs of the epoxy system cured by PEG-MI-b-TDI. The second at near the α relaxation peak of epoxy network. The relaxation peak of the neat MI cured epoxy located at the highest temperature, which was due to no soft structure in the epoxy matrix.

DSC Analysis
The activities of the epoxy systems were related with both epoxy resins and curing agents. The measurements of reaction heats were significant to select resin matrix, curing agent type, and dosage. Figure 5 showed the DSC curves of different curing agents cured epoxy resins. The curing temperatures were listed in Table IV.

As seen in Figure 5, there was one significant curing exothermic peak, respectively, at the same heating rate. The location of curing exothermic peak and reaction heat were diverse with different curing agents. The temperature of the exothermic peak was the lowest when the neat MI cured E-44, which indicated that the curing agent was more activated, whereas the curing agents of blocked isocyanates had been cut down at a certain extent.

Scanning Electron Microscopic Analysis
The fractured surfaces of different curing agents cured epoxy samples from charpy impact test were studied by SEM. The morphology pattern of MI cured epoxy [Figure 6(a)] showed smooth and MI-b-TDI cured E-44 showed glassy fractured surfaces with ripples [Figure 6(b)]. PEG-MI-b-TDI cured E-44
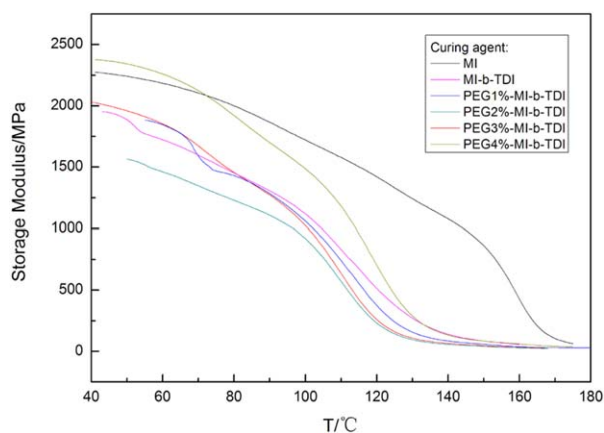

Figure 4. Effect of different curing agents on storage modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
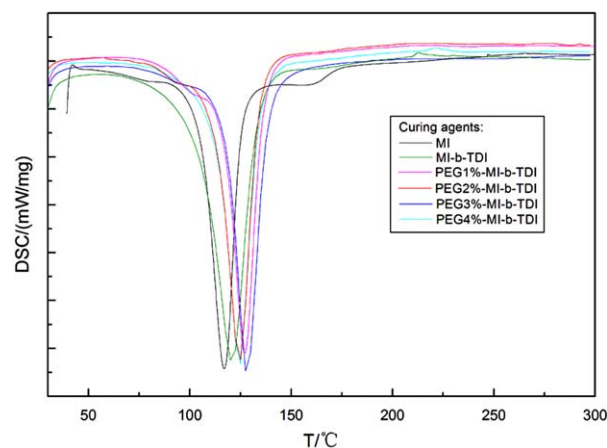

Figure 5. DSC curves of different curing agents with PEG-400 as soft segments cured epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
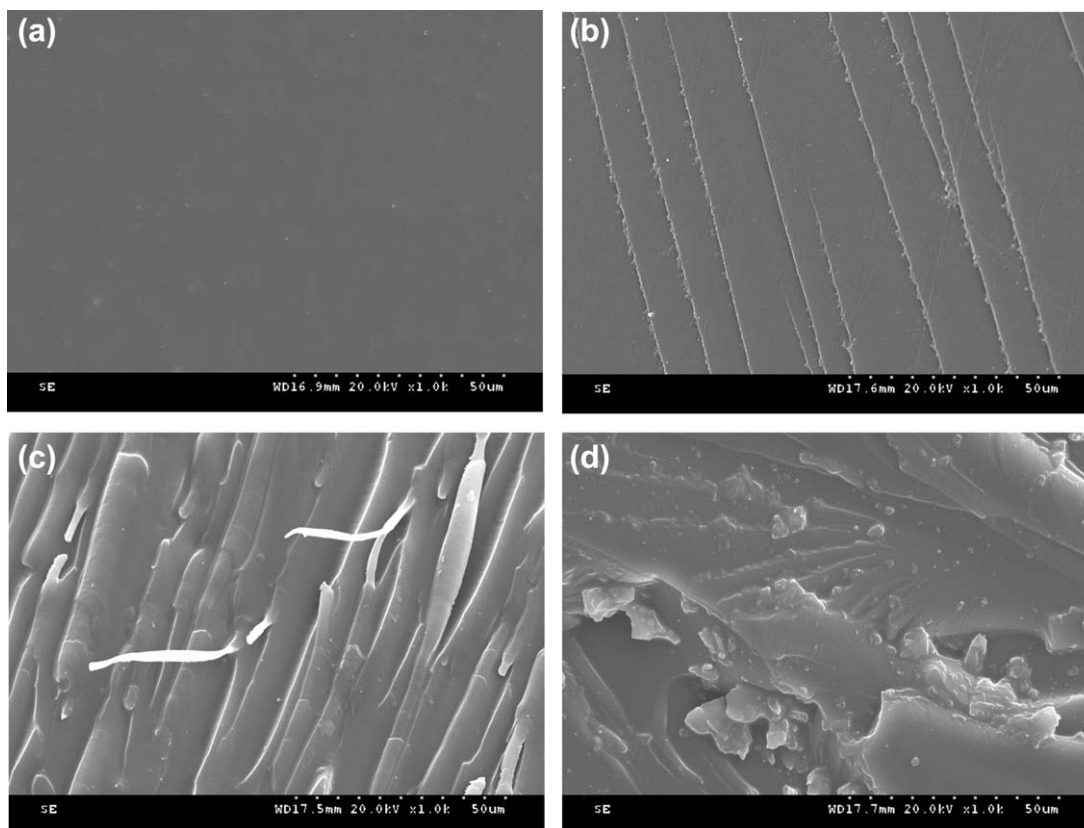
Figure 6. SEM micrographs of epoxy resins with PEG-400 as soft segments cured by different curing agent. Curing agent: (a) MI; (b) MI-*b*-TDI; (c) PEG-MI-*b*-TDI ($n_{OH} : n_{NCO}$ is 1 : 100); (d) PEG-MI-*b*-TDI ($n_{OH} : n_{NCO}$ is 4 : 100).

