

Physical, Mechanical, and Thermal Properties of Polyurethanes Based on Hydroxyalkylated Cardanol–Formaldehyde Resins

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Received 4 May 2004; accepted 10 January 2005

DOI 10.1002/app.22016

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyurethanes are synthesized using three different hydroxyalkylated cardanol–formaldehyde resins, diphenylmethane diisocyanate (MDI), and a commercial polyol (PPG-2000). These polyurethanes are found to be tough and crosslinked. A polyurethane prepared using a higher mole ratio of cardanol/formaldehyde of hydroxyalkylated cardanol–formaldehyde resin is found to possess

better thermal and mechanical properties than the polyurethane prepared from a lower mole ratio. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 284–288, 2005

Key words: polyurethanes; hydroxyalkylated cardanol–formaldehyde resin; diphenylmethane diisocyanate; poly(propylene glycol); mechanical properties

INTRODUCTION

Naturally available cashew nut shell liquid (CNSL) is an abundant agricultural by-product whose main component, cardanol (a meta-substituted phenol), acts as an excellent monomer for polymer production. Several patents have been taken out on the production of polymeric materials based on phenolic resin with polyisocyanates and additives.^{1–6} The synthesis and curing behavior of crosslinked polymers from CNSL⁷ and from cardanol⁸ have been described. A self-crosslinkable monomer from cardanol has also been reported.⁹ The synthesis and characterization of rigid polyurethanes using hydroxyalkylated cardanol–formaldehyde resins and 4,4'-dicyclohexylmethane diisocyanate (HMDI) have been described.¹⁰ In the present work, tough polyurethanes are synthesized using hydroxyalkylated cardanol–formaldehyde resins, diphenylmethane diisocyanate (MDI), and a commercially available polyol, poly(propylene glycol) (PPG-2000). The physical, mechanical, and thermal properties of these polyurethanes are also studied.

EXPERIMENTAL

MATERIALS

The CNSL for isolation of cardanol was procured from M/S Vijayalakshmi Cashew Company (Quilon, India).

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Formaldehyde for formylation and methanol for dissolving the catalyst were obtained from M/S BDH Ltd. Glutaric acid, MDI, and epichlorohydrin for epoxidation were obtained from M/S E Merck. PPG-2000 was received from Aldrich Chemicals (Milwaukee, WI). Dibutyltin dilaurate was received from Fluka Chemie.

Synthesis of polyurethanes

Cardanol was separated from technical CNSL by liquid chromatography on silica gel H 60 (thin layer chromatography type). The monoene constituent of cardanol was separated by the argentation method.¹¹ Cardanol–formaldehyde resins were prepared from cardanol and formaldehyde with three different mole ratios: 1 : 0.9, 1 : 0.8, and 1 : 0.6. These cardanol–formaldehyde resins were epoxidized and hydrolyzed to obtain hydroxyalkylated cardanol–formaldehyde resin and then characterized.¹² In the present work, these already synthesized hydroxyalkylated cardanol–formaldehyde resins were treated with MDI and PPG-2000, keeping the isocyanate index (NCO/OH, mol/mol) constant at 1.4 in a nitrogen atmosphere. The formulations of the three polyurethanes, CR₁EHMP, CR₂EHMP, and CR₃EHMP, where 1, 2, and 3 represent the polyurethanes prepared from 1 : 0.9, 1 : 0.8, and 1 : 0.6 mole ratios of cardanol/formaldehyde resins, are presented in Table I. The hydroxyalkylated cardanol–formaldehyde resin, MDI, PPG-2000, and the catalyst dibutyltin dilaurate (0.12%) were mixed at

TABLE I
Formulations of Polyurethanes Based on Hydroxyalkylated Cardanol Formaldehyde Resin

Polyurethane	Diisocyanate (MDI)		Hydroxyalkylated cardanol formaldehyde resin		Polypropylene glycol 2000	
	mol	Concn mol × functionality	mol	Concn mol × functionality	mol	Concn mol × functionality
CR ₁ EHMP	0.680	1.260	0.07	0.70	0.10	0.20
CR ₂ EHMP	0.476	0.952	0.06	0.48	0.10	0.20
CR ₃ EHMP	0.294	0.588	0.05	0.30	0.10	0.20

room temperature in a small plastic cup and poured into a mold for 24 h.

Spectral analysis of polyurethanes

IR spectral analysis was carried out for polyurethanes by the KBr pellet method using a Jasco 410 FTIR spectrophotometer.

