FT-IR Studies on the Curing Behavior of Polycardanol from Naturally Renewable Resources

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ABSTRACT: In the present study, the curing behavior of polycardanol prepared by enzymatic oxidative polymerization of thermally treated cashew nut shell liquid, which can be available from naturally renewable resources, was explored in the presence of methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate (Co-Naph). The curing behavior was monitored varying Co-Naph concentration and curing temperature by means of Fourier transform infrared (FT-IR) spectroscopy. The result revealed that the characteristic absorption bands were significantly affected by the given curing condition, resulting mainly from the unsaturated moiety in the polycardanol molecule. The extent of curing of polycardanol strongly depended on curing temperature, showing a typically sigmoidal curve reaching almost 1.0 upon processing at 200°C for 120 min. The thermal curing conditions for preparing polycardanol with an optimal state of cure were provided in the work. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2774–2778, 2011

Key words: polycardanol; FT-IR absorption; curing behavior; the extent of curing; methyl ethyl ketone peroxide; cobalt naphthenate

INTRODUCTION

With increasing environmental awareness, social consciousness, and globally upcoming environmental issues, biomass-based products obtainable from naturally renewable resources have been increasingly attracted attention in academia and industry during the last decade. Many research efforts have been devoted to replace petroleum-derived organic materials to environmentally-benign materials derived from renewable resources, particularly like plants.[1–3]

Polycardanol is one of the promising candidates as a polymer material derived from naturally renewable resources. It can be obtained by enzymatic oxidative polymerization of thermally treated cashew nut shell liquid (CNSL) using peroxidase secreted from the basidiomycete fungus.[4,5] CNSL constitutes nearly one-third of total cashew nut weight. Basically, polycardanol is originated from cardanol.

Cardanol, which can be produced by thermal treatment of 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] Polycardanol, which is an oily soluble polymer, is normally dark brown, highly viscous, and thermally curable. As advantages over conventional phenol-based thermosetting resins, it has no volatile organic compounds (VOC).[6] Therefore it has potential as an environmentally-benign green composite matrix resin as well as a glossy formaldehyde-free coating material and a finish.[3,7,8]

Understanding of the curing behavior of such an environmentally-benign thermosetting resin is critically important to obtain optimal properties of resulting resin and/or composite materials as well as to determine appropriate thermal conditions to process it.[9–11] Polycardanol with unsaturated double bonds in the repeating unit can be thermally cured with the presence of appropriate peroxides and/or cobalt naphthenate, as found typically in unsaturated polyester resins.[12–14] Fourier transform infrared (FT-IR) spectroscopy is a powerful tool for monitoring chemical reactions that occur during thermal curing. This technique has been successfully utilized in a number of polymer studies including curing,[15] aging,[16] crosslinking,[17] as well as structural identification.[18,19]

The objectives of the present study are primarily to understand the curing of polycardanol and ultimately to find out optimal curing conditions for successfully processing polycardanol composites with cellulose-based natural fibers. Prior to accomplishing our ultimate objective, in the present work we, for the first time, dealt with the curing behavior of polycardanol in the absence and presence of initiator and accelerator and also with the effect of curing temperature on monitoring the appearance and disappearance of characteristic absorption bands of polycardanol.

EXPERIMENTAL

Materials

Polycardanol, which was prepared by enzyme-catalyzed oxidative polymerization, was kindly supplied by Korea Research Institute of Chemical Technology, Daejeon, Korea. Its number-average molecule weight (M_n) was 1610 and the weight-average molecule weight (M_w) was 7220. The viscosity was in the range of 16,000–34,800 cps. The chemical structure of polycardanol used in this work can be found in the previous report.[14]

Methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate (Co-Naph) were used as initiator and accelerator, respectively. MEKP of 1.0 wt % was used. Three different Co-Naph concentrations of 0.1, 0.2, and 0.3 wt % were used. Curing processes of polycardanol were performed at 120, 140, 160, 180, 190, 200, 220, and 240°C for 120 min in a convection oven, respectively. Curing of polycardanol at 200°C for 240 min was also conducted for comparison.

Analysis

FT-IR spectroscopy (300E Jasco) was also utilized to monitor the change of chemical groups upon curing. Clear potassium bromide (KBr) discs were molded from the powder and a pure KBr disc was used as the background. A very small amount of liquid-state polycardanol resin containing MEKP in the absence and presence of Co-Naph was coated on the KBr disc to form a thin film of the resin on it. Then each KBr disc coated with polycardanol was individually cured in the range of 120–240°C in an air-circulating oven according to prescheduled thermal profiles. The KBr disc coated with neat polycardanol without MEKP and Co-Naph were also ready for comparison. FT-IR spectra were collected from an identical spot of the sample in the disc. The discs were always kept in a desiccator prior to each measurement. The resolution and the number of scans were 4 and 50 cm^{-1}, respectively. FT-IR measurements were performed at ambient temperature.

