Crosslinking and ozone degradation of thermosetting resins based on maleic anhydride/diene copolymer and polyfunctional alcohols

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ABSTRACT: Crosslinking and de-crosslinking reactions of an alternating copolymer of maleic anhydride (MAn) and 2,4-dimethyl-1,3-pentadiene (DMPD) by thermal curing with polyfunctional alcohols as the crosslinkers and subsequent ozone degradation are reported in this article. The ring-opening reaction of an anhydride group by polyfunctional alcohols produces network polymers with an ester linkage. The rate of crosslinking reaction depends on the curing conditions, i.e. the structure of the used alcohols and the curing temperature and time. The crosslinking density of the alcohol-cured copolymers is low due to a slow reaction between the anhydride and hydroxy groups, being different from the corresponding epoxy-cured copolymer with a dense network structure reported in a previous article. The insoluble resins are readily de-crosslinked and solubilized by ozone degradation. The polymer surface modification by ozone is also investigated. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42763.

INTRODUCTION

Alternating radical copolymerization is used for controlled polymer synthesis and functional materials design due to several advantages, such as the production of a high-molecular-weight copolymer in a high yield and a well-defined alternating sequence structure independent of the comonomer ratio in the feed.[1,2] The radical copolymerization of maleic anhydride (MAn) as the electron-accepting monomer combined with an electron-donating olefin provides a high-molecular-weight alternating copolymer.[3–5] The anhydride moiety introduced in the copolymer main chain is further used for the synthesis of various functional polymers.[6–8] Differing from the facile formation of alternating copolymers with olefins, MAn readily reacts with 1,3-diene compounds to predominantly yield Diels-Alder adducts, but not alternating copolymers. Recently, it was reported that 3-methylenecyclopentene as the cyclic 1,3-diene monomer including a reactive exomethylene moiety produced an alternating copolymer during radical copolymerization with an electron-accepting N-substituted maleimide in a high yield.[9] This was because Diels-Alder reaction was totally suppressed due to the fixed s-trans conformation of the cyclic diene monomer. More recently, it was also demonstrated that 2,4-dimethyl-1,3-pentadiene (DMPD) and several other methyl-substituted dienes similarly produced the corresponding alternating copolymers with MAn.[10] The predominant copolymer formation was discussed based on the reactivity of the diene monomers with a twisted diene structure, which was disadvantageous to undergo Diels-Alder reaction. An anhydride moiety in each repeating unit of the copolymers was available for the postpolymerization reaction, such as crosslinking using an epoxy compound.[10,11] On the other hand, an alternative diene monomer unit including a carbon-to-carbon double bond was reacted with ozone, leading to the polymer chain scission, re-crosslinking of the epoxy-cured resins, and polymer surface modification during oxidative ozonolysis.[10] Reworkable UV- and thermally-cured polymer materials are often used as adhesives, printing, coatings, mounting of electronic parts, and composite materials with high performances in various application fields.[12–24] Polymer surface modification, especially, the fabrication of polymer surfaces with high hydrophilicity is important for adhesives, painting, and coatings.

In this article, we report the crosslinking reactions using the alternating copolymers of MAn and DMPD, i.e. poly(MAn-*alt*-DMPD) (PMAD) with polyfunctional alcohols as the crosslinkers and the degradation of the crosslinked products (Scheme 1). We investigated the network polymer formation of PMAD with polyfunctional alcohols by thermal curing and the subsequent ozone degradation of the crosslinked polymers in order to induce the cleavage of a carbon-to-carbon double bond in the polymer chains, leading to the solubilization of the networked polymers by de-crosslinking reaction.
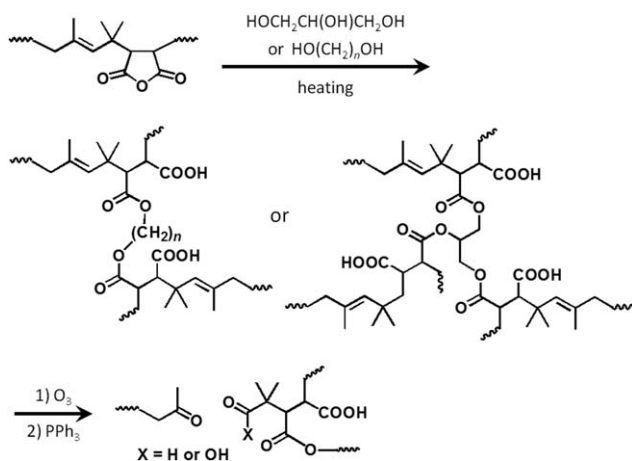
Scheme 1. Crosslinking reaction of PMAD with polyfunctional alcohols and subsequent ozone degradation.

