J Therm Anal Calorim (2010) 99:277–284
DOI 10.1007/s10973-009-0171-8

Curing behavior of polycardanol by MEKP and cobalt naphthenate using differential scanning calorimetry

Qun Zhou · Donghwan Cho · Bong Keun Song · Hyun-Joong Kim

Abstract In this study, polycardanol, which was synthesized by enzymatic oxidative polymerization of thermally treated cashew nut shell liquid (CNSL) using fungal peroxidase, was partially or fully cured using methyl ethyl ketone peroxide (MEKP) as initiator and cobalt naphthenate (Co-Naph) as accelerator. The curing behavior of polycardanol was extensively investigated in terms of curing temperature, curing time, concentration of initiator and accelerator, and the monomer-to-polymer conversion of polycardanol by means of differential scanning calorimetry (DSC). The curing behavior significantly depends on the thermal condition given and it was monitored with the change of the exotherms as a function of temperature. The optimal conditions for fully curing polycardanol are 1 wt% MEKP, 0.2 wt% Co-Naph, curing time 120 min, and curing temperature 200 °C. This study suggests that a polycardanol with high monomer-to-polymer conversion would be useful for processing a polycardanol matrix composite under the optimal conditions of curing.

Keywords Polycardanol · Curing behavior · Differential scanning calorimetry · Initiator · Accelerator · The extent of curing

Q. Zhou · D. Cho (✉)
Department of Polymer Science and Engineering,
Kumoh National Institute of Technology, Gumi,
Gyungbuk 730-701, Korea
e-mail: dcho@kumoh.ac.kr

B. K. Song
Korea Research Institute of Chemical Technology,
Daejeon 305-343, Korea

H.-J. Kim
Program in Environmental Materials Science,
Seoul National University, Seoul 151-921, Korea

Introduction

During the past years, there have been increasing demands for developing polymer materials available from renewable resources, which are environmentally benign and sustainable, due to gradual depletion of petroleum and environmental consciousness. There have been a number of research efforts to replace petroleum-derived raw materials to polymeric materials renewable from plants as natural resource.

Cardanol, which can be obtained by thermal treatment of cashew nut shell liquid (CNSL), is a phenol derivative mainly composed of the *meta* substitute of a C15 unsaturated hydrocarbon chain with one to three double bonds [1, 2]. CNSL constitutes nearly one-third of the total nut weight. Thus, a large amount of CNSL is formed as a by-product of the mechanical processes used to render the cashew kernel edible and its total production approaches one million tons annually [3]. CNSL has industrially potential applications such as resins, friction lining materials, and surface coatings.

Recently, Kim et al. [4, 5] reported that the enzymatic oxidative polymerization of thermally treated CNSL using peroxidase secreted from the basidiomycete fungus, *Coprinus cinereus*, produced very efficiently an oily soluble polymer, which is called polycardanol. Polycardanol is normally dark brown, highly viscous, and thermally curable. It has no volatile organic compounds (VOC) so that it has potential as a composite matrix resin as well as a glossy formaldehyde-free coating material and a finish [4]. Understanding of the cure behavior of such a thermosetting resin is critically important to know optimal conditions and properties of the cured product [6, 7]. Based on the chemical structure of polycardanol with unsaturated double bonds, it may be thermally cured with peroxides and/or cobalt naphthenate (Co-Naph) as typically in an unsaturated polyester resin [8–10]. However the curing behavior of polycardanol has not been extensively studied yet. In particular, no differential scanning calorimetry (DSC) studies on polycardanol have been found.

Recently, a number of papers on biocomposites dealing with natural resources have been published increasingly [11–13]. In particular, a composite material consisting of polycardanol and plant-based natural fibers is now being an interesting issue due to use of all environmentally friendly constituents without volatile organic compounds (VOC) in the composite. Up to date, only a few papers on natural fiber composites with CNSL have been reported [14–16], but not with polycardanol. The ultimate purpose of our research dealing with polycardanol is to process natural fiber-reinforced polycardanol matrix composites. In a fiber-reinforced polymer composite material, information on the thermal behavior of a thermosetting matrix resin is substantially significant to successfully make a composite and also to exhibit its good properties. Consequently, the objective of the present work is primarily to characterize the dynamic and isothermal curing behaviors of polycardanol under various thermal curing conditions like curing temperature, curing time, and initiator and accelerator concentrations by means of DSC and to determine the optimal curing conditions of polycardanol. The study will provide useful information on the determination of thermal parameters for processing natural fiber/polycardanol composites.