showed very rough [Figure 6(c,d)].[24] When PEG content was 1% [Figure 6(c)], the whole systems were a homogeneous phase structure. However, when PEG content was 4% [Figure 6(d)], there were many particles among the matrix. That might be unreacted PEG. From Figure 6, the toughness of the PEG-MI-*b*-TDI cured E-44 could be improved effectively.

CONCLUSIONS

In this study, PEG was used for soft segment of MI blocked isocyanate, which was used for functional curing agents of epoxy resins. These could be synthesized by TDI, PEG-400, and MI. When the molar ratio of OH was 1% of NCO, an optimum content of PEG into the epoxy resin could offer higher toughening and impact strength than those of the neat MI and MI-*b*-TDI cured epoxy resins, respectively. The toughness of the PEG-MI-*b*-TDI cured E-44 could be improved effectively without sacrificing the tensile shear strength. With the incorporation of the PEG-400, the glass transition temperature of epoxy system could decrease as well.

ACKNOWLEDGMENTS

REFERENCES

1. Emel, Y.; Özdemir, Ö.; Tülay, Y. İ.; Abdülkadir, K.; Attila, G. *Polym. Bull.* **2007**, *58*, 503.

2. Lou, C. H.; Kong, X. Z.; Wang, J. X.; Ma, L. Q. *J. App. Polym. Sci.* **2012**, *125*, 578.

3. Zhang, Y.; Shang, C. Y.; Yang, X.; Zhao, X. J.; Huang, W. *J. Mater. Sci.* **2012**, *47*, 4415.

4. Blanco, I.; Oliveri, L.; Cicala, G.; Recca, A. *J. Therm. Anal. Calorim.* **2012**, *108*, 685.

5. Akbari, R.; Beheshty, M. H.; Shervin, M. *Iran. Polym. J.* **2013**, *22*, 313.

6. Zhang, X. G.; Zhang, B.; Sun, M. M.; Li, J. H.; Wang, L.; Qin, C. L. *Pigment Resin Technol.* **2012**, *41*, 104.

7. Yang, X. T.; Yi, F. P.; Xin, Z. R.; Zheng, S. X. *Polymer* **2009**, *50*, 4089.

8. Samanta, B.; Maity, T.; Banthia, A. K. *Pigment Resin Technol.* **2009**, *38*, 143.

9. Cengiz, C.; Guneri, A.; Cevdet, K. *Polym. Bull.* **2004**, *51*, 429.

10. Kong, J.; Ning, R. C.; Tang, Y. S. *J. Mater. Sci.* **2006**, *41*, 1639.

11. Kong, J.; Tang, Y. S.; Zhang, X. J.; Gu, J. W. *Polym. Bull.* **2008**, *60*, 229.

12. Kinlooch, A. J.; Taylor, A. C. *J. Mater. Sci.* **2006**, *41*, 3271.

13. Wang, M. H.; Yu, Y. F.; Li, S. J. *Sci. China Ser. B: Chem.* **2007**, *50*, 554.

14. Yan, C.; Xiao, K. Q.; Ye, L.; Mai, Y. W. *J. Mater. Sci.* **2002**, *37*, 921.

15. Becu, L.; Taha, M.; Maazouz, A.; Merle, G. *J. Mater. Sci.* **2002**, *37*, 41.

16. Ormaetxea, M.; Forcada, J.; Mugika, F.; Valea, A.; Martin, M. D.; Marieta, C.; Goyanes, S.; Mondragon, I. *J. Mater. Sci.* **2001**, *36*, 845.

17. Lou, C. H.; Gu, J. Y.; Di, M. W.; Ma, L. Q.; Wang, Y. Z.; Liu, X. J. *Iran. Polym. J.* **2011**, *20*, 247.

18. Sankar, G.; Nasar, A. S. *Eur. Polym. J.* **2009**, *45*, 911.

19. Subramani, S.; Park, Y. J.; Lee, Y. S.; Kim, J. H. *Prog. Org. Coat* **2003**, *48*, 71.

20. Gnanarajan, T. P.; Iyer, N. P.; Nasar, A. S.; Radhakrishnan, G. *Eur. Polym. J.* **2002**, *38*, 487.

21. Yin, L. G.; Liu, Y. L.; Ke, Z.; Yin, J. H. *Eur. Polym. J.* **2009**, *45*, 191.

22. Li, A. F.; Fan, G. D.; Chen, H.; Zhao Q. *Res. Chem. Intermed.* **2013**, *39*, 3565.

23. Jin, H.; Zhang, Y. G.; Wang, C. S.; Sun, Y. F.; Yuan, Z. R.; Pan, Y. Q.; Xie, H. F.; Cheng, R. S. *J. Therm. Anal. Calorim.* **2014**, *117*, 773.

24. Szeluga, U.; Moryc, P. *J. Therm. Anal. Calorim.* **2013**, *114*, 137.