EXPERIMENTAL

Materials

Commercially available MAn (Kishida Chemicals Co.) was used after sublimation under reduced pressure. DMPD was purchased from Tokyo Chemical Industry Co. and used as received. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was purchased from Wako Pure Chemicals Co., and recrystallized from methanol. Cyclohexanone (Nacalai Tesque) was distilled under reduced pressure. Polyfunctional alcohols as the crosslinkers were used as received (Wako Pure Chemicals Co. or Tokyo Chemical Industry Co.). The solvents were distilled before use.

Synthesis of PMAD

PMAD was prepared by the radical alternating copolymerization of MAn and DMPD in chloroform in the presence of AMVN by the procedure described as follows.[10] The reaction mixture was poured into a large amount of diethyl ether/n-hexane mixture (4/1 volume ratio) to precipitate the copolymers after copolymerization. The isolated copolymer was dried in $vacuo$ at 110°C. The copolymer yield was 73.3% for the copolymerization under the following conditions: [MAn] = [DMPD] = 1.0 mol/L and [AMVN] = 20 mmol/L at 40°C for 10 h. The isolated PMAD was further purified by a repeated precipitation procedure using acetone and a diethyl ether/n-hexane mixture. The ¹H NMR spec-

Figure 1. ¹H NMR spectrum of PMAD used for the crosslinking reactions in this study.

trum of PMAD is shown in Figure 1. The composition of the obtained PMAD was determined based on the intensity ratio of the peaks due to the MAn and DMPD repeating units, which were observed at 2.6–3.3 and 2.1–2.6 ppm, respectively, in the ¹H NMR spectrum; MAn/DMPD = 50.0/50.0 in mol %. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of PMAD were determined to be 1.30×10^4 and 1.65, respectively, by size exclusion chromatography (SEC).

PMAD

¹H NMR (CDCl₃, 400 MHz) δ 5.1–5.3 (CH=), 2.6–3.3 (CH), 2.1–2.6 (CH₃), and 0.8–1.5 (CH₃).

General Procedures

The NMR spectra were recorded using JEOL ECS-400 and ECX-400 FT NMR spectrometers. The IR spectra were recorded using a JASCO FT-IR410 spectrometer. For the preparation of a sample for the IR measurement, the solution of PMAD (50 mg) and an alcohol (8–23 mg) in cyclohexanone (0.53 mL) was spin-coated (1000 rpm, 30 s) on a Si plate to obtain a thin film. SEC was carried out using Chromatoscience CS-300C, JASCO PU-2080PLUS, JASCO DG-2080-53, JASCO RI-2031-PLUS, TOSOH TSK-gel columns, GMH$_{HR}$-N and GMH$_{HR}$-H, and tetrahydrofuran as the eluent. The M_n and M_w/M_n values were determined by calibration with standard polystyrenes. The thermogravimetric analysis (TG) was carried out using Shimadzu TGA-50 in nitrogen at the heating rate of 10°C/min to determine the onset temperature of decomposition (T_{d5}) and the 50% weight-loss temperature (T_{d50}). The maximum decomposition temperature (T_{max}) was determined from the differential TG curves. The differential scanning calorimetry (DSC) was carried out using Shimadzu DSC-60 in nitrogen at the heating rate of 10°C/min to determine the glass transition temperature (T_g). Spin-coated films were prepared using a Mikasa 1H-D7 spin coater. Film thickness was determined by interferometric measurement using a Nanometrics Nanospec AFT M-3000 series. Ozone gas was generated using Ozone Mart O3 Clear (Earth Walker Trading Co., Japan).