RESULTS AND DISCUSSION

Effect of MEKP and Co-Naph on the spectrum of uncured polycardanol

Figure 1 displays FT-IR spectra of uncured polycardanol in the absence and presence of MEKP and Co-Naph. The spectrum obtained from neat polycardanol (A) was compared with the spectra from uncured polycardanols containing 1.0 wt % MEKP only (B) and both 1.0 wt % MEKP and 0.2 wt % Co-Naph (C).

Neat and uncured polycardanols exhibited characteristic absorption peaks primarily based on two chemical moieties in the molecule. One was based on the aromatic moiety and the other on the unsaturated moiety therein. It was obvious that a strong and broad absorption band centering near 3400 cm^{-1} was due to hydrogen-bonded O—H stretching vibration in the molecule. The small and sharp absorption peak at 3010 cm^{-1} was ascribed to typical sp^2 C—H stretching of the unsaturated hydrocarbon and the peaks in the range of 3,000–2,850 cm^{-1} to sp^3 C—H stretching in the polycardanol chain. The absorption band around 1680 cm^{-1} was due mainly to stretching of C=C bonds in the unsaturated moiety. The bands near 1600 and 1470 cm^{-1} were resulted from the C=C stretching in the aromatic moiety. It was likely that the band around 1460 cm^{-1} responsible for C—H bending vibration in the saturated hydrocarbons was overlapped with the C=C stretching band in the aromatic moiety. The peaks in the range of 1300–1100 cm^{-1} were due mainly to C—O stretching in the ether linkage as well as to C—O stretching in the secondary alcohol groups in the aromatic moiety of the molecule. It seemed that the multiple absorption peaks in the
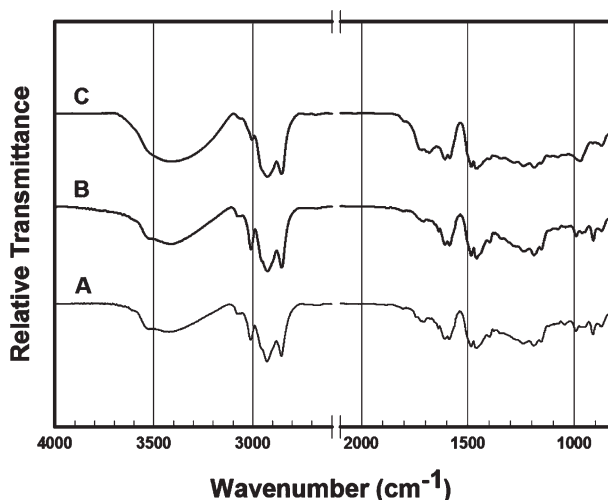

Figure 1 FT-IR spectra of uncured polycardanols: (A) neat, (B) with 1 wt % MEKP and no Co-Naph, (C) with 1 wt % MEKP and 0.2 wt % Co-Naph.

range of 1000–850 cm^{-1} were attributed to *m*-substituted phenol in the aromatic moiety and C—H vibration of conjugated *cis*-trans double bond, nonconjugated *trans* double bond and terminal vinyl group in the unsaturated moiety.

There was no significant change in the absorption band measured with the uncured polycardanol containing 1.0 wt % MEKP only, compared to the result from neat polycardanol. However, it was found that in the presence of Co-Naph with MEKP the spectrum of the uncured polycardanol was changed more or less in the two characteristic absorption positions at 3010 cm^{-1} and near 1720 cm^{-1}. That is, the band at 3010 cm^{-1} was decreased while the band near 1720 cm^{-1} was increased. It indicated that incorporating Co-Naph into polycardanol with MEKP may be useful for monitoring the curing behavior of a polycardanol system, focusing on the appearance and disappearance of the two characteristic peaks by means of FT-IR spectroscopy.