Determination of crosslink density and molecular weight between crosslinks

The density of the polyurethanes was determined according to ASTM D 792. The swelling coefficient was determined from the solubility parameter of polyurethanes, and the crosslink density (v_e) or effective number of moles of crosslinked units per gram of polyurethane was determined using the modified Flory Rehner equation:

$$v_e = \frac{-1 \left[V_r + \lambda V_r^2 + \ln(1 - V_r) \right]}{V_s \left[\frac{\rho_r (V_r^{1/3} - V_r/2)}{M_c} \right]} = \frac{1}{M_c}$$

where V_s is the molar volume of the solvent; V_r is the volume fraction of polyurethane in the swollen polymer, which is equal to $1/1 + Q$, where Q is the swelling coefficient; λ is the solvent interaction parameter; ρ_r is the density of the polyurethane; and M_c is the molecular weight between neighboring crosslinks.

Mechanical properties

The tear strength of the polyurethanes was determined in a Zwick universal testing machine (model 1497) using angle tear test specimens (dies) at a crosshead speed of 100 mm/min according to ASTM D 624-81. The tensile strength was measured on the same instrument at a crosshead speed of 100 mm/min using dumbbell-shaped test specimens punched out from cast polyurethane sheets according to ASTM D-412. The indentation hardness

(Shore A) was measured using a hardness tester (Durometer) according to ASTM D 2240-81. The tensile strength, percentage of elongation, and modulus at break were calculated.

Thermal properties

The thermal properties of the polyurethanes were determined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Dupont 2100 and Mettler Toledo thermal analyzers were used for the TA. The samples were heated from ambient temperature to 800°C at a heating rate of 10°C/min under atmospheric conditions in the DTA analyzer. The decomposition temperature was checked for all polyurethanes. The TGA was carried out at a heating rate of 10°C/min. The samples were heated from ambient to 800°C under a nitrogen atmosphere. The weight loss was noted for all polyurethanes.

RESULTS AND DISCUSSION

Synthesis of polyurethanes

The condensation reaction between hydroxyalkylated cardanol-formaldehyde resins and diisocyanate can lead to the formation of stable urethane linkages. The branching and crosslinking in the present polyurethanes are possible because of the higher isocyanate index (1 : 1.4) and the multifunc-

TABLE II
Characterization of Networks of Polyurethanes

Polyurethane	Density (g/cc)	Swelling coefficient in DMA Q	Crosslink density ($\times 10^{-5}$)	Molecular weight between crosslinks (mol^{-1})
CR ₁ EHMP	1.12	1.35	1.2076	828.09
CR ₂ EHMP	1.11	1.44	1.0919	915.83
CR ₃ EHMP	1.10	1.53	0.9973	1002.70

TABLE III
Mechanical Properties of Polyurethanes

Polyurethane	Tear properties			Tensile properties			Hardness Shore A
	Tear strength (kN/m)	Elongation (%)	Tear modulus (kN/m)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	
CR ₁ EHMP	115	90	127.78	28.82	19.21	150	67
CR ₂ EHMP	112	100	112.00	26.64	17.19	155	62
CR ₃ EHMP	100	110	90.91	24.49	15.02	163	53

tional nature of the hydroxyalkylated resins. The polyurethanes synthesized in the present work possess a variety of groups along the polymer chain, including urethane, allophanate, hydrocarbon chain, aromatic ring, and unreacted hydroxyl groups. The formation of crosslinked products clearly indicates the completion of the condensation reaction, leading to stable products.

Spectral properties of polyurethanes

The IR spectrum of the polyurethanes showed characteristic absorptions at 3414, 1743, and 1543 cm^{-1} , corresponding to urethane linkage (—NH stretching), C=O stretching (bonded) in urethane, and N—H bending in urethane, respectively.

Crosslink density and molecular weight between crosslinks

Polyurethane CR₁EHMP is found to possess higher crosslink density and lower molecular weight between crosslinks in comparison with CR₂EHMP and CR₃EHMP (Table II). This may be due to the fact that the CR₁EH resin, having 10 hydroxyl groups, enables the increased condensation of isocyanate and hydroxyl groups, hence the higher crosslink density and lower molecular weight in the CR₁EHMP polyurethane.