Thermal Curing

A mixture of PMAD, an alcohol ([anhydride]/[hydroxy] = 1/1 molar ratio), and cyclohexanone (10 wt % to the polymer) as the solvent was put in an aluminum pan, then prebaked at 60°C for 5 min to remove the solvent, followed by curing at a determined temperature. The insoluble fraction was determined after removing a soluble fraction by immersing the samples in a pan into acetone for 15 min. Epoxy-cured PMAD was prepared according to a similar method. A mixture of PMAD, bisphenol A diglycidyl ether (BADGE) ([anhydride]/[epoxy] = 1/1 molar ratio), N,N′-dimethylbenzylamine (3 wt % to the epoxy compound), and cyclohexanone was put in an aluminum pan, then prebaked at 60°C for 5 min, followed by curing at 180°C for 1 h. The insoluble fraction was determined to be 99.6% after removing a soluble fraction by immersing the samples in a pan into acetone for 15 min.

Ozonolysis

The ozonolysis of the cured copolymers was carried out by bubbling ozone-containing air in acetone at 0°C or by blowing ozone-containing air without any solvent at room temperature.
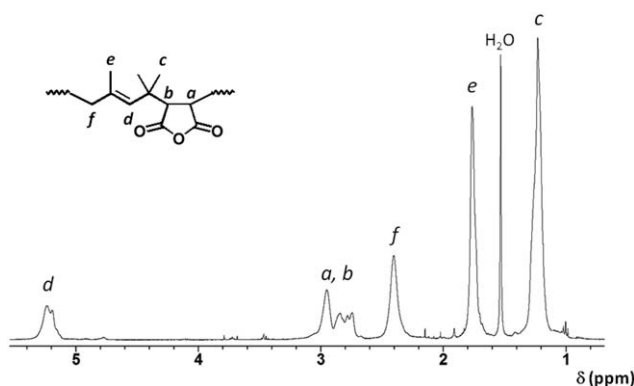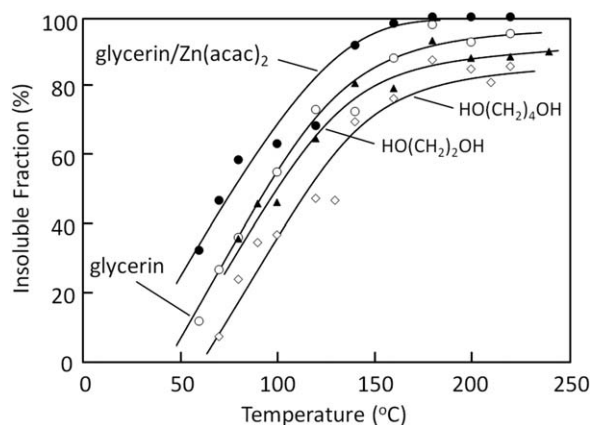
Figure 2. Temperature dependence of the insoluble fraction of alcohol-cured PMAD during thermal curing. (◇) 1,4-butanediol, (▲) ethylene glycol, (○) glycerin, and (●) glycerin with $Zn(acac)_2$. Curing conditions: [anhydride]/[hydroxy] = 1/1 in molar ratio for 0.5 h. Dissolution in acetone for 15 min after thermal curing.

After ozonolysis for a determined time, the produced ozonides were reacted with 5 wt % triphenylphosphine in acetone at room temperature for 10 min. The insoluble fraction was determined based on the residual weight of the glycerin-cured PMAD or a change in the film thickness for the epoxy-cured PMAD (an initial film thickness was ca. 0.8 μm).

RESULTS AND DISCUSSION

Thermal Curing

The thermal curing of PMAD using diethylene glycol and 1,4-butanediol as the diols was carried out under various temperature conditions. A change in the insoluble fraction values for each curing system is shown in Figure 2, as the function of the

Table I. The Insoluble Fraction of PMAD Cured Using Polyfunctional Alcohols as Crosslinkers

