

Cardanol–Glycols and Cardanol–Glycol-Based Polyurethane Films

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ABSTRACT: The syntheses of cardanol–glycols (CGs) and CG-based polyurethane (CGPU) films have been investigated. The characterization of CGs and CGPU films were determined by IR, $^1\text{H-NMR}$ spectra as well as a swelling test and DSC studies. The increase of molecular weight of glycols leads to a decrease of cardanol content in CGPUs and hence decreases crosslinking density of the films, which strongly affects the swelling property and glass transition temperature. The autooxidation-polymerization of CGPUs through the double bonds of the cardanol side chain, catalyzed by cobalt salt, resulting the crosslinking films was also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 507–510, 1997

INTRODUCTION

In the last 10 years, considerable attention has been paid in the synthesis of polymers based on cardanol,^{1–4} natural alkyl phenol from Cashew nut shell liquid, which is well known to exist as a mixture of four components differing in the degree of unsaturation in the metha side chain: 3-(pentadecyl)-phenol, 3-(8-pentadecenyl)-phenol, 3-(8,11-pentadecadienyl)-phenol, and 3-(8,11,14-pentadecatrienyl)-phenol.⁵ There have been a large number of publications on modification of cardanol using the reactivity of hydroxyl phenol group,^{6–10} for example, a formation of films based on epoxy and partially blocked isocyanates with cardanol,¹¹ whereas reports concerning the attempted polymerization of cardanol and its derivatives through the double bonds are very limited.^{12,13} Recently, the synthesis of epoxy flexibilizers, based on cardanol, glycols, and epichlorhydrine, for inhibition of composite propellants has been reported.¹⁴ In this study, cardanol first reacted with glycols in the presence of sulfu-

ric acid. However, sulfonation and polymerization³ of cardanol as well as etherification of glycols may also occur in the presence of a high concentration of sulfuric acid at high temperature.

In this work, the formation of cardanol–glycols (CG) with different molecular weights of glycols in the presence of phosphoric acid as a catalyst was investigated. The synthesis and characterization of the polyurethane films based on CGs and toluene diisocyanate are also reported.

EXPERIMENTAL

Materials

Ethylene glycol (EG), diethylene glycol (DEG), poly(ethyleneglycol)s (PEG-200, PEG-600, and PEG-1000), and 1,4-toluenediisocyanate (TDI) are laboratory-grade chemicals, supplied from Fluka. Cardanol was obtained by distillation of CNSL in vacuum at 2–6 mm Hg, 225–230°C. The density, viscosity, and hydroxyl value of cardanol are 0.9415 g/cm³ (25°C), 75 cP (25°C) and 196 mg KOH/g, respectively.

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Table I Composition of CGs and CGPU Films

CG Sample	Glycol	Yield (%)	Molecular Weight	CGPU Sample	OH/NCO Molar Ratio	Cardanol Content (%)
CG1	EG	82	638	CGPU1	1/1	74.3
CG2	DEG	86	682	CGPU2	1/1	70.4
CG3	PEG200	74	792	CGPU3	1/1	62.4
CG4	PEG600	61	1188	CGPU4	1/1	44.1
CG5	PEG1000	47	1614	CGPU5	1/1	33.6

Synthesis of CG

CG was synthesized by the reaction of 2 mol cardanol with 2 mol glycol in the presence of phosphoric acid 60% (2% by total weight) as a catalyst in a round bottom flask equipped with thermometer, stirrer, and cooler under nitrogen atmosphere at 150°C for 12 h. Phosphoric acid and unreacted glycol were removed from the obtained product by washing with hot water. Unreacted cardanol was extracted by a mixture of ethanol-ether-water. Finally, CG was dried in vacuum at 60°C for 3 h. The composition of the reaction is shown in Table I.

Preparation of the CGPU Films

CGPU films were prepared by the reacting of CGs with TDI in benzene at 50°C for 2–3 h. In all reactions, the OH/NCO molar ratio was maintained as 1 : 1. The films were solvent cast and cured at 60°C for 2 h and then postcured at 100°C for 2 h with and without the presence of cobalt octoate 10% (0.05% by total weight). As shown in Table I, the increase of molecular weight of glycols decreases the cardanol content in the obtained films.