Experimental

Polycardanol, which was prepared by enzyme-catalyzed oxidative polymerization from a renewable resource using a fungal peroxidase, was kindly supplied in the prepolymer state by the Korea Research Institute of Chemical Technology, Daejeon, Korea. The number-average molecule weight of polycardanol was 1,610 and the weight-average molecule weight was 7,220. The viscosity was in the range of 16,000–34,800 cps. Figure 1 shows the typical chemical structure of polycardanol used in this work. A polycardanol resin with the monomer-to-polymer conversion of 91.1% was mostly used for examining the curing behavior throughout this work. In addition, polycardanol resins with different monomer-to-polymer conversions of 85.6% and 97.1% were also supplied and used for comparison. The chemistry and synthesis of polycardanol have been described in detail elsewhere [4].

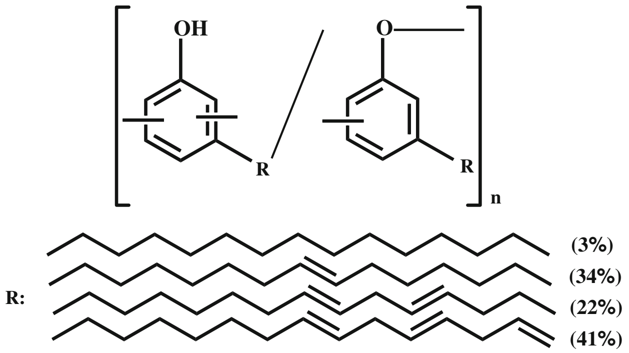

Fig. 1 Chemical structure of polycardanol

Methyl ethyl ketone peroxide (MEKP) as initiator and Co-Naph as accelerator were used, respectively. Curing processes of polycardanol were conducted by varying temperature (100–220 °C), time (30–90 min), and concentration of the initiator (0.5–3 wt%) and the accelerator (0.1–0.3 wt%) concentrations. Uncured polycardanol was also studied for comparison with partially or fully cured polycardanol.

Polycardanol resins were cured in an ordinary oven in the absence and the presence of MEKP or Co-Naph according to pre-scheduled conditions. Each sample of 10–20 mg was placed in an aluminum pan and sealed tightly. A DSC (200F3 Maia®) was performed in the range of 60–240 °C with a heating rate of 10 °C/min, purging nitrogen gas at 50 mL/min.

Results and discussion

Curing behavior of polycardanol in the absence of accelerator

Figure 2 shows the DSC curves of polycardanol resins with 1 wt% MEKP cured at different curing temperatures for 90 min. No accelerator was added here. The small

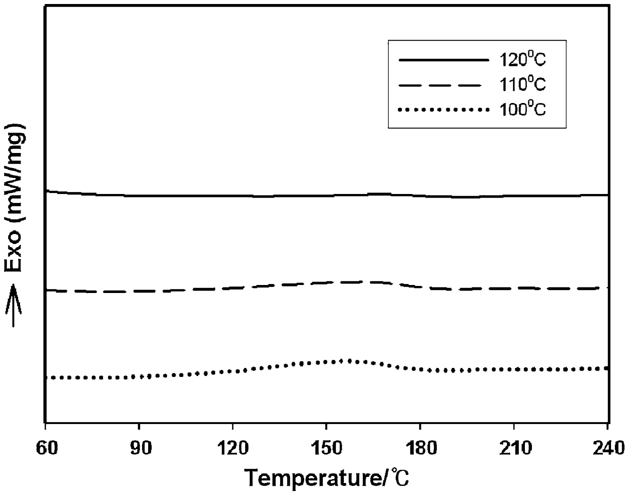

Fig. 2 DSC curves of polycardanol with 1 wt% MEKP cured at different temperatures for 90 min

exotherm with a maximum near 155 °C, which was found upon curing polycardanol at 100 °C for 90 min, almost disappeared upon curing at 120 °C for 90 min. This points out that the MEKP of 1 wt% or higher may be used for initiating the curing reaction of polycardanol as long as the curing temperature is higher than 120 °C for 90 min. However, the obtained polycardanol sample was not hard enough to play a role as composite matrix resin although the exothermic peak almost disappeared after curing at 120 °C for 90 min. Therefore it was necessary that further curing process should be followed to harden the polycardanol. To find out an appropriate concentration of MEKP for fully curing polycardanol, the curing processes were conducted at various MEKP concentrations under different isothermal curing conditions.

Figure 3 displays the effect of isothermal curing time on the exothermic behavior of polycardanol at various MEKP concentrations in the absence of accelerator. Four MEKP concentrations of 0.5, 1, 2, and 3 wt% were used. Three isothermal curing times given at 120 °C were 30, 60, and 90 min. The DSC curve of each cured sample was compared with the uncured sample.

The small exothermic peak with a maximum near 150 °C in the range of 120–175 °C was observed for the uncured samples. The exothermic peak was due to the presence of unreacted, further thermally curable molecules in the polycardanol sample. It can also be seen that the exothermic peak was decreased with increasing isothermal curing time and almost disappeared after 90 min. This means that polycardanol can be almost cured under the thermal conditions given, but not fully cured. Also, it was found that with increasing curing time the exothermic peak position was shifted to higher temperature and the area of the exothermic peak became smaller. This was because the small amount of the unreacted molecules remaining in the polycardanol even after the primary curing was additionally cured at the temperature lower than 120 °C during the DSC measurement.

