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ORIGINAL PAPER

Synthesis and application on UV-curable epoxy/dendritic maleate resin

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Abstract The dendritic polyester, dendritic maleate, and epoxy/dendritic maleate resins were synthesized and analyzed by acid value, hydroxyl value, FT-IR, TGA, and DSC. The dendritic maleate and epoxy/dendritic maleate resins were applied in UV-curable coating, and the properties of the UV-curable coatings were compared. With the introduction of epoxy resin, the epoxy/dendritic maleate resin formed larger cross linked structure and more cavities which helped to improve the properties of coating. The epoxy/dendritic maleate resin exhibited higher thermal decomposition temperature and T_g. The coating based on equal content of epoxy resin and dendritic maleate had higher gel content and better properties such as impact strength, adhesive strength, flexibility, pencil hardness, and solvent resistances. The SEM figures showed that the epoxy/dendritic maleate resin could form more cavities and improve the toughness of coating.

Keywords Dendritic polyester · Maleate · Epoxy resin · Coating ·
Thermal properties · Mechanical properties

Introduction

The development of new coating systems has been pushed forward by new demands on technical performance and environmental concerns [1]. UV-curable technology, for its fast curing speed and environmental friendliness, has been developed fast

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during the past decade [2, 3]. The new resin has been presented, and significant improvement has been obtained. Some new polymers have been developed by the introduction of new reactive groups or new backbone structures [4, 5]. The polymer structure can be divided into several subgroups ranging from linear to highly branched or side chain grafted structures. Also there is an increasing interest in modifying the properties of polymer by changing the macromolecular structure [6].

Dendritic polyester as a kind of new functional material is built from monomers containing three or more reactive groups. They have high geometric symmetry, accurate structure, and a large number of end groups which make them show the lower viscosity [7, 8], higher reactivity [9, 10], and better mutual solubility than their linear counterparts [11]. Their advantages on constructing supramolecular network give them potential application in the UV-curable coating. They would be a wonderful prepolymer and provide the base structure to link the different molecules. Modifying their end groups has a large influence on the properties of the UV-curable coating [12, 13]. Nowadays various dendritic polyesters have been developed on using the reactive groups to build the dendritic blocks, and the system will be modified suitably with the introduction of a rigid or a flexible unit. However, the reports about the dendritic polyester applied in UV-curable coating are still very less. The cost and the lack of appropriate modified system limited the application of dendritic polyester for UV-curable coating in industrial field.

Epoxy resins are used extensively for their relatively low cost and good qualities, which are welcomed as a matrix for high temperature composites, mechanical, chemical, and corrosion resistance [14, 15]. A favorable property of epoxy resins is the low viscosity in the uncured state that enables them to be processed without the use of high pressure equipments [16]. Epoxy resins can be widely used as coatings, electronic materials, and adhesives. But the main disadvantage in their applications is their inherent brittleness. The highly cross-linked structure of epoxy resin affects the durability [17–19].

Directly introducing the epoxy resin into the structure of dendritic polyester and changing the chemical structure of dendritic polyester with cross-linked network is a unique way for the modification of dendritic polyester. It would composite the excellent properties of dendritic polyester and epoxy resin, and brings actual importance such as lower price, less consumption of solvents, faster curing speed, and better toughness for UV-curable coating. Some of hyperbranched polymers have been explored as low-viscosity tougheners for epoxy resins to increase the fracture toughness properties [20, 21]. Hydroxyl functionalized hyperbranched polymers can effectively toughen epoxy resins without compromising the ease of process ability [22, 23]. In fact, the reactive end groups control the final morphology because of their solubility with the epoxy resin. All of these theoretical researches provide the possibility of building the network about epoxy/dendritic polyester. Varying the linked units is a very powerful tool for designing the final properties of epoxy/dendritic polyester network and help to improve the properties of UV-curable coating.