Characterization

IR and ¹H-NMR spectra were recorded on a Perkin-Elmer spectrophotometer 457 and on a Bruker WM 250 spectrometer, using CDCl₃ as solvent with tetramethyl silane as an internal standard, respectively. The swelling test was performed according to Collins' method.¹⁵ Differential scanning calorimetry analyses were carried out on a Perkin-Elmer DCS-7 under dry nitrogen atmosphere. The sample was first scanned to 100°C, thereafter cooled and recorded a second time at a heating rate of 5°C/min. The glass tran-

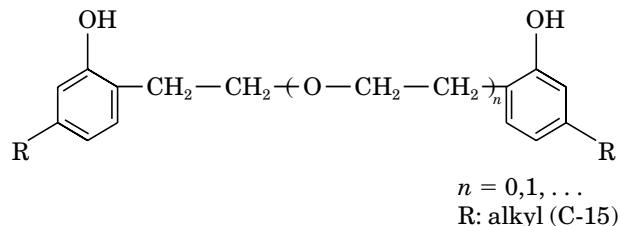
sition temperature (T_g) was determined at the second scan.

RESULTS AND DISCUSSION

The IR spectra of all CGs showed the stretching vibrations of —OH group at 3380 cm⁻¹, C—H of double bonds in the side chain of cardanol at 2995 cm⁻¹, C—H of the phenyl group at 1460 cm⁻¹, and C—O—C of ether groups in glycols at 1080–1200 cm⁻¹ (except for the case of EG). In the ¹H-NMR spectra of CGs the peaks were assigned for different protons (δ , ppm): 0.82 (CH₃), 1.15–1.58 (CH₂), 1.65–2.14 (—CH₂—CH=CH), 2.25–2.69 (—CH₂—Ar), 3.66 (—CH₂—O) (except for the case of EG), 5.12–5.45 (CH₂=CH—, CH=CH—), 6.81–7.35 (aromatic).¹⁶ It should be mentioned that when the higher concentration of phosphoric acid and/or higher temperatures were used, the IR spectrum showed a stretching vibration of an ether group, although it was in the case of EG. This may be explained by the fact that the etherification reaction between EGs happens at the same time.

The determined number-average molecular weight of CGs is shown in Table I. It is clear that the number-average molecular weight of CGs increases with the increase in molecular weight of glycols.

The molecular weight, IR, and NMR data are highly in agreement with the structure of CG, as proposed by Agrawal and Satpute,¹⁴ which can be written as



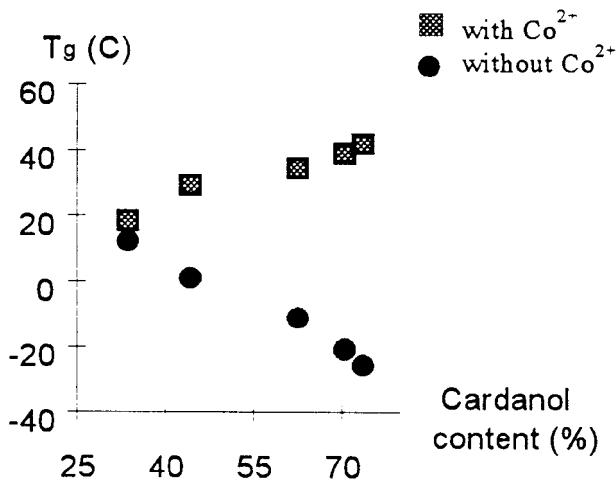


Figure 1 Influence of cardanol content on the T_g of the films.

It also can be seen from Table I that the increase of molecular weight of glycols decreases the reaction yield. This can be explained by the decrease of reactivity of glycol as the chain length increases. However, the boiling point of the reaction mixture decreases according to the amount of water produced by the reaction; in the case of EG, the boiling point of the reaction cannot reach the value 150°C after reacting for 2 h. This is the reason for the lower yield of CG1 compared to that of CG2.