Crosslinker	Temperature (°C)	Time (h)	Insoluble fraction (%)
	Thermal curing conditions[a]		
Ethylene glycol	180	0.5	87.4
1,4-Butanediol	180	0.5	93.1
Glycerin	100	0.5	54.9
	140	0.33	54.2
	140	0.5	72.6
	140	1.0	65.3
	160	0.5	88.0
	180	0.5	97.7
	200	0.5	92.7
	220	0.5	95.2
Glycerin/$Zn(acac)_2$	140	0.5	91.8
	160	0.5	98.1
	180	0.5	~100
BADGE (epoxy)	180	1.0	99.6

[a] [Anhydride]/[hydroxy] = 1/1 in molar ratio.
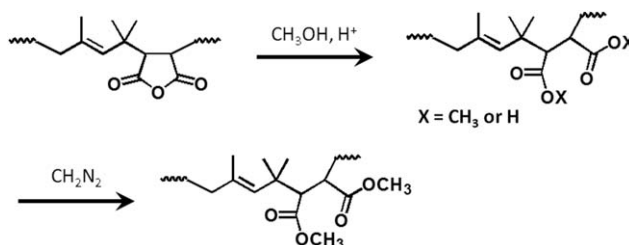
Scheme 2. Polymer reactions of PMAD with methanol and diazomethane.

curing temperature. The curing time was constant as 0.5 h. The crosslinking reaction proceeded when a curing temperature was higher than 50°C and the insoluble fraction gradually increased as the temperature increased. The amount of the insoluble products depended on both the curing temperature and time, as summarized in Table I. The crosslinking reaction hardly achieved a 100% yield under the curing conditions using difunctional alcohols as the crosslinkers in this study. This was contrast to the previously reported results for the rapid crosslinking reaction of the epoxy-cured system to quantitatively produce insoluble polymer networks.[10]

The reactivity of the anhydride group incorporated in the polymer chain was investigated using methanol as a model reaction in a solution; i.e. under reflux conditions in a toluene and methanol mixture (1/10 in volume ratio) in the presence of a small amount of H_2SO_4, followed by methylation with diazomethane (Scheme 2). The detection of the remaining anhydride moiety in the IR spectrum of the product indicated the incomplete reaction process of the anhydride group with methanol even after the 2-h reflux in chloroform [Figure 3(a,b)]. The quantitative ring-opening reaction of the anhydride groups required the harder reaction conditions, such as reflux in toluene for 5 h. The peak due to the anhydride moiety was not observed in the spectrum of the isolated product [Figure 3(c)]. In the literature, the reactivity of functional groups, such as anhydride, acyl chloride, and isocyanate groups, was reduced when they were incorporated as a part of the polymer repeating structure.[25–30]
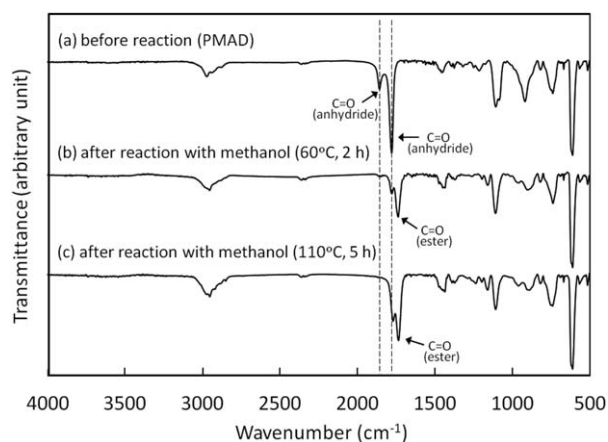

Figure 3. IR spectra of (a) PMAD before curing, (b) after reaction with methanol in chloroform under reflux condition for 2 h, and (c) after reaction with methanol in toluene under reflux condition for 5 h.
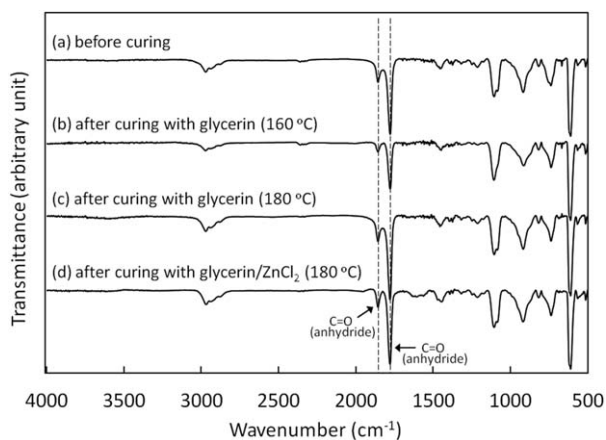
Figure 4. IR spectra of (a) PMAD before curing, (b) after curing with glycerin ([anhydride]/[hydroxy] = 1/1 in molar ratio) at 160°C for 0.5 h, (c) after curing with glycerin ([anhydride]/[hydroxy] = 1/1 in molar ratio) at 180°C for 0.5 h, and (d) after curing with glycerin ([anhydride]/[hydroxy] = 1/1 in molar ratio) in the presence of $Zn(acac)_2$ (5 mol %) at 180°C for 0.5 h.