The present work aims to study the synthesis of the epoxy/dendritic maleate resin and its application in UV-curable coating. The synthesis and characterization of dendritic polyester with 12 terminal hydroxyl groups and dendritic maleate with 12 terminal carboxyl groups are addressed. The different epoxy/dendritic maleate resins are prepared for UV-curable coatings, and the properties of coatings are evaluated.

Experimental

Materials

Phthalic anhydride (PA, 97%), trimethylol propane (TMP, 97%), stannous chloride ($SnC1_2$), tetraethylammonium bromide (TEAB), *N*,*N*-dimethyl formamide (DMF), maleic anhydride (MA, 97%), and epoxy resin (E44 6101) were procured from the Third Reagent Co. (Beijing, China). Glycidol (GLY, 97%), β-hydroxyethyl methacrylate (HEMA, 99%), silane coupling agent, and α,α-dimethyl-α-hydroxyl acetophenone (Darocure 1173) were purchased from Aladdin (Shanghai, China).

Polymerization

Synthesis of dendritic polyester

Dendritic polyesters were synthesized by two-step procedures as shown in Fig. 1. First, TMP (5 g), PA (23.4 g), and catalytic amount of $SnC1_2$ were put into DMF (20 mL). The mixture was left stirring at 90 °C until the acid value was not changed. Second, the mixture of GLY (12.7 g) and catalytic amount of TEBA was added dropwise at 100 °C. The reaction was ended at a constant acid value. By separating the residual GLY and DMF through vacuum distillation, the polyester DHBP1 with 6 terminal hydroxyl groups was gained. Repeating above procedures, the polyester DHBP2 with 12 terminal hydroxyl groups was synthesized from the polyester DHBP1 (5 g), PA (7.4 g), and GLY (6.44 g).

The polyester DHBP1: ^{1}H-NMR ($CDCl_3$; δ, ppm) = 7.52–8.08 (Ar–$\underline{H}$), 4.31–4.35 (–O–C$\underline{H}_2$–CH–), 3.99 (–C–C$\underline{H}_2$–O–), 3.78–3.82 (–CH_2–C$\underline{H}$–), 3.56–3.58 (–CH–C$\underline{H}_2$–OH), 1.51 (–C$\underline{H}_2$–CH_3), 0.93 (–C–C$\underline{H}_3$).

The polyester DHBP2: ^{1}H-NMR ($CDCl_3$; δ, ppm) = 7.53–8.08 (Ar–$\underline{H}$), 5.12 (–CH_2–C$\underline{H}$–CH_2–), 4.46 (–O–C$\underline{H}_2$–CO–), 4.35 (–O–C$\underline{H}_2$–CH–), 4.26–4.29 (–O–C$\underline{H}$–CH_2–), 3.98 (–C–C$\underline{H}_2$–O–), 3.8–3.84 (–CH_2–C$\underline{H}$–), 3.57–3.62 (–CH–C$\underline{H}_2$–OH), 1.25 (–C$\underline{H}_2$–CH_3), 0.89 (–C–C$\underline{H}_3$).

Synthesis of dendritic maleate

The dendritic maleate (DHBP2-MA) was synthesized from the polyester DHBP2 (7 g) and MA (4.2 g). TEAB was served as catalyst. The mixture was left stirring at 70 °C until the acid value was not changed. The procedure was shown in Fig. 2. The polyester DHBP2-MA had 12 terminal carboxyl groups.