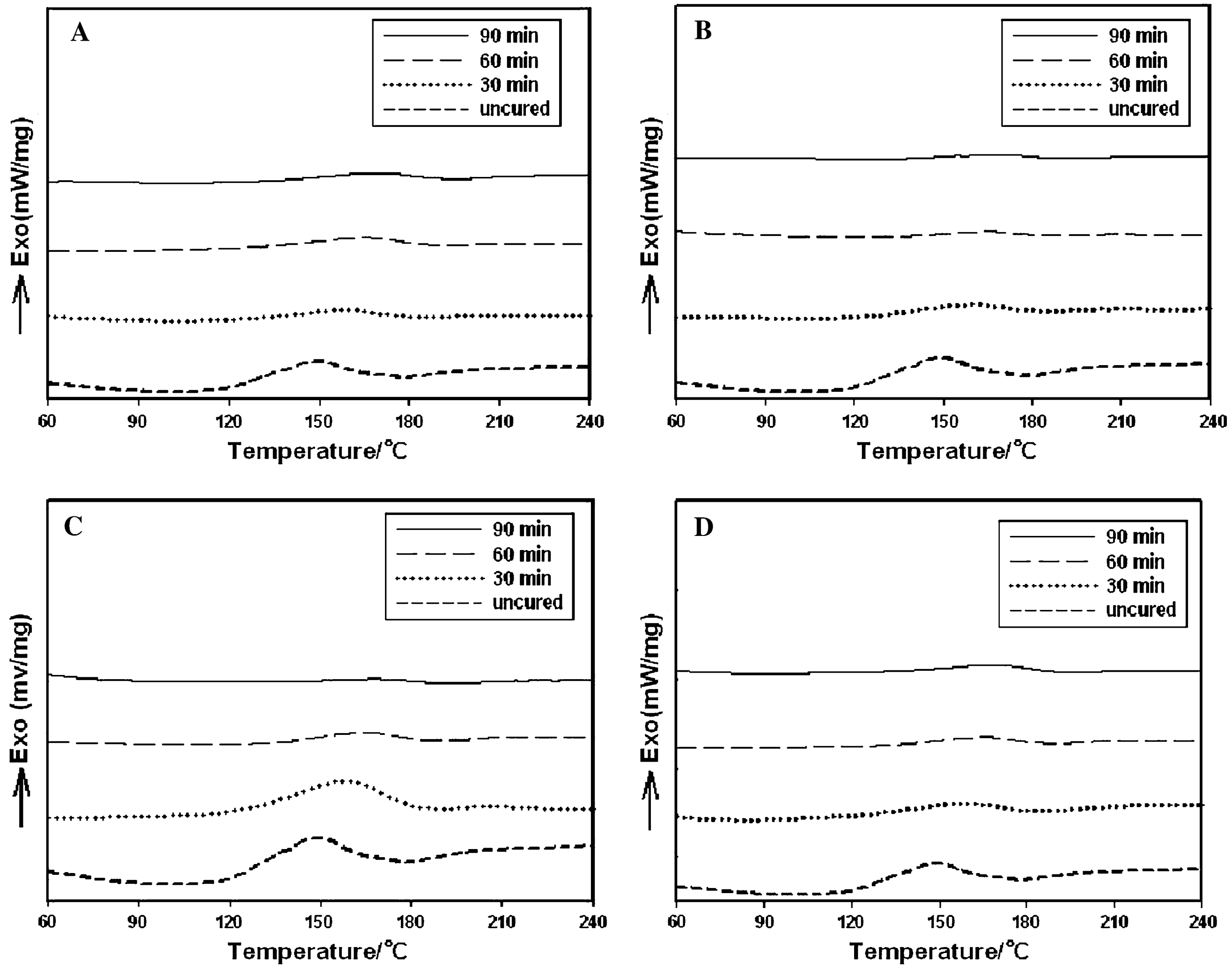

Fig. 3 DSC curves of polycardanol with **a** 0.5 wt%, **b** 1 wt%, **c** 2 wt%, and **d** 3 wt% of MEKP cured at 120 °C for different curing times

The result indicates that most of the curing reaction of polycardanol may be occurred with 0.5 or 1 wt% MEKP at 120 °C for 90 min. Although the polycardanol sample was mixed with MEKP of low concentration by agitating, the curing time of 90 min was not long enough to let the MEKP molecules accomplish the reaction of the polycardanol molecules. As a result, the polycardanol could not be cured completely, showing a very small exotherm. When the concentration of MEKP was higher than 2 wt%, the very small exothermic peak was still found even after curing for 90 min. The change of the exothermic peak position and intensity implies that the molecular chains of MEKP can move more freely and then react with polycardanol by increasing the curing temperature.