In this study, we also used glycerin as a trifunctional crosslinker in order to efficiently increase the insoluble fraction. High crosslinking efficiency was observed for the reaction using glycerin as shown in Figure 2 and Table I, when it was compared with those for the reaction systems using the diols. We further
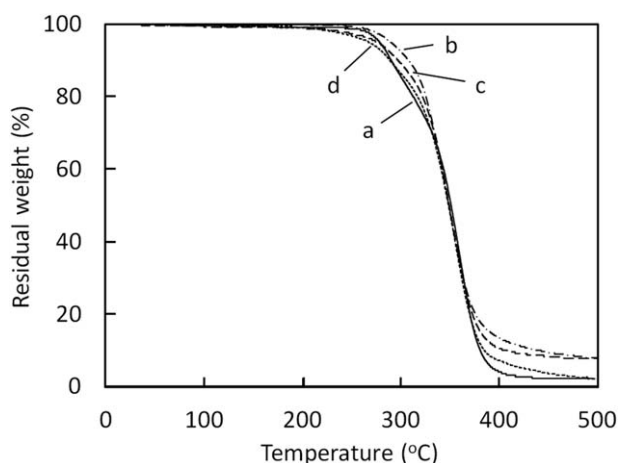

Figure 5. TG curves of PMAD (a) before curing (———) and after curing with (b) ethylene glycol (——- ——), (c) 1,4-butanediol (– – –), and (d) glycerin (········). TG measurement was carried out in a nitrogen stream at a heating rate of 10°C/min.

revealed that $Zn(acac)_2$ accelerated esterification and yielded the quantitative insoluble fraction, while a soluble polymer partially remained even at a high temperature such as 180°C during the reaction in the absence of $Zn(acac)_2$. It was reported that Lewis acids such as $Zn(acac)_2$ functioned as the high efficient catalyst for the transesterification of the reversible crosslinked network polymers.[31] The IR spectroscopy revealed that the most anhydride groups in the PMAD remained even after the reaction with glycerin at 180°C for 0.5 h in the absence and presence of $Zn(acac)_2$ (Figure 4). The peaks due to the remaining anhydride group were observed at 1562 and 1641 cm^{-1} with a considerable intensity after the curing reactions, while no characteristic peak due to an ester moiety as the ring-opening product was detected. This result indicated that the formation of a very small amount of crosslinking points by the ring-opening reaction of the anhydrides with alcohols was enough to change the solubility of PMAD, i.e. the achievement for the 100% yield of the insoluble fraction.

Thermal Stability

The thermal stability of the alcohol-cured copolymers was evaluated by TG analysis. Judged from the TG thermograms shown in Figure 5 and the determined decomposition temperatures therefrom, T_{d5}, T_{d50}, and T_{max}, and the residual weight at 500°C summarized in Table II, it was concluded that the thermal stability of the crosslinked PMAD was similar to that of the linear PMAD before crosslinking; The T_{d5}, T_{d50}, and T_{max} values were 271–290, 348–349, and 351–360°C, respectively, independent of the presence or absence of the network structures. This was because the alcohol-cured PMAD had a loose crosslinking structure due to the low conversion of the anhydride group during a thermal curing process. This is contrast to the excellent thermal stability of polymers containing imide groups.[32–35] Actually, the reaction of PMAD with polyfunctional amines followed by a post-curing reaction provided thermally stable crosslinked polymers including maleimide repeating structures. The results for the reactions of PMAD using various polyfunctional amines will be separately reported in combination with the results for the copolymerization of maleimides and diene monomers including DMPD to produce alternating maleimide copolymers.