Effect of Co-Naph concentration on the spectrum of cured polycardanol

Three concentrations of cobalt naphthenate 0.1, 0.2, and 0.3 wt % were used to examine the effect of Co-Naph concentration on the FT-IR spectrum of cured polycardanol. The result was compared with the uncured one, as seen in Figure 2. The polycardanols with 1.0 wt % MEKP and Co-Naph at different concentrations were cured at 200°C for 240 min. Three characteristic absorption bands at 3010 cm^{-1}, around 1720 cm^{-1} and in the range of 1500–900 cm^{-1} observed in the uncured polycardanol were distinctly changed after curing. The peak at 3010 cm^{-1}
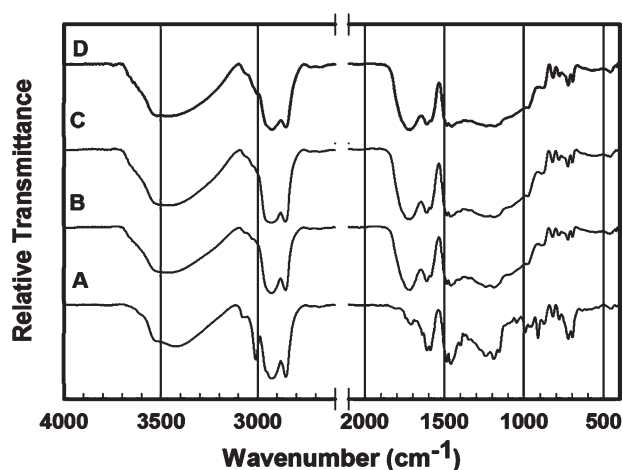

Figure 2 FT-IR spectra of polycardanols cured at different Co-Naph concentrations: (A) uncured, (B) 0.1 wt % Co-Naph, (C) 0.2 wt % Co-Naph, (D) 0.3 wt % Co-Naph. Curing was done at 200°C for 240 min in the presence of 1 wt % MEKP.

originated from the unsaturated moiety in the molecule completely disappeared and the band centering near 1200 cm^{-1} became smaller and broader. On the other hand, the peak centering at about 1720 cm^{-1} was markedly developed after curing, reflecting C=O stretching vibrations of aldehydes and ketones in the range of 1725–1715 cm^{-1}. It was noted that the spectral change in the range of 1500–900 cm^{-1} was also resulted from the structural change by crosslinking between the unsaturated double bonds in the polycardanol molecule upon curing. However, it seemed that varying the Co-Naph concentration did not influence the spectral change significantly.

It has been found that curing polycardanol at 200°C for 240 min may cause the change of the cured polycardanol from dark brown to black. The result also confirmed that varying the Co-Naph concentration from 0.1 to 0.3 wt % did not influence significantly the curing behavior of polycardanol and the duration of 240 min at 200°C was too long to complete the curing. The earlier report[14] studied using DSC revealed that there was no distinct exothermic peak found from polycardanol samples with 0.1–0.3 wt % Co-Naph. And polycardanol with 0.2 wt % Co-Naph and 1.0 wt % MEKP cured at 200°C exhibited the DSC curve without any indication of exothermic peak, reflecting complete curing of the resin. The FT-IR study also demonstrated that 0.2 wt % Co-Naph may be appropriate for assisting MEKP to cure polycardanol successfully. Combining the results, it was worth examining the spectral change of polycardanol containing 1.0 wt % MEKP and 0.2 wt % Co-Naph by varying temperatures with a shorter curing time.

Effect of cure temperature on the spectrum of polycardanol

The FT-IR spectra for polycardanols with 1.0 wt % MEKP and 0.2 wt % Co-Naph cured at different cure temperatures are shown in Figure 3. With increasing cure temperature from 120 to 190°C the absorption band was varied particularly at 3010 cm^{-1}, 1725–1715 cm^{-1}, and 1000–900 cm^{-1}. The absorption peaks at 3010 cm^{-1} and in the range of 1000–900 cm^{-1} were ascribed to the unsaturated moiety in the polycardanol molecule. The peak at 1725–1715 cm^{-1} was due to C=O stretching vibrations of aldehydes and ketones in the molecule.