It was obvious that the curing conditions given were not adequate for processing polycardanol as a composite matrix resin because they did not make the polycardanol consolidated enough and, as a result, the mechanical resistance of the polycardanol to manual tension was very poor. The exothermic peak shifted to higher temperature indicates that only adding an initiator to polycardanol was not effective enough for full curing. Therefore, Co-Naph was added to the MEKP to accelerate the curing reaction of polycardanol.

Effect of accelerator on the curing behavior of polycardanol

Figure 4 compares the DSC result examined for uncured polycardanol in the absence and the presence of accelerator. From the DSC curves, it was observed evidently that after adding 1 wt% MEKP and 0.2 wt% Co-Naph to polycardanol, the exothermic peak position was shifted to lower temperature and the enthalpy change was greater than that of uncured polycardanol with 1 wt% MEKP only. It was obvious that the change of the exothermic peak was due to the addition of Co-Naph, indicating that it accelerates the curing reaction in the lower temperature region.

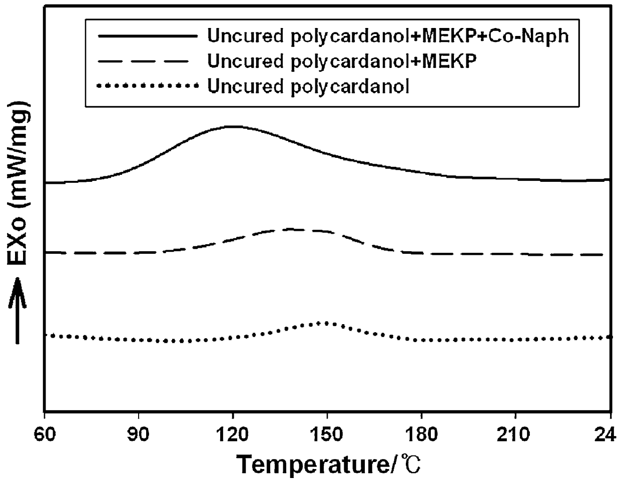

Fig. 4 DSC curves of neat polycardanol and uncured polycardanol resins with 1 wt% MEKP in the absence and the presence of 0.2 wt% Co-Naph

Figure 5 depicts the DSC curves of polycardanol cured isothermally from 120 to 200 °C with 1 wt% MEKP and 0.2 wt% Co-Naph, respectively. The curing time at each temperature was varied from 30 to 120 min. The exothermic peak with the maximum between 120 and 125 °C disappeared after curing for 30 min (a) and for 60 min (b) at 200 °C. The maximum peak was slightly shifted to lower temperature with increasing curing temperature. As found from the occurrence of exothermic reaction, the curing reaction was not completed at the temperatures lower than 200 °C. The exothermic peak intensities observed with the curing time of 30 min are similar to those with the curing time of 60 min, whereas they are significantly decreased upon curing at the same temperature for 120 min, as shown in Fig. 5c.

It was obvious that the exothermic peak intensity was greatly reduced in the temperature range between 180 and 200 °C in the presence of Co-Naph. The polycardanol samples cured at 200 °C for both 30 and 60 min were not hard enough even though the endothermic peaks completely disappeared, whereas the sample cured at 200 °C for 120 min was hard enough to be a matrix resin. Consequently, it was considered that the curing time of 120 min at 200 °C may be appropriate for consolidating a polycardanol and it is useful for processing the composite.

The polycardanol cured at 190 °C for 120 min in Fig. 5c exhibited a broad small exotherm. It indicates that 190 °C was not high enough for completely curing polycardanol. The result demonstrates that 200 °C is a critical temperature, at which polycardanol can be fully cured. It was noted that there was no exotherm observed with the samples cured at above 200 °C, as shown in Fig. 6. This means that no further reaction took place in the polycardanol exposed to the temperature higher than 200 °C and the crosslinking of polycardanol with the monomer-to-polymer conversion of 91.1% may be accomplished at 200 °C for 120 min. The DSC curves obtained at 200, 220, and 240 °C were similar to each other. It was concluded that the temperature higher than 200 °C for curing polycardanol was not necessary for producing natural fiber-reinforced polycardanol composites because the temperature may degrade cellulose-based natural fibers during processing [17].