Ozone Degradation

The ozone degradation of the crosslinked PMAD was carried out in acetone at 0°C and a change in the insoluble fraction was determined as the function of the time. The results are shown in Table III. The both results of the glycerin-cured and epoxy-cured PMADs are shown as the comparison. The unsaturated carbon-to-carbon double bond included in the main chain of

Table II. Thermal Stability of PMAD Cured Using Polyfunctional Alcohols as Crosslinkers

Crosslinker	T_{d5} (°C)	T_{d50} (°C)	T_{max} (°C)	Residual weight at 500°C (%)
PMAD before crosslinking	278	349	360	4.1
PMAD after curing with ethylene glycol	290	349	350	7.8
PMAD after curing with 1,4-butanediol	280	349	351	7.7
PMAD after curing with glycerin	271	348	355	2.0

Table III. Change in the insoluble Fraction of the Glycerin- and Epoxy-Cured PMADs During Ozone Degradation in Acetone at 0°C

Polymer (curing conditions)	Time (min)	Insoluble fraction (%)
Glycerin-cured PMAD (200°C, 0.5 h)	0	92.7
	5	88.1
	8	60.3
	9	52.3
	10	17.5
	15	8.0
Epoxy-cured PMAD (180°C, 1 h)	0	>99
	5	98.6
	10	96.8
	15	94.8
	20	92.0
	30	90.6
	40	88.2
	50	82.6
	60	80.1

Table IV. Change in Insoluble Fraction and Water Contact Angle of the Cured PMAD Films During Ozone Degradation in Air at Room Temperature

Polymer (curing conditions)	Time (min)	Insoluble fraction (%)	Water contact angle (degree)
Glycerin-cured PMAD (180°C, 0.5 h)	0	100	
	10	98.2	
	20	95.9	
	30	94.0	
Glycerin-cured PMAD (200°C, 2 h)	0		80.0+2.1
	10		78.9+0.7
	20		74.3+1.5
	30		71.2+1.8
	40		69.6+2.2
	50		69.0+1.0
	60		68.8+0.8
Epoxy-cured PMAD[a] (180°C, 1 h)	0	100	77.9+1.2
	10	99	71.4+0.4
	30	97	69.6+0.4

[a] Cited from Ref. 10.

PMAD reacted with ozone to produce ozonides, and then the scission of the polymer chains occurred during the work-up procedures using triphenylphosphine as the reducing agent, according to the reactions shown in Scheme 3. This resulted in the re-solubilization of the crosslinked polymers. The insoluble fraction values of the crosslinked PMAD rapidly decreased during ozonolysis for several minutes, while re-solubilization slowly occurred for the epoxy-cured PMAD that included a high-density network structure. In our previous article, rapid re-solubilization was reported for the epoxy-cured PMAD system using a spincoat thin-film (thickness 0.8 μm).[10] The difference in the re-solubilization rates was due to the sample shape, spin-coat film or bulk solid. The former had a larger relative surface area. When we tried to evaluate the re-solubilization process of the alcohol-cured PMAD using spincoat films, it was difficult to determine insoluble fraction values after ozonolysis for a few minutes. Thus, the low crosslinking density of the alcohol-cured polymers was favored for a re-solubilization process because less-frequent chain scission was enough to solubilize the crosslinked PMAD during ozonolysis.

