

Rigid Polyurethane Foam Prepared from a Rape Seed Oil Based Polyol

YAN HONG HU, YUN GAO, DE NING WANG, CHUN PU HU, STELLA ZU, LIEVE VANOVERLOOP, DAVID RANDALL

Institute of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Huntsman Polyurethanes (China) Ltd., 452 Wen Jing Road, Minhang Economic and Technological Development Zone, Shanghai 200245, China

Huntsman Polyurethanes, Everslaan 45, B-3078 Everberg, Belgium

Received 22 March 2001; accepted 11 July 2001

ABSTRACT: A new kind of polyol based on rape seed oil for use in rigid polyurethane foam was synthesized and characterized. The synthesis of such a polyol was divided into two steps. The first step was the hydroxylation of the double bonds existing in the long chains of the unsaturated aliphatic hydrocarbon of rape seed oil with peroxy acid. The second step was use of the alcoholysis of the hydroxylated rape seed oil with triethanolamine to increase the hydroxyl value of the product. The reaction process was monitored by means of a novel on-line infrared spectrometer. Rigid polyurethane foam was produced with this rape seed oil based polyol and some physical properties of the foam were examined and compared with a reference foam. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 591–597, 2002; DOI 10.1002/app.10311

Keywords: rigid foam; polyurethane; rape seed oil

INTRODUCTION

Rigid polyurethane (PU) foam is one of the most important insulating materials used today in the construction industry and is the sole insulant used in the global appliances (refrigerators, freezers, etc.) industry. A general review of the rigid PU industry and the physics of heat transfer in cellular materials can be found in refs. ¹ and ².

Today these foams are based on polymeric methylene diphenyl diisocyanate (polymeric MDI) and either polyether or polyester polyols. The polyether polyol can be based on a number of different starting materials to which alkylene oxides (propylene oxide (PO) and/or ethylene oxide (EO)) were added. The starting materials that are currently used are either natural products such

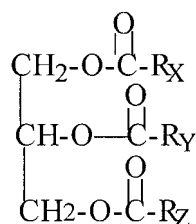
as sucrose or sorbitol or specifically produced organic chemicals such as ethylene diamine or industrial waste streams such as *o*-toluene diamine.

Polyesters used in rigid foams were based on industrial waste streams such as the mixtures of adipic, glutamic, and succinic acid (from nylon production), the distillation residues of dimethyl terephthalate, and the depolymerized poly(ethylene terephthalate) from scrap bottles or films. However, very little work was done by using natural product based polyesters. The environmental and sustainability aspects of using oil-based polyols are of great importance to the PU industry and consequently research work aimed at identifying natural product components of polyethers and polyesters is of interest. In the early days of rigid PU foam production, castor oil was used as the polyol component³ and the three hydroxyl groups on every molecule of castor oil could react with the —NCO groups of isocyanate.

Correspondence to: C. P. Hu (cphu@guomai.sh.cn).

Journal of Applied Polymer Science, Vol. 84, 591–597 (2002)
© 2002 John Wiley & Sons, Inc.

Another important renewable resource is rosin. Rosin contains abietic and pimaric acids and the levopimaric acid can easily react with maleic anhydride to form maleopimaric anhydride, which can then be converted into a polyester polyol by reacting with a diol.⁴ In addition to castor oil and rosin, one abundant natural product is vegetable oil. However, in the chemical structure of vegetable oil, there are no functional groups suitable to react with isocyanate and hence to form urethane bonds. Vegetable oil has the general formula:



where *R* represents a long aliphatic chain containing at least one double bond. It was observed⁵ that treatment with KMnO_4 or a peroxy acid will convert the double bond to an epoxy and subsequently to one or two hydroxy functional groups. Such a functionalization of the double bonds is an effective method for broadening the scope of the application of vegetable oil. This potential for functionalization, and the free availability of rape seed oil, has made it a prime candidate for the production of fine chemicals.⁶ However, there is no published work on its use in PUs.

In the present work, peroxy acid treatment of rape seed oil followed by alcoholysis produced a highly (OH) functionalized product. The reaction was monitored by a novel on-line infrared spectrometer. The rigid PU foam was produced from the rape seed oil based polyol and the physical properties of the foam were measured and compared to reference material.

EXPERIMENTAL

Materials

Rape seed oil (iodine value: 97.92 mg KOH/g; acid value: 0.47 mg KOH/g; saponification value: 172.69 mg KOH/g) was supplied by Kunsan Agricultural Oil Factory, China. Hydrogen peroxide (wt content: 35%), formic acid (wt content: 85%), and triethanolamine (wt content: $\geq 85\%$) were laboratory reagents supplied from different manufacturers in China. The latter was dried under vacuum before use. For preparation of rigid PU foam, the isocyanate SuprasecTM 2085 (functionality of NCO: 2.85; NCO content: 30.2%) was provided by Huntsman Polyurethanes. As a reference polyol, the polyester polyol DaltolacTM P744 (hydroxyl value: 360 mg KOH/g, acid value: 0.57 mg KOH/g, viscosity at 25°C: 650 mPa s) was also supplied by Huntsman Polyurethanes. (Daltolac and Suprasec are trademarks of Huntsman ICI Chemicals LLC.)