The height of the peak centering near 3400 cm^{-1}, which was due to O—H stretching of the aromatic moiety in the polycardanol molecule, did not change significantly but the peak position was shown at a higher frequency region with increasing curing temperature, shifting about 100 cm^{-1} from 120 to 190°C. The peaks at 1300–1100 cm^{-1} due to C—O stretching in the aromatic moiety did not change meaningfully.
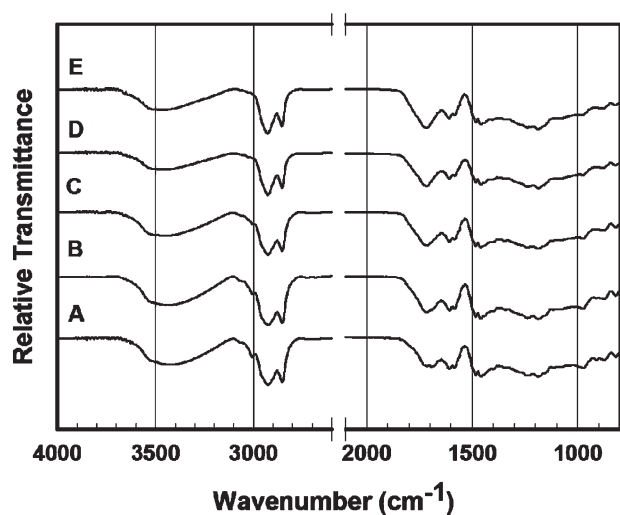
Figure 3 FT-IR spectra of polycardanols containing 1 wt % MEKP and 0.2 wt % Co-Naph cured at different temperatures for 120 min: (A) 120°C, (B) 140°C, (C) 160°C, (D) 180°C, (E) 190°C.

Figure 4 compares a spectrum of polycardanol cured at 200°C for 120 min and two spectra of polycardanols cured additionally at 220 and 240°C, respectively. It can be said that the polycardanol sample exposed to 220 or 240°C was postcured. As can be seen, postcuring at 220°C did not change the spectrum whereas postcuring at 240°C somewhat changed the absorption band, exhibiting a less intensive peak height at each characteristic spectral position in comparison with the band of the sample cured at 200°C.

The disappearance and appearance of some characteristic absorption bands of polycardanol upon thermal curing were examined quantitatively.
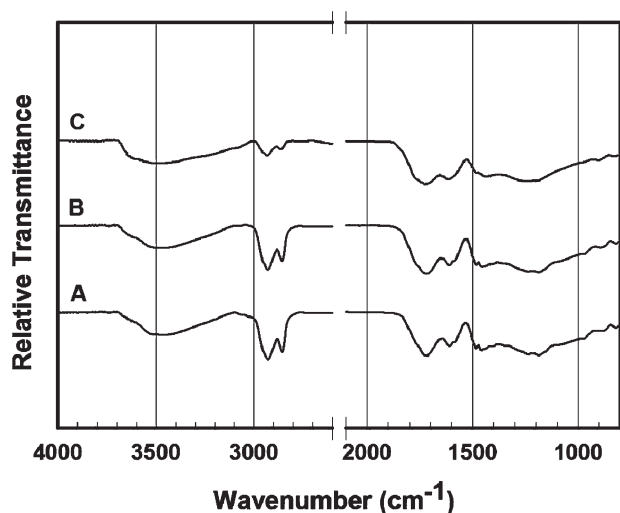

Figure 4 FT-IR spectra of the polycardanols cured at (A) 200°C and postcured at (B) 220°C and (C) 240°C.
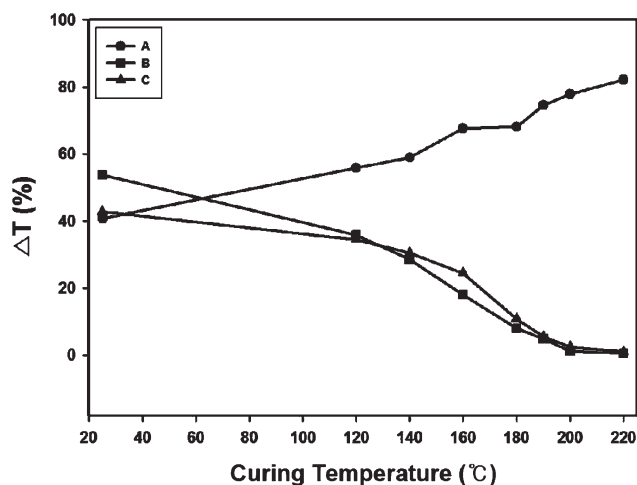

Figure 5 Variation of the $\Delta T(\%)$ values obtained from three characteristic absorption bands of polycardanol as a function of curing temperature. (A) from 1725–1715 cm^{-1}, (B) from 3010 cm^{-1}, (C) from 1000–900 cm^{-1}.