^{1}H-NMR($CDCl_3$, δ, ppm) = 8.07–7.32 (Ar–$\underline{H}$), 6.34–6.32 (–C$\underline{H}$=C$\underline{H}$–), 4.59 (–CH_2–C$\underline{H}$–CH_2–), 4.51 (–O–C$\underline{H}_2$–CO–), 4.47 (–O–C$\underline{H}_2$–CH–), 4.43–4.29

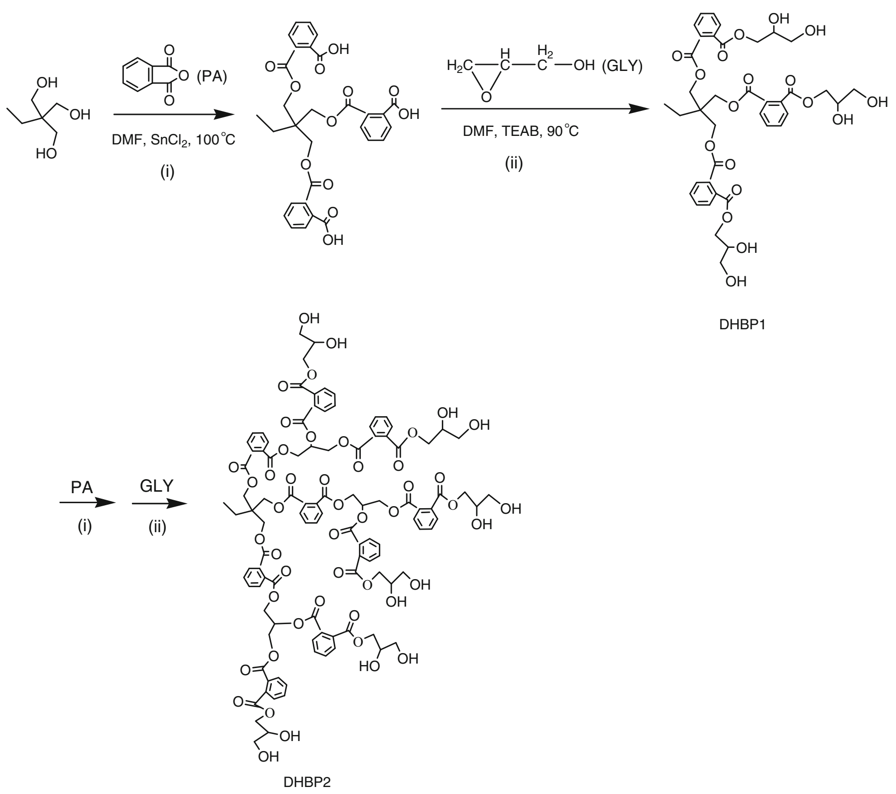

Fig. 1 Synthesis of dendritic polyester DHBP2

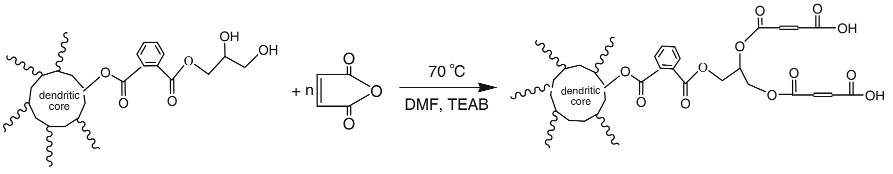

Fig. 2 Synthesis of dendritic maleate

$(-O-C\underline{H}-CH_2-)$, 3.21 $(-C-C\underline{H}_2-O-)$, 3.04–2.94 $(-CH_2-C\underline{H}-)$, 2.89–2.88 $(-CH-C\underline{H}_2-OH)$, 1.27 $(-C\underline{H}_2-CH_3)$, 0.96 $(-C-C\underline{H}_3)$.

Synthesis of epoxy/dendritic maleate resin

Epoxy/dendritic maleate resins 1–3 were synthesized from the dendritic maleate DHBP2-MA and E44. TEAB was served as catalyst. The mixture was left stirring at 80 °C until the acid value was not changed. Resins 1–3 with different amount of epoxy resins were synthesized according to the same general procedure as described in Fig. 3. Data on resins 1–3 were listed in Table 1.