The polymer surface modification by ozone degradation was also investigated. The ozonolysis modified the surface of the

cured PMAD by the introduction of polar functional groups such as an aldehyde and carboxylic acid (Scheme 3). Table IV summarizes the results for changes in the insoluble fraction and water contact angles of the glycerin-cured and epoxy-cured PMAD spincoat films during ozonolysis in air at room temperature. The re-solubilization of the cured PMADs proceeded in air at a rate lower than that in a solution because the reaction proceeded only at a solid polymer surface in the latter case. Figure 6 shows a difference in the water contact angles before and after the ozonolysis. The contact angle value of the glycerin-cured PMAD was 80° and it decreased to ca. 70° after

Scheme 3. Mechanism for ozone degradation of PMAD.
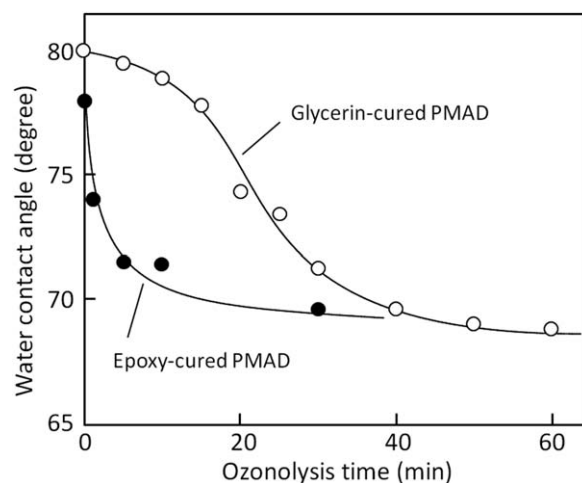
Figure 6. Change in water contact angles during ozonolysis of glycerin- and epoxy-cured PMADs.

ozonolysis for 60 min. A similar change in the water contact angles was observed for the epoxy-cured PMAD; it decreased to 70° during the 30-min ozonolysis. This indicated the surface modification similarly proceeded independent of the crosslinking densities of the cured PMAD. However, a change in the water contact angle for the epoxy-cured PMAD at the initial stage of the reaction was much faster than that for the glycerin-cured PMAD, as shown in Figure 6. The water contact angle value for the glycerin-cured PMAD slowly changed at the initial stage and the rate of the change gradually accelerated after the reaction for 10 min. The final water contact angle values were similar for the both systems. This was possibly due to the faster degradation of the epoxy-cured PMAD than that of the alcohol-cured one due to the ozonolysis of aromatic moieties included in the epoxy-cured PMAD.[36–38] Furthermore, the difference in the chemical structure of the crosslinking points should also be considered, i.e. the epoxy-cured PMAD included a large number of polar groups, such as a hydroxy group, in the polymer network structure and the surface property was more sensitively influenced by the polar groups after polymer chain scission during the ozonolysis. In contrast, the glycerin-cured PMAD included a small number of crosslinking points and polar functional groups in the networks. They led to a difference in the fashion for a decrease in the water contact angle in Figure 6.

CONCLUSION

It was demonstrated that the anhydride group of PMAD reacted with polyfunctional alcohols to produce crosslinked polymers by thermal curing. The insoluble fraction increased as an increase in the curing temperature and time. The crosslinking rate was enhanced in the presence of a Lewis acid such as $Zn(acac)_2$ and the insoluble fraction reached 100%. The crosslinking density of the cured PMAD by the polyfunctional alcohols was low and ozone degradation readily induced the re-solubilization of the crosslinked PMAD within several minutes. The re-solubilization rate of the alcohol-cured crosslinked PMAD was much higher than that of the epoxy-cured PMAD with a high crosslinking density. It was also shown that the hydrophilicity of the cured film surfaces increased after ozonolysis. It has been demonstrated that the two functional repeating units incorporated in the main chain of PMAD, i.e. the anhydride group and the double bond, can be orthogonally used for the crosslinking and de-crosslinking, respectively.

REFERENCES

1. Cowie, J. M. G. Ed. Alternating Copolymers; Plenum Press: New York, **1985**.

2. Badi, N.; Chan-Seng, D.; Lutz, J.-F. *Macromol. Chem. Phys* **2013**, *214*, 135.

3. Trivedi, B. C.; Culbertson, B. M. Maleic Anhydride; Springer: New York, **1982**.

4. Rätzsch, M. *Prog. Polym. Sci.* **1988**, *13*, 277.

5. Klumperman, B. *Polym. Chem.* **2010**, *1*, 558.

6. Chernikova, E.; Terpugova, P.; Bui, C.; Charleux, B. *Polymer* **2003**, *44*, 4101.

7. Maeda, H.; Sawa, T.; Konno, T. *J. Control. Release* **2001**, *74*, 47.

8. Pompe, T.; Zschoche, S.; Herold, N.; Salchert, K.; Gouzy, M.-F.; Sperling, C.; Werner, C. *Biomacromolecules* **2003**, *4*, 1072.