Three concentrations of Co-Naph, 0.1, 0.2, and 0.3 wt% were used to find out the amount of accelerator and the temperature suitable for curing polycardanol. Figure 7 shows the DSC curves of polycardanol resins with 1 wt% MEKP and different Co-Naph concentrations cured isothermally at 200 °C for 120 min. No distinct exotherm was observed in the all three samples, as can be seen. It seems

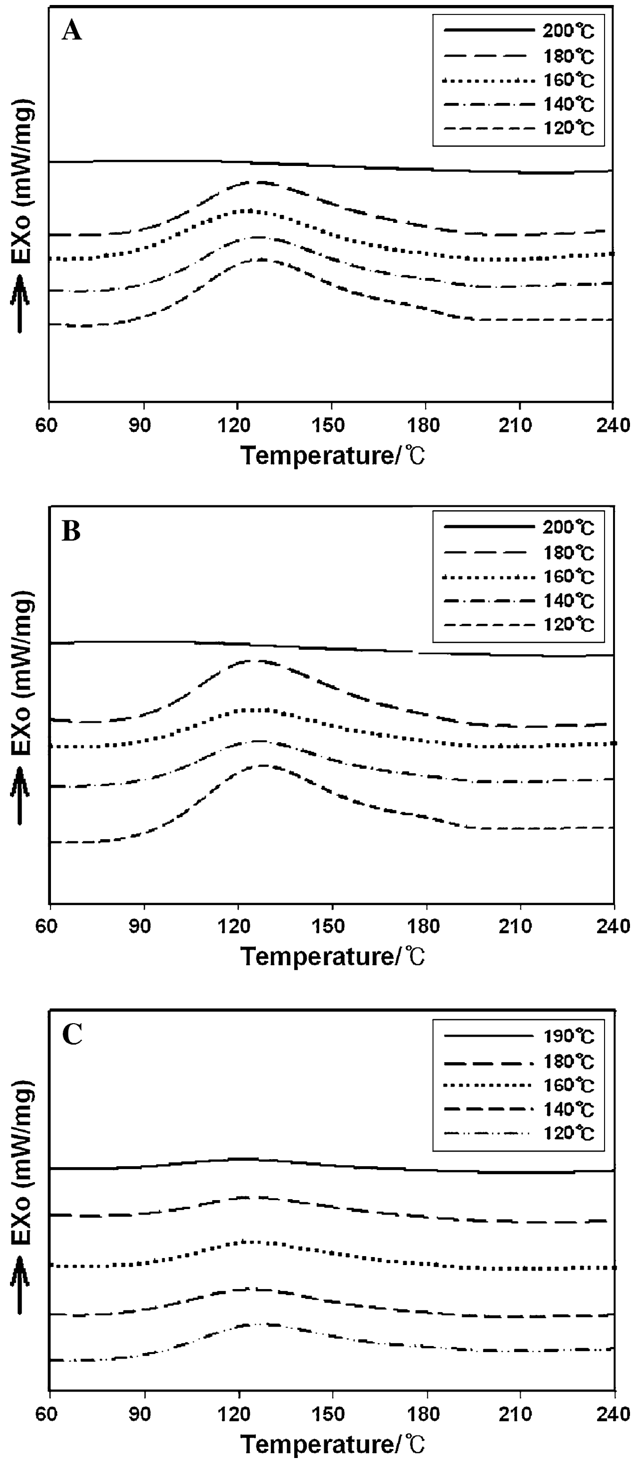

Fig. 5 DSC curves of polycardanol resins in the presence of 1 wt% MEKP and 0.2 wt% Co-Naph cured at different temperatures for **a** 30 min, **b** 60 min, and **c** 120 min

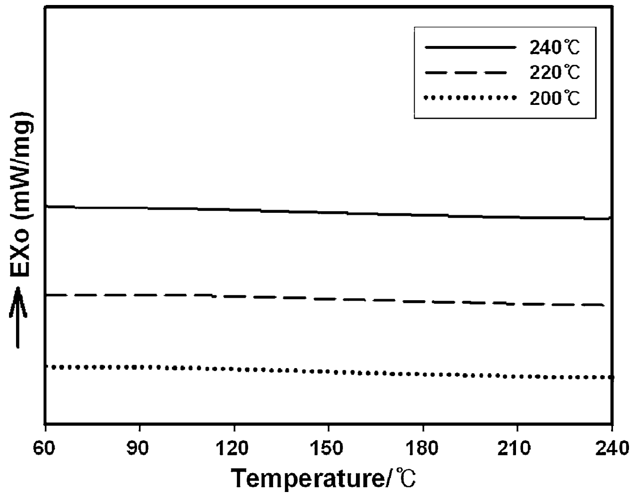

Fig. 6 DSC curves of polycardanols in the presence of 1 wt% MEKP and 0.2 wt% Co-Naph cured at 200, 220 and 240 °C for 120 min, respectively