Figure 5 depicts the variation of the absorption peak of polycardanol as a function of curing temperature. The $\Delta T(\%)$ values were calculated from the difference of the percent transmittance values between the absorption maximum and the minimum in close proximity to the peak observed from polycardanol samples cured at different temperatures, as done with different thermosetting resin systems in an earlier study.[11]

It was noticeable that the $\Delta T(\%)$ values at 3010 cm^{-1} and in the range of 1000–900 cm^{-1} due to the unsaturated moiety were decreased with increasing curing temperature and almost disappeared at 190°C. Also, the peak at 1725–1715 cm^{-1} due to C=O stretching vibrations was increased slightly with increasing curing temperature, resulting in the increase of $\Delta T(\%)$. Consequently, it was likely that the aromatic moiety in the polycardanol molecule did not contribute to changing significantly the absorption band during the curing process whereas the unsaturated moiety contributed to the appearance and disappearance of the characteristic absorption bands, reflecting an important role in the crosslinking of polycardanol.

The extent of curing of polycardanol

FT-IR analysis also provides useful information on the extent of curing of polycardanol, as studied with other thermally curable polymer systems.[11,15,20] The extent of curing (X) can be calculated from the change in the area of the absorption peak specified at a representative wavenumber by the following equation.[21]

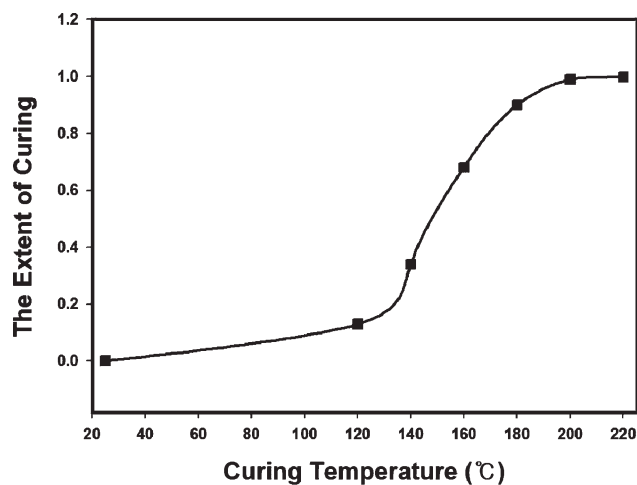$$X = 1 - (\Delta A_r / \Delta A_t)$$

Figure 6 The extent of curing of polycardanol as a function of curing temperature.

where ΔA_r is the peak area of the absorption band obtained from each polycardanol sample partially cured at different temperatures and ΔA_t is the total peak area of the absorption band from uncured polycardanol. The X values are expressed in fraction. The absorption bands in the range of 1000–900 cm^{-1} were not considered in the calculation of the extent of curing because they were overlapped with each other.

Figure 6 represents the variation of the extent of curing of polycardanol as a function of curing temperature, determined at a specified wavenumber of 3010 cm^{-1}, at which exhibited a distinct change of $\Delta T(\%)$, as shown in Figure 5. The peak area of the absorption band centered at 3010 cm^{-1} was decreased with increasing curing temperature from 25 to 220°C. Comparing the total peak area ($\Delta A_t = 1$) determined for uncured polycardanol at 25°C, the relative ratio ($\Delta A_r/\Delta A_t$) of the peak area for partially or fully cured polycardanol was 0.87 at 120°C, 0.64 at 140°C, 0.33 at 160°C, 0.09 at 180°C, 0.02 at 200°C, and 0 at 220°C. The variation of the extent of curing obtained from the peak near 1720 cm^{-1} showed a similar tendency to the result from the peak at 3010 cm^{-1}. The result typically exhibited a sigmoidal curve representing the variation of the extent of curing of a thermosetting resin system. It was also noted that polycardanol was cured slowly at the initial stage, partially cured with a much faster rate in the range of 130–180°C, and completely cured at 200°C showing a maximum value of the extent of curing close to 1.0.

CONCLUSIONS

FT-IR studies with thermally curable polycardanol obtainable from naturally renewable resources revealed that the characteristic absorption bands were resulted from the unsaturated moiety in the polycardanol molecule and they significantly depended on the curing condition given. It was noted that the appearance and disappearance of the characteristic absorption peaks particularly near 3010 and 1720 cm^{-1} with varying curing temperature provided a useful indication for monitoring the curing behavior of polycardanol.

The extent of curing of polycardanol strongly depended on curing temperature, exhibiting a sigmoidal pattern. It has been suggested that polycardanol be cured at between 190 and 200°C for 120 min in the presence of 1.0 wt % MEPK and 0.2 wt % Co-Naph to attain an optimal state of polycardanol used in the present work. Postcuring of polycardanol can also be performed at a temperature below 240°C if necessary. In addition, it has been remarked that combining the present FT-IR study and the previous DSC study may provide complementary information not only on curing neat polycardanol resin but also on processing polycardanol in a composite system.

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