Mechanical properties

The mechanical properties of the polyurethanes, especially tensile strength and tear strength, are largely influenced by the presence of aromatic groups, long

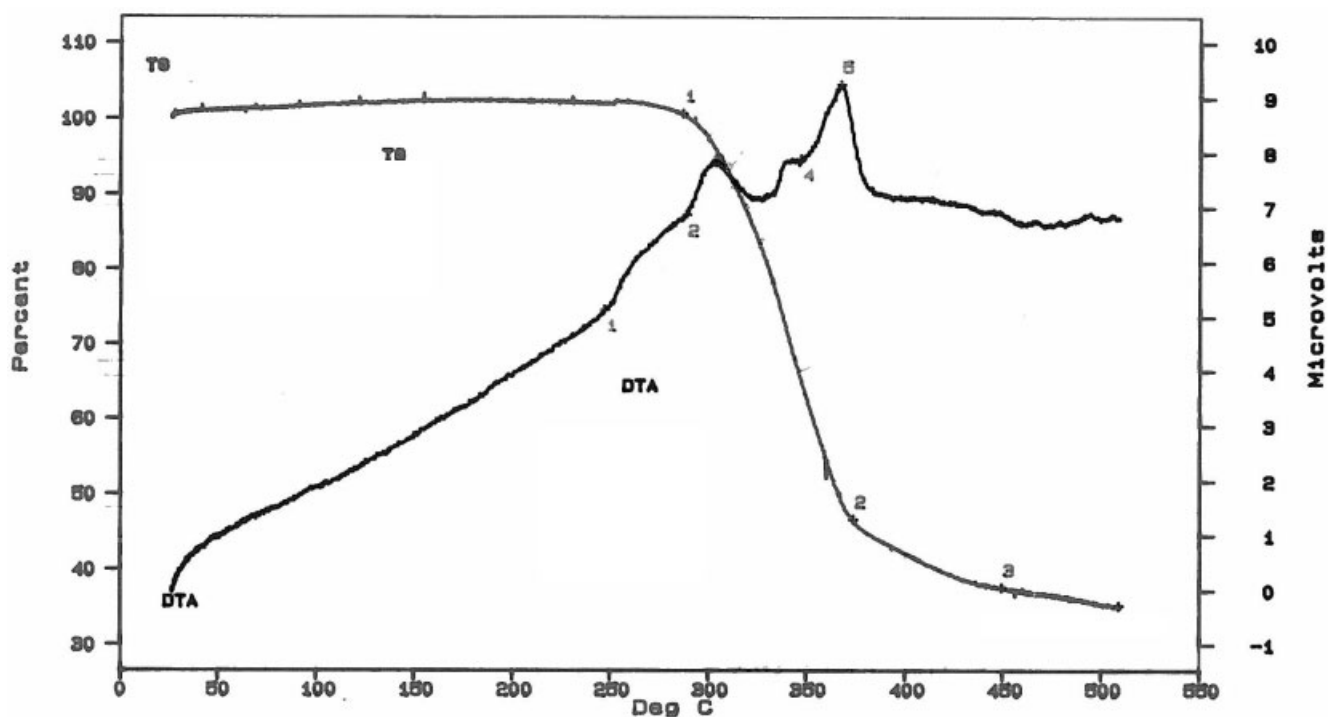


Figure 1 The TGA/DTA results for CR1EHMP.

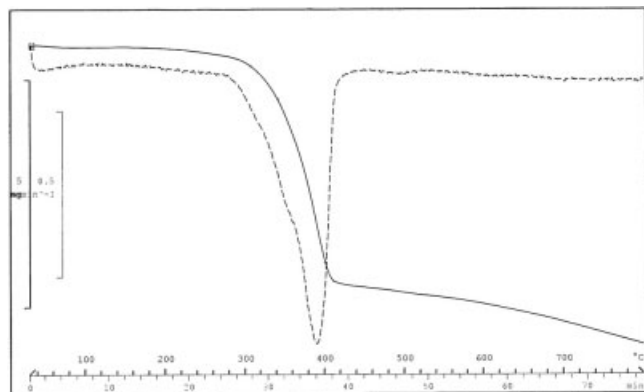


Figure 2 The TGA/DTA results for CR2CEHMP.

alkyl side chains, crosslinking, and so forth. The mechanical properties of the polyurethanes are presented in Table III. The higher tensile and tear strength observed in CR₁EHMP is attributed to the lower molecular weight between the crosslinks and higher crosslink density. The higher Shore A hardness of CR₁EHMP may be due to the higher concentration of phenyl rings in comparison with that of CR₃EHMP.