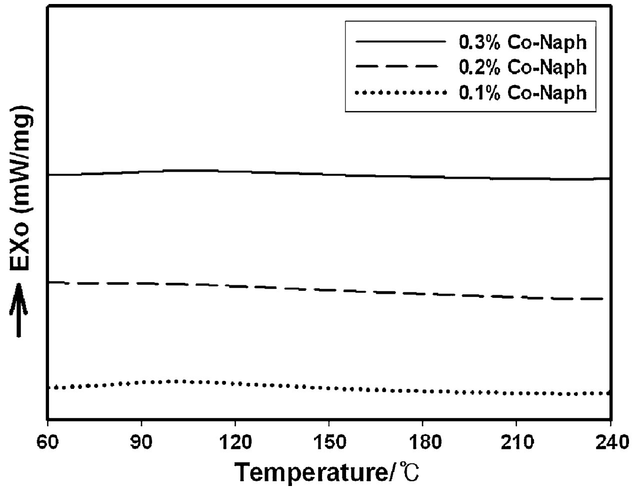

Fig. 7 DSC curves of polycardanol with 1 wt% MEKP and with different Co-Naph concentrations cured at 200 °C for 120 min

that among the three samples the polycardanol sample with 0.2 wt% Co-Naph provided a curve without any indication of the exotherm as a function of temperature. It may be said that 0.2 wt% Co-Naph may be suitable for assisting the MEKP to cure the polycardanol. Consequently, the final curing conditions of polycardanol have been determined as follows: 1 wt% MEKP, 0.2 wt% Co-Naph, curing temperature 200 °C, and curing time 120 min.

Effect of the conversion of polycardanol on the curing behavior

Polycardanol resins with three different monomer-to-polymer conversions were used to compare their curing behavior. Figure 8 displays the DSC curves of polycardanol resins with the conversions of 85.6% (a) and 97.1% (b), respectively. Each sample was prepared at different curing temperatures for 120 min in the presence of 1 wt% MEKP and 0.2 wt% Co-Naph. The results from Fig. 2 to Fig. 7

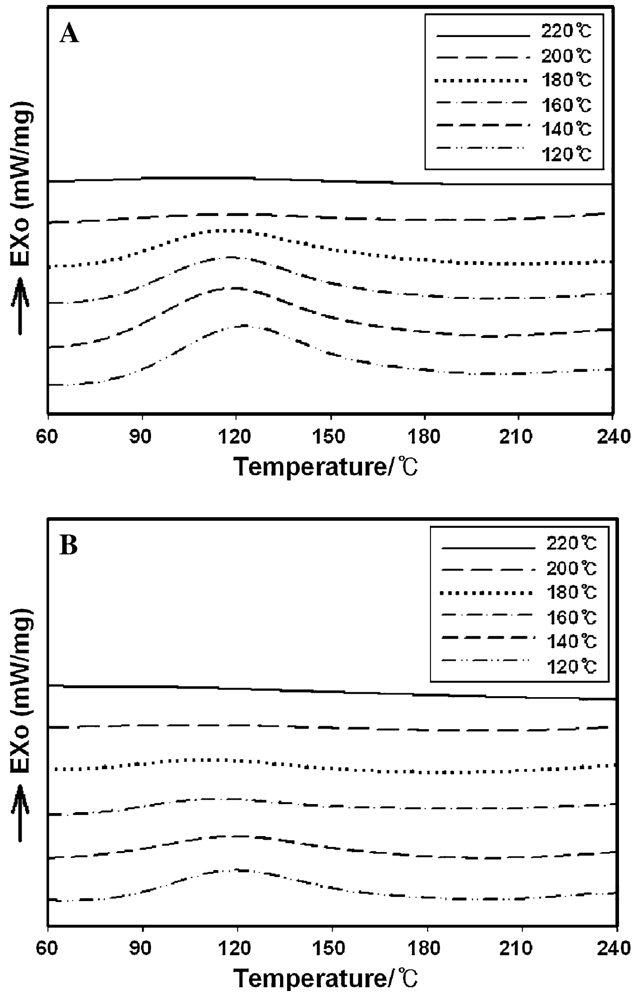

Fig. 8 DSC curves of polycardanol resins with the monomer-to-polymer conversions of **a** 85.6% and **b** 97.1% cured at different curing temperatures for 120 min in the presence of 1 wt% MEKP and 0.2 wt% Co-Naph, respectively

were from a polycardanol with a monomer-to-polymer conversion of 91.1%. Compared with the polycardanol of 91.1% conversion, the polycardanol of 85.6% conversion exhibited greater exotherms at the corresponding curing conditions, whereas that of 97.1% conversion showed smaller exotherms at each curing temperature. In the both cases, the exotherm was gradually decreased with increasing curing temperature. There was a significant change in the exotherm between 180 and 200 °C. As a result, it was obvious that 200 °C may be a critical temperature for completely curing polycardanol, as mentioned earlier, regardless of the monomer-to-polymer conversion.