9. Yamamoto, D.; Matsumoto, A. *Macromolecules* **2013**, *46*, 9526.

10. Tsujii, A.; Namba, M.; Okamura, H.; Matsumoto, A. *Macromolecules* **2014**, *47*, 6619.

11. Auvergne, R.; Caillol, S.; David, G.; Boutevin, B.; Pascault, J.-P. *Chem. Rev.* **2014**, *114*, 1082.

12. Ogino, K.; Chen, J.-S.; Ober, C. K. *Chem. Mater.* **1998**, *10*, 3833.

13. Wang, L.; Li, H.; Wong, C. P. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3771.

14. Shirai, M.; Morishita, S.; Okamura, H.; Tsunooka, M. *Chem. Mater.* **2002**, *14*, 334.

15. Malik, J.; Clarson, S. J. *Int. J. Adhes. Adhesives* **2002**, *22*, 283.

16. Mcelhanon, J. R.; Russick, E. M.; Wheeler, D. R.; Loy, D. A.; Aubert, J. H. *J. Appl. Polym. Sci.* **2002**, *85*, 1496.

17. Ebe, K.; Seno, H.; Horigome, K. *J. Appl. Polym. Sci.* **2003**, *90*, 436.

18. Trenor, S. R.; Long, T. E.; Love, B. J. *J. Adhes.* **2005**, *81*, 213.

19. González, L.; Ferrando, F.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. *Prog. Org. Coat.* **2009**, *65*, 175.

20. Liu, W.; Wang, Z.; Xiong, L.; Zhao, L. *Polymer* **2010**, *51*, 4776.

21. Sato, E.; Tamura, H.; Matsumoto, A. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2594.

22. Imato, K.; Nishihara, M.; Kanehara, T.; Amamoto, Y.; Takahara, A.; Otsuka, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 1138.

23. Inui, T.; Sato, E.; Matsumoto, A. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2124.

24. Kloxin, C. J.; Bowman, C. N. *Chem. Soc. Rev.* **2013**, *42*, 7161.

25. Otsu, T.; Tajima, T. *Kobunshi Ronbunshu* **1974**, *31*, 181.

26. Otsu, T.; Matsumoto, A.; Nakamura, K. *J. Appl. Polym. Sci.* **1992**, *45*, 1889.

27. Bruch, M.; Mäder, D.; Bauers, F.; Loontjens, T.; Mülhaupt, R. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1222.

28. Yamasaki, R.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 5215.

29. Seto, R.; Matsumoto, K.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 5221.

30. Tsuchiya, K.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 699.

31. Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. *Science* **2011**, *334*, 965.

32. Matsumoto, A.; Kubota, T.; Otsu, T. *Macromolecules* **1990**, *23*, 4508.

33. Hisano, M.; Takeda, K.; Takashima, T.; Jin, Z.; Shiibashi, A.; Matsumoto, A. *Macromolecules* **2013**, *46*, 7733.

34. Matsumoto, A. In Sequence-Controlled Polymers: Synthesis, Self-Assembly, and Properties, ACS Symposium Series; Lutz,

J.-F.; Meyer, T.; Ouchi, M.; Sawamoto, M., Eds.; American Chemical Society: Washington, D.C., **2014**; Vol. *1170*, Chapter 20, p 301.

35. Matsumoto, A.; Hisano, M.; Yamamoto, D.; Yamamoto, H.; Okamura, H. *Kobunshi Ronbunshu* **2015**, *72*, 243.

36. Singh, B.; Sharma, N. *Polym. Deg. Stab.* **2008**, *93*, 561.

37. Haack, L. P.; Straccia, A. M.; Holubka, J. W.; Bhurke, A.; Xie, M.; Drzal, L. T. *Surf. Inter. Anal.* **2000**, *29*, 829.

38. Sham, M.-L.; Li, J.; Ma, P.-C.; Kim, J.-K. *J. Comp. Mater.* **2009**, *43*, 1537.