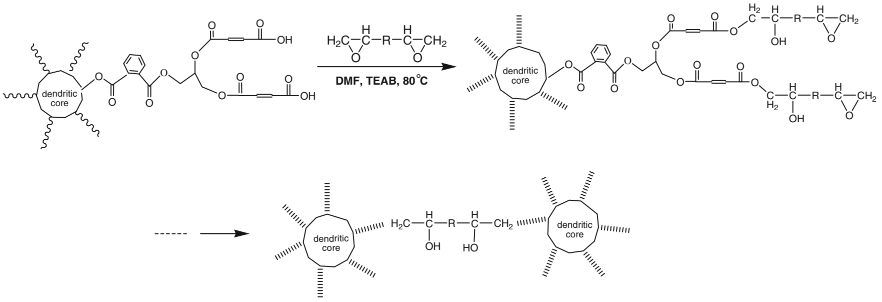

Fig. 3 Synthesis of epoxy/dendritic maleate resin

Table 1 Formulations of the epoxy/dendritic maleate resins 1–3

Sample	Epoxy group: carboxyl group (mol:mol)	Main end groups of resin
Resin 1	0.5:1	Carboxyl group, hydroxyl group
Resin 2	1:1	Hydroxyl group
Resin 3	2:1	Epoxy group, hydroxyl group

Preparation of UV-curable coating

UV-curable coatings of DHBP2-MA and resins 1–3 were prepared by a general procedure. Resin (89 wt%) was mixed with HEMA (3 wt%), silane coupling agent (3 wt%), and Darocure 1173 (5 wt%) at room temperature. The mixture was coated on sample plate with applicator and cured under a 1000 W UV lamp (lamp distance for 50 cm). The coating was cooled, and its properties were measured according to the standard methods.

Measurements

The acid value was measured with chemical titration. The sample (0.1–0.2 g) was added in the mixture of acetone (10 mL) and alcohol (10 mL), and phenolphthalein was used as indicator. The acid value and percent conversion were calculated by the consumed volume of NaOH (0.1 mol/L).

The hydroxyl value was measured with chemical titration according to the method of Anhydride-Sulfuric acid. The sample (0.2–0.4 g) was added in the mixture of acetic anhydride and sulfuric acid, and phenolphthalein was used as indicator. The hydroxyl value was calculated by the consumed volume of NaOH (0.5 mol/L).

^{1}H-NMR spectra were obtained on a Varian Unity Inova-400 MHz spectrometer using $CDCl_3$ as solvent, and Me_4Si was used as internal standard at room temperature.

Fourier transform infrared (FT-IR) spectra were taken on a Thermo Nicolet Nexus 670 spectrometer by scanning 20 times with a resolution of 4 cm^{-1} within a spectral range of 400–4000 cm^{-1}.

The thermal decomposition profiles of the samples were studied with DG/DTA 6200 at a constant rate of 10 °C/min in nitrogen atmosphere from 30 to 600 °C.

Differential scanning calorimetric measurements (DSC) of the samples were performed with Dupont 1090B instrument under nitrogen at a heating rate of 10 °C/min from −80 to 100 °C.

The gel contents were measured by $(w_2/w_1) \times 100\%$, where w_1 represented the mass of coating through UV curing and w_2 represented the mass of coating immersed in acetone after 3 h.

The mechanical properties including impact strength, adhesive strength, flexibility, and pencil hardness were studied. Impact strength test was carried out by QCJ coating impact tester according to GB/T 1732-93. Adhesive strength test was performed by QFZ coating adhesion tester according to GB/T 1720-89. Flexibility test was done with QTZ coating cone bend tester according to GB/T 1731-93. Hardness test was recorded with pencil hardness according to GB/T 6739-86.

The solvent resistances on UV-curable coating such as acid resistance, alkali resistance, acetone resistance, and toluene resistance were studied according to the standard methods.

The fracture surfaces of the UV-curable coatings were studied with SEM HITACHI-S 4800, Japan. The thickness of coating was about 15 μm and the surface coated with gold before fractographic examination.