It can be seen from Fig. 9 that the peak temperatures found for polycardanol resins with three different monomer-to-polymer conversions were shifted to lower temperatures with increasing curing temperature, more significantly in the polycardanol of 97.1% conversion, indicating that the effect of Co-Naph added to MEKP was

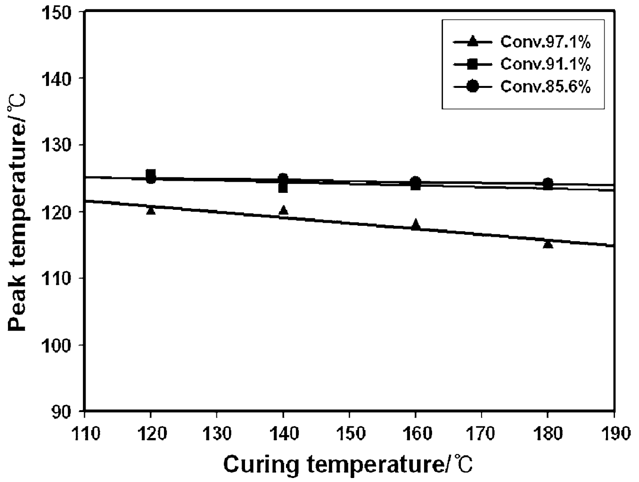

Fig. 9 Variation of the exothermic peak temperature for polycardanol resins with different conversions as a function of curing temperature

greater in the polycardanol of high conversion than in that of low conversion. The result suggests that a polycardanol of high monomer-to-polymer conversion may be more useful as a polymer matrix resin than that of low conversion because it would lower the curing temperature and also it would shorten the curing time for composite processing.

Figure 10 depicts the variation of the heat of curing reaction for polycardanols with different monomer-to-polymer conversions as a function of curing temperature. The heat of reaction was gradually decreased with increasing curing temperature to 200 °C. The highest conversion resulted in the lowest heat of curing reaction. The ΔH value reached almost zero at 200 °C, which means that the curing reaction was completed at the temperature. Figure 11 illustrates the variation of the extent of curing for

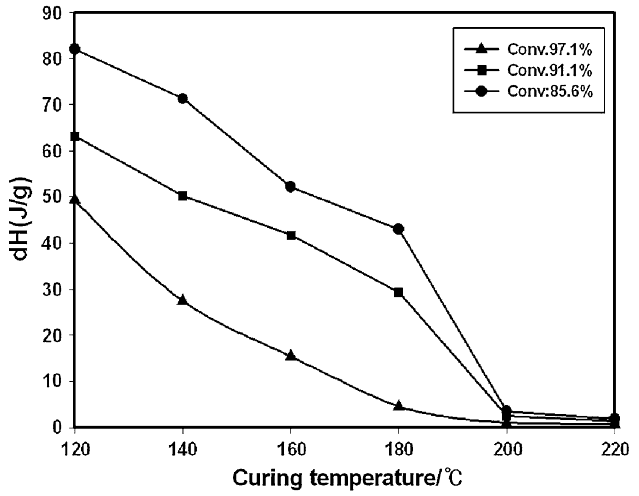

Fig. 10 Variation of the heat of curing reaction for polycardanol resins with different conversions as a function of curing temperature

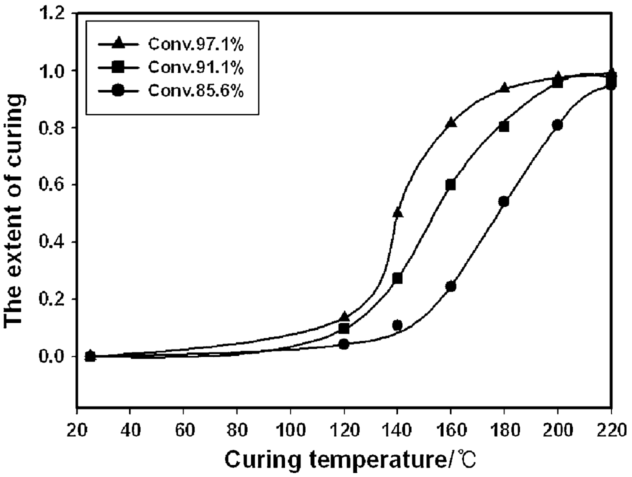

Fig. 11 Variation of the extent of curing for polycardanol resins with different conversions as a function of curing temperature

polycardanols with different monomer-to-polymer conversions as a function of curing temperature. The extent of curing (X) of a thermosetting resin can be determined from the change of the heat of curing reaction [18, 19] using the following equation. Therefore the extent of curing was directly related with the change of the exothermic peak area

$$X = 1 - (\Delta H_r/\Delta H_t)$$

where ΔH_r is the residual heat of exothermic reaction obtained from the partially cured sample and ΔH_t is the total heat of the exothermic reaction for an initially uncured sample. The polycardanol with high conversion exhibited the higher extent of curing than that with low conversion over the entire temperature range, indicating an S-shape curve, which can be typically observed in thermosetting resins. Polycardanol can be cured slowly and partially in the low temperature range up to about 120 °C. The curing was accelerated in the range of 130–140 °C. The extent of curing reaches a plateau region above 200 °C as a consequence of the absence of exothermic reaction and of the complete curing described earlier.