The IR spectra of the CGPU films indicate that there is an additional peak at 1720 cm^{-1} assigned to carbonyl group of urethane group,¹¹ whereas the peak at 3380 cm^{-1} (OH group) disappears. The absorbance of carbonyl group of urethane at 1635 cm^{-1} was also observed. In the NMR spectra of the CGPU films a new peak appears at $\delta = 6.70$ (multiplet) assigned to the NH-proton in urethane group.¹⁷

In the case of the samples using cobalt octoate, the characteristic peak at 2995 cm^{-1} for the double bonds of cardanol side chain was nearly absent in the IR spectrum. Furthermore, these films were totally insoluble in various solvents, whereas the films without cobalt salt dissolved weakly in methylethylketone and cyclohexanone. The results of swelling studies, as illustrated in Figure 1, indicate that in the case of the films using cobalt salt (Co^{2+} films), swelling ratios are very low, and the higher the cardanol content in CGPU films, the lower the swelling ratio will be, in contrast to the films without cobalt salt (normal films). In the case of the normal films, the long alkyl chain of cardanol reduces the structural density of the films and hence increases the swelling ratio as

the cardanol content increases. In contrast, the decrease of the swelling ratio according to the increase of cardanol content in the case of Co^{2+} films might be due to the crosslinking formation during curing. It is well known that cardanol can be auto-oxidation leading to polymerization and resulting crosslinked products. Tyman suggested that under atmospheric oxygen cardanol can undergo hydroperoxidation through the triene double bonds, giving rise to allylic radical centers that would combine to form conjugated intermediates leading to propagation reactions and crosslinking.¹³ Organic salts of cobalt, manganese, and lead are known to catalyze the autooxidation reactions of allylic systems.^{18,19} The crosslinking mechanism of poly(cardanylacrylate) was also studied by George and Pillai.¹⁶ In general, the higher the cardanol content, the higher the crosslinked density will be. The high crosslinked density should relate to the low swelling ratio. Therefore, the CGPU1 and CGPU2 samples containing the highest cardanol content have the lowest swelling ratio.

In DSC studies, it should be mentioned that the first scan for some samples having the T_g above room temperature showed an endothermic peak overlapping with the T_g . After cooling down and repeating the second scan, only the T_g appeared. This endotherm may be due to enthalpy relaxation because these samples were glassy and transparent. It is clear that the polymer chains are frozen in a nonequilibrium conformation in the glassy state; however, some motion occurs even in the glassy state at a temperature moderately below T_g .²⁰ As a result of these restricted motions, a slow relaxation of the nonequilibrium

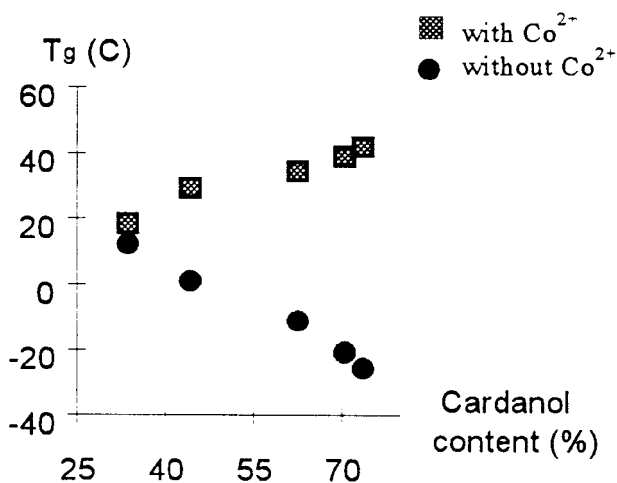


Figure 2 Influence of cardanol content on the swelling value of the films.

state toward the equilibrium state takes place. This process, which is accompanied by a decrease in enthalpy and free volume, is known as physical aging or enthalpy relaxation.

Figure 2 shows the T_g of the polyurethane films. The extension of the glycol chain increases the T_g of the normal films while it decreases the T_g of the Co^{2+} films. Since the long alkyl chain of cardanol can play a role of a plasticizer/flexibilizer and the extension of the glycol chain related to a decrease of the cardanol content, the increase in the glycol chain length increases the T_g of the normal films. Cobalt salt catalyzes autooxidation polymerization of double bonds in cardanol; therefore, the increase of cardanol content improves the crosslinking of the Co^{2+} films. The higher the crosslink density, the higher the T_g will be.

CONCLUSION

Cardanol-glycol can be produced by the reaction of cardanol and glycols in the presence of phosphoric acid as a catalyst. The characterization of the polyurethane films based on CGs is influenced by the type of glycol used. Crosslinked CGPU films can be formed through autooxidation polymerization of double bonds in the cardanol side chain as cobalt salt is used.

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