Results and discussion

The acid value was tracked in the processing of reaction, and the reaction was ended according to the constant acid value. Comparing the acid value of beginning and ending, the percent conversion can be defined. The final product such as DHBP1, DHBP2, and epoxy/dendritic maleate resins with terminal hydroxyl groups could be defined by the analysis of the hydroxyl value, while the product such as DHBP2-MA with terminal carboxyl groups could be defined by the analysis of the acid value. Table 2 showed the percent conversion and the content of hydroxyl groups or carboxyl groups about polyester DHBP1, DHBP2, DHBP2-MA, and epoxy/dendritic maleate resins 1–3. The reactions could be conducted totally, and the percent conversions were ideal. Compared to the theory values, the measured values of samples basically coincided with the designs of reactions. The excess reactant in the system of epoxy/dendritic maleate resin had not been separated away. The optimum polymer would be chosen by comparing the properties of the UV-curable coating.

FT-IR spectroscopy was used to determine the functional groups present in the polymers. The different characteristic peaks on DHBP2 polymer, dendritic maleate, and epoxy/dendritic maleate resins were shown in Fig. 4. The DHBP2 polymer indicated a wide hydroxyl peak at 3340 cm^{-1} because of its terminal hydroxyl groups. The dendritic maleate exhibited the characteristic peaks of double bond at 1638 and 820 cm^{-1}, and at the same time the hydroxyl peak had almost disappeared. The epoxy/dendritic maleate resins showed the characteristic peaks of epoxy resin at 1509, 1247, and 916 cm^{-1}. The hydroxyl peak appeared at

Table 2 Percent conversion and the content of hydroxyl group or carboxyl group about sample

Sample	Percent conversion (%)	Hydroxyl group (g/mol)	Carboxyl group (g/mol)	Theory value (g/mol)
DHBP1	99.4	121.95	–	133
DHBP2	94.7	166.67	–	178
DHBP2-MA	91.1	–	274.57	276
Resin 1	84.9	746.31	–	777
Resin 2	87.2	489.32	–	501
Resin 3	86.6	482.07	–	501

3446 cm^{-1} after the epoxy group connecting with the terminal carboxyl group. The resin 1 which had less epoxy contents exhibited low hydroxyl peak, while resin 3 which had excess epoxy contents exhibited high hydroxyl peak and epoxy peak.

Figure 5 displayed the TGA thermograms of the DHBP2 polymer, dendritic maleate, and epoxy/dendritic maleate resins. All samples showed good thermal stability, and the temperature data were reported in Table 3. The aromatic structures produced thermal stability at low temperature. As the linear chains were added on the branched units, the onset decomposition temperature of the dendritic maleate was earlier than the DHBP2 polymer. While the linear maleate structure would form cross-linked network by grafting or linking different carbons at high temperature, as a result, the dendritic maleate was more stable at high temperature than DHBP2 polymer. The introduction of epoxy resin further increased the tightness of network,