Thermal properties

The thermal properties of the polyurethanes in this study are influenced mainly by long alkyl side chains in the phenyl ring, unreacted dihydroxy propyl chain ends, the geometry of the molecule, the molecular weight between crosslinks, the degree of segments in the flexible sequence, the flexible polyether polyol segments, and elastically active branch points. The flexible soft segments are polyol segments that start either

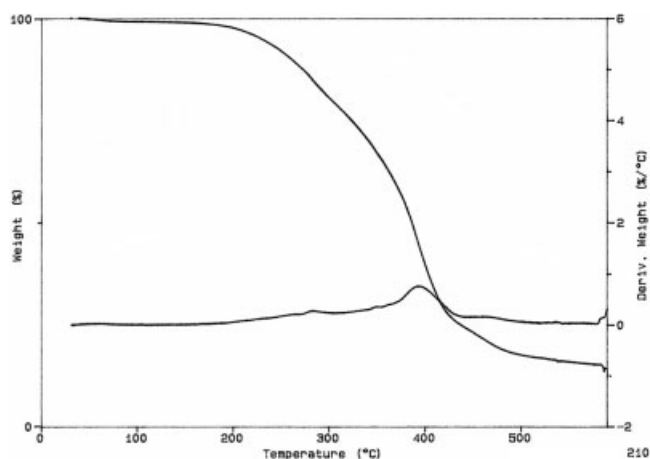


Figure 3 The TGA/DTA results for CR3CEHMP.

TABLE IV
Thermogravimetric Analysis Data of Polyurethanes

Polyurethane	Weight loss at various temperatures				
	100°C	200°C	300°C	400°C	450°C
CR ₁ EHMP	0.0	0.0	1.0	57.3	62.6
CR ₂ EHMP	0.0	0.8	3.1	60.0	70.0
CR ₃ EHMP	0.4	2.1	19.0	61.5	80.0

from urethane or allophanate linkages. The elastically active branch points comprise biuret and allophanate.

The DTA curves of these polyurethanes (Figs. 1–3) do not show any endothermic peak for softening. There are two exotherms: a weak one at around 300°C and a strong one above 300°C for decomposition. The weak exotherm may be due to the cleavage of the meta-substituted alkyl side chain in the phenyl ring. This is conforms well with the result reported earlier.¹³ The second degradation was followed in the main chain of the polyurethanes.

The TG data of polyurethanes (Table IV) show that these polyurethanes invariably possess higher thermal stability. In these cases, only 10% weight loss occurs at a relatively higher temperature. CR₁EHMP has higher thermal stability than CR₃EHMP. This may be due to the fact that CR₁EHMP is stereochemically more stable than CR₃EHMP.

CONCLUSION

Polyurethanes based on hydroxyalkylated cardanol-formaldehyde resins were found to be tough and possessed higher thermal stability and mechanical strength. Polyurethanes prepared using a higher mole ratio of cardanol/formaldehyde of hydroxyalkylated cardanol-formaldehyde resin have better thermal and mechanical strength compared to that of the polyurethane having a lower mole ratio of cardanol/formaldehyde. This may be attributable to the presence of higher crosslink density in the former.

The first author (C.V.M.) thanks the University Grants Commission, New Delhi, the Director of Collegiate Education, Chennai, and the Principal, Rani Anna Government College for Women, Tirunelveli, for selection under the FIP program.

References

1. Robert, L. U.S. Pat. 4,698,377 (1987).
2. Akio, I.; Shigetoshu, A.; Isao, K.; Kkazuuo, T. Jpn. Pat. 62,241,914 (1987).
3. Toshaki, N.; Yukio, S.; Kazuichi, I. Jpn. Pat. 63,142,016 (1988).
4. Noriimasa, Y.; Noratake, S. Jpn. Pat. 63/97/641 (1988).

5. Tsutomu, N.; Koichi, K.; Yoshi, M.; Yokki, Jpn. Pat. 63/213/512 (1988).
6. Hisamitsu, I.; Yukio, S. Jpn. Pat. 63/264/616 (1988).
7. Ikeda, R.; Tanake, H.; Uyama, H.; Kobayashi, S. *Polymer* 2002, 43, 3475.
8. John, G.; Pillai, C. K. S. *J Polym Sci Part A: Polym Chem* 1993, 31, 1069.
9. John, G.; Pillai, C. K. S. *Makromol Chem Rapid Commun* 1992, 13, 255.
10. Sathyalekshmi, K.; Gopalakrishnan, S. *Plast Rubber Compos* 2000, 29(2), 63.
11. Sood, S. K.; Tyman, J. H. P.; Durrani, A.; Johnson, R. A. *Lipids* 1986, 21, 241.
12. Mythili, C. V.; Malar Retna, A.; Gopalakrishnan, S. *J Curr Sci*, to appear.
13. Sathyalekshmi, K. In *Polymer Science—Recent Advances*; Bhardwaj, I. S., Ed.; Allied Pub. Ltd.: New Delhi, 1994; Vol. 2, p 862.