Conclusions

The curing behavior of polycardanol was extensively explored varying curing temperature, curing time, concentration of initiator and accelerator, and the monomer-to-polymer conversion of polycardanol by means of DSC. In conclusions, the curing behavior of polycardanol strongly depended not only on curing temperature and time but also on the concentration of initiator and accelerator used. It was demonstrated that 200 °C may be a critical temperature for completely curing polycardanol. Full curing of polycardanol was attained at 200 °C for 120 min in the presence of 1 wt% MEKP and 0.2 wt% Co-Naph. Such the behavior was explored by monitoring the disappearance of the exothermic peak that depends on the concentration of MEKP and Co-Naph used. The result also suggests that a polycardanol with high monomer-to-polymer conversion would be more useful for a matrix resin than that with low conversion because it lowers the curing temperature and shortens the curing time for processing the composite. The heat of reaction of polycardanol was gradually decreased with increasing curing temperature, whereas the extent of curing was increased with increasing curing temperature, showing a typical S-shape curve. The polycardanol with the highest conversion resulted in the lowest heat of curing reaction and the greatest extent of curing.

Acknowledgment This work was financially supported by the Korea National Cleaner Production R&D Program.

References

1. Ikeda R, Tanaka H, Uyama H, Kobayashi S. A new crosslinkable polyphenol from a renewable resource. Macromol Rapid Commun. 2000;21:496–9.
2. Kim YH, An ES, Park SY, Song BK. Enzymatic epoxidation and polymerization of cardanol obtained from a renewable resource and curing of epoxide-containing polycardanol. J Mol Catal B. 2007;45:39–44.
3. Park SY, Kim YH, Song BK. Polymer synthesis by enzyme catalysis. Polym Sci Technol. 2005;16:342–53.
4. Kim YH, Won K, Kwon JM, Jeong HS, Park SY, An ES, et al. Synthesis of polycardanol from a renewable resource using a fungal peroxidase from *Coprinus cinereus*. J Mol Catal B. 2005;34:33–8.
5. Won K, Kim YH, An ES, Lee YS, Song BK. Horseradish peroxidase-catalyzed polymerization of cardanol in the presence of redox mediators. Biomacromolecules. 2004;5:1–4.
6. Sharma P, Choudhary V, Narula AK. Curing and thermal behaviour of epoxy resin in the presence of a mixture of imide-amines. J Therm Anal Calorim. 2008;94:805–15.
7. Jovičić MC, Radičević RŽ, Budinski-Simendić JK. Curing of alkyds based on semi-drying oils with melamine resin. J Therm Anal Calorim. 2008;94:143–50.
8. Ikeda R, Tanaka H, Uyama H, Kobayashi S. Synthesis and curing behaviors of a crosslinkable polymer from cashew nut shell liquid. Polymer. 2002;43:3475–81.
9. Tawfik SY, Asaad JN, Sabaa MW. Effect of polyester backbone structure on the cured products properties. Polym Test. 2003;22:747–59.
10. Nazareth da Silva AL, Teixeira SCS, Widal ACC, Coutinho FMB. Mechanical properties of polymer composites based on commercial epoxy vinyl ester resin and glass fiber. Polym Test. 2001;20:895–9.
11. Kim H-S, Choi S-W, Lee B-H, Kim S, Kim H-J, Cho CW, et al. Thermal properties of bio-flour-filled polypropylene bio-composites with different pozzolan contents. J Therm Anal Calorim. 2007;89:821–7.
12. Lee HS, Cho D, Han SO. Effect of natural fiber surface treatments on the interfacial and mechanical properties of henequen/polypropylene biocomposites. Macromol Res. 2008;16:411–7.

13. Kim H-S, Kim H-J, Cho D. Thermal analysis of hydrolysis and degradation of biodegradable polymer and bio-composites. J Therm Anal Calorim. 2009;96:211–8.
14. Mwaikambo LY, Ansell MP. Hemp fibre reinforced cashew nut shell liquid composites. Compos Sci Technol. 2003;63:1297–305.
15. Aziz SH, Ansell MP. The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites: part 2-cashew nut shell liquid matrix. Compos Sci Technol. 2004;64:1231–8.
16. Maffezzoli A, Calo E, Zurlo S. Cardanol based matrix biocomposites reinforced with natural fibres. Compos Sci Technol. 2004;64:839–45.
17. Zhou Q. Studies on cure behavior of polycardanol and various natural fiber/polycardanol biocomposites. Master Thesis, Kumoh National Institute of Technology, Gumi, Korea; 2008.
18. Pryde CA. IR studies of polyimides. I. Effects of chemical and physical changes during cure. J Polym Sci A. 1989;27:711–24.
19. Cho D, Drzal LT. Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material. II. Thermal characterization. J Appl Polym Sci. 2000;75:1278–87.