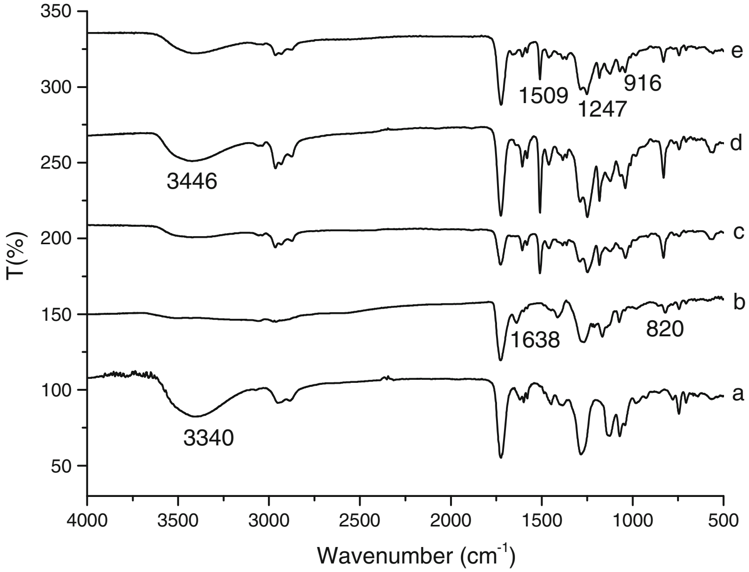

Fig. 4 The FT-IR spectra of (*a*) DHBP2 polymer, (*b*) dendritic maleate, (*c*–*e*) epoxy/dendritic maleate resins 1–3

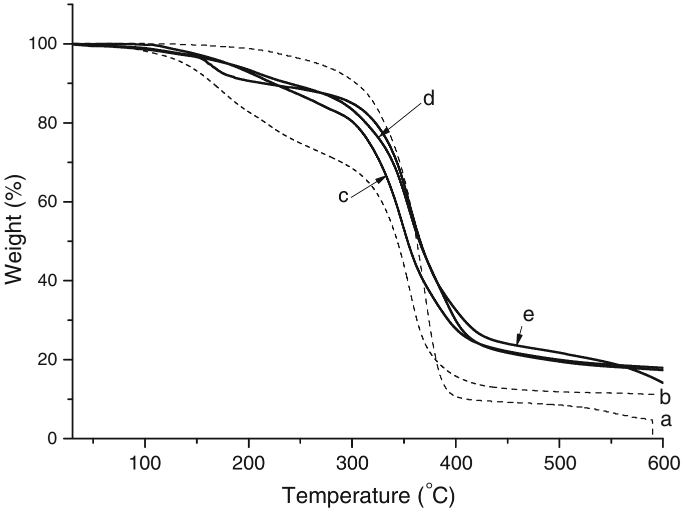

Fig. 5 TGA curves of (*a*) DHBP2 polymer, (*b*) dendritic maleate, (*c–e*) epoxy/dendritic maleate resins 1–3

Table 3 TGA data of the DHBP2 polymer, dendritic maleate, and resins 1–3

Sample	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{85\%}$ (°C)
DHBP2	291.3	374.1	383.5
DHBP2-MA	166.1	343.1	514.6
Resin 1	222.7	353.9	796.9
Resin 2	237.5	364.5	788.8
Resin 3	210.8	365.4	616.4

and the resins 1–3 showed higher decomposition temperature than the dendritic maleate.

In DSC curves, obvious phase transitions were found in Fig. 6. The glass transition temperature (T_g) of the DHBP2 polymer was −28.4 °C. The introduction of maleic anhydride increased the linear chain of branched unit which improved the flexibility of the system, and the dendritic maleate had a lower T_g at −42.5 °C. The epoxy/dendritic maleate resin formed a cross network which took more rigidity to the system and T_g of resins 1–3 exhibited a clear increase. Compared to the resins 1 and 3, the resin 2 had a higher T_g because of the equal mole of epoxy group and carboxyl group could help to form the effective cross-linked network. The T_g of resins 1, 2, and 3 were −0.69, 1.12, and −4.07 °C, respectively.

The gel content and mechanical properties of the UV-curable coating like impact strength, adhesive strength, flexibility, and pencil hardness were reported in Table 4. The C=C in polymer could trigger the forming of cross-linked network during the UV curing. The gel content reflected the cross-linked degree of UV-curable coating. With the introduction of epoxy resin, the polymer shaped larger cross-linked structure and had more cavities which helped to increase the

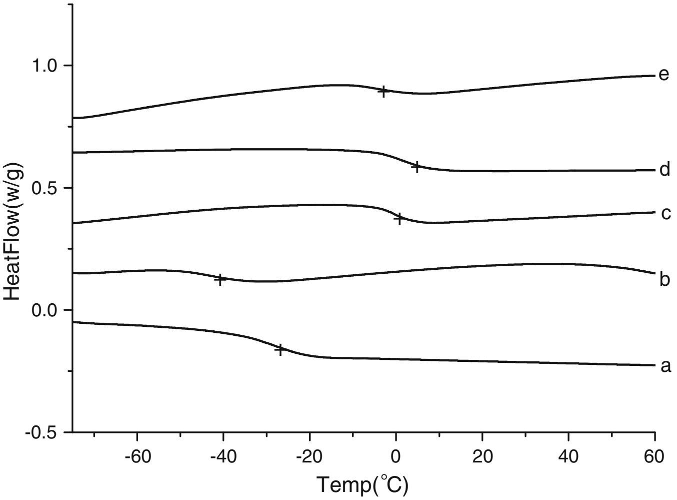

Fig. 6 DSC curves of (*a*) DHBP2 polymer, (*b*) dendritic maleate, (*c*–*e*) epoxy/dendritic maleate resins 1–3

Table 4 The property data of the UV-curable coating

Sample	Gel content (%)	Impact strength (kg cm)	Adhesive strength (grade)	Flexibility (cm)	Pencil hardness
DHBP2-MA coating	98.33	30	6	2	6B
Resin 1 coating	98.74	40	3	4	H
Resin 2 coating	99.58	50	1	7	2H
Resin 3 coating	99.18	47	2	6	H

cross-linked degree of UV-curable coating and took higher gel content. Compared to the resins 1 and 2, the resin 3 had low content of C=C which led to some decrease of the gel content. The larger cross-linked structure of epoxy/dendritic maleate resin also improved the mechanical properties of coating such as impact strength, adhesive strength, flexibility, and pencil hardness. The resin 2 possessed more effective cavity and its coating exhibited better mechanical properties than others.

The solvent resistances on UV-curable coatings such as acid resistance, alkali resistance, acetone resistance, and toluene resistance were shown in Fig. 7. The solvent resistance was an evaluation of coating for resisting corrosivity. The small molecule with ester was easily decomposed by acid and alkali, while the polymer with benzene ring and ester had some dissolubility in acetone and toluene. The coating of DHBP2-MA showed low alkali resistance because of its terminal carboxyl groups. The compactness of coating could provide higher solvent resistance. With the enhancement of cross-linked network, the epoxy/dendritic maleate resin got better solvent resistances than dendritic maleate. Resin 2 had the best compactness and exhibited a higher solvent resistance than others.

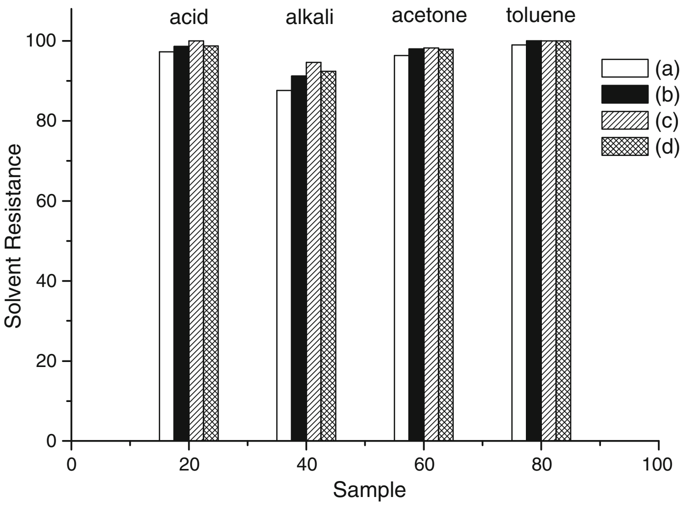

Fig. 7 The solvent resistances of UV-curable coating based on (*a*) dendritic maleate, (*b–d*) epoxy/dendritic maleate resins 1–3

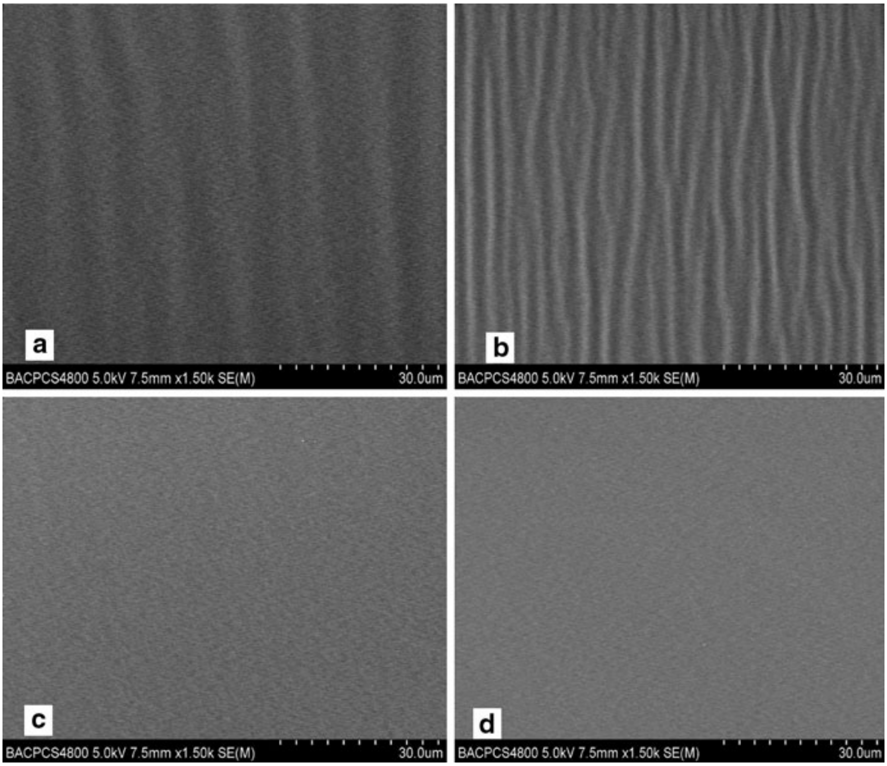

Fig. 8 SEM micrographs of UV-curable coating based on (**a**) dendritic maleate, (**b–d**) epoxy/dendritic maleate resins 1–3

Figure 8 presented the SEM micrographs on the fracture surface of the UV-curable coating. The surface morphology of the coating was improved by the different compactness of epoxy/dendritic maleate resin, which was consistent with the thermal and coating properties studies. The fracture surface of dendritic maleate coating exhibited more orientation which accounted for its poor impact strength and adhesive strength. With the introduction of epoxy resin, the coating of epoxy/dendritic maleate resin formed more cavities. It helped to reduce the brittleness and give more toughness to coating. The excessive epoxy resin in resin 3 could not increase the effective cavities of coating, and the fracture surface did not exhibited obvious change.

Conclusions

In this study, the dendritic polyester DHBP2, dendritic maleate, and epoxy/dendritic maleate resins were synthesized and analyzed by acid value, hydroxyl value, FT-IR, TGA, and DSC. The dendritic maleate and epoxy/dendritic maleate resins were applied in UV-curable coating, and the properties of the UV-curable coatings were compared. With the introduction of epoxy resin, the epoxy/dendritic maleate resin formed larger cross-linked structure and more cavities which helped to improve the properties of coating. The epoxy/dendritic maleate resin exhibited higher thermal decomposition temperature and T_g. The coating of resin 2 based on equal content of epoxy resin and dendritic maleate had higher gel content and better properties such as impact strength, adhesive strength, flexibility, pencil hardness, and solvent resistances. Furthermore, the SEM figures showed that the fracture surface of resin 2 coating had more effective cavities than other samples. It was consistent with the studies on thermal and mechanical properties of coating.

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