Hydroxylation of Rape Seed Oil

H_2O_2 solution and formic acid were added to a flask equipped with stirrer, thermometer, and thermoregulator. The temperature of the reactants was raised to 40°C; the rape seed oil was added dropwise and the temperature of the reactants was controlled from 40 to 50°C. After the rape seed oil had been added, the reaction was continued for 1 h at 40°C. Thereafter, the reactants in the flask were allowed to stand overnight at room temperature. The final product divided into two layers in the flask. The bottom layer of acid phase was removed, and the upper layer was directly distilled under vacuum to eliminate the remaining water and acid to get the hydroxylated rape seed oil, as reported in the literature.⁷ The preferable formulation was $\text{C}=\text{C}/\text{H}_2\text{O}_2$ (mol) = 1/

Table I Raw Materials and Formulation of Rigid Polyurethane Foam

Raw Material	Type	Part by Weight
Polyol	^a	100
Surfactant	B8462	3.72
Catalyst for trimerization	LB	3.13
Catalyst for foaming	SFC	0.65–1.00
	Water HCFC	
Foaming agent	141b	29
Flame retardant	TCPP	11.83
Isocyanate	'Suprasec' TM 2085	246

^a Rape seed oil based polyol or 'Daltolac'TM P744.

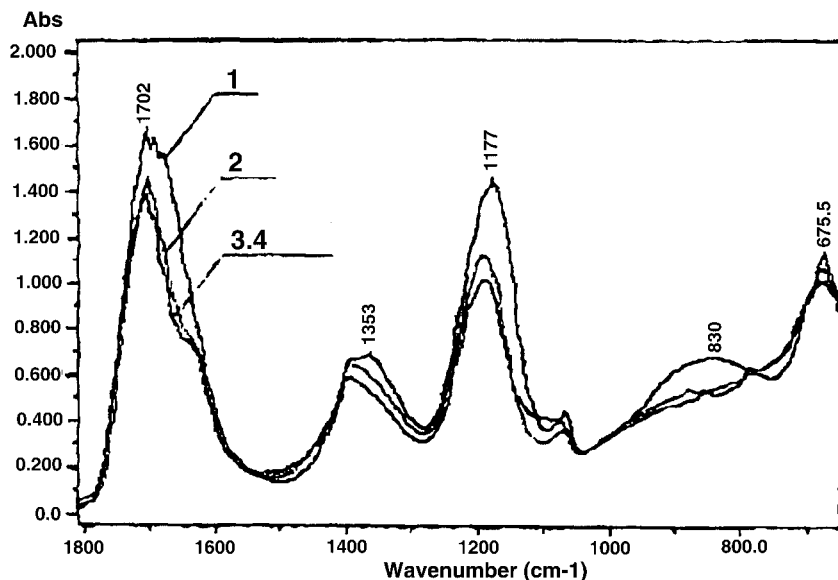


Figure 1 Infrared spectra recorded during the reaction of formic acid with hydrogen peroxide.

0.667; $\text{H}_2\text{O}_2/\text{HCOOH}$ (mol) = 1.4. The yield of the hydroxylated rape seed oil was 95%.

Alcoholysis of the Hydroxylated Rape Seed Oil

The hydroxylated rape seed oil, dry triethanolamine, and catalyst (LiOH) were added together in a flask. The stirrer was set in motion, and the temperature of the reaction was raised to 150°C in 0.5 h. Then, the reaction continued for 90 min at this temperature. The reaction was stopped when the acid value of the reactants became < 1 mg KOH/g. The formulation was that hydroxylated rape seed oil/triethanolamine = 1/3 (mol ratio) and the amount of LiOH = 0.2% (by weight) of the total reactants.

Rigid PU Foam

Table I lists the formulation used for preparing rigid PU foam. All of the raw materials, except isocyanate, were first well mixed in a plastic beaker. Then, the isocyanate was added into the beaker and mixed with high-speed stirring (2000 rpm) for 6 s. To measure the reaction behavior of the foaming system, approximately 35 g of total formulation were mixed in a 500-mL beaker and allowed to react and expand in the beaker while the reaction behavior was measured.

To make foam for the measurement of physical properties, 420 g of the rape seed oil were mixed in a 1000-mL beaker and the mixture was then

quickly poured into an open mold ($200 \times 200 \times 300$ mm).

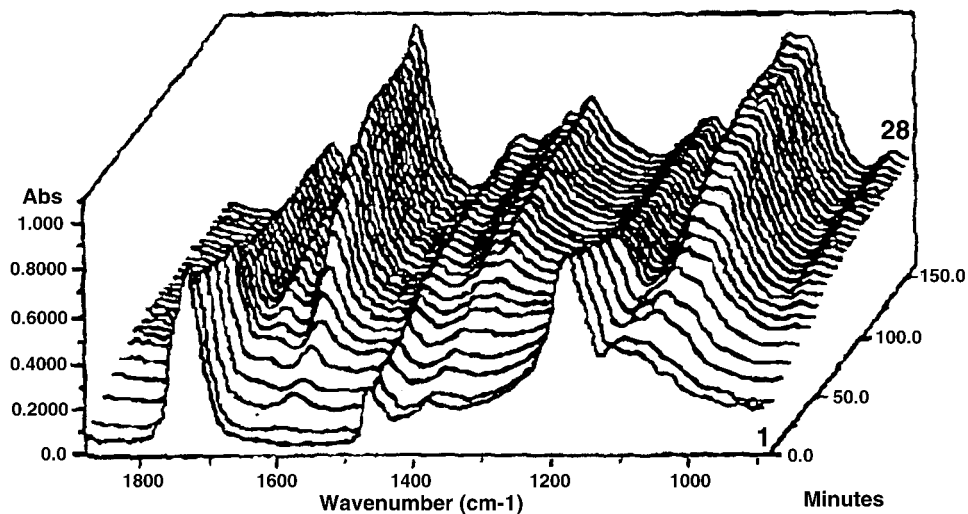
Characterization and Measurement

An infrared spectrometer type React IR1000, developed by ASI Applied System Co., was used to monitor the reaction process directly. This instrument was equipped with a cylindrical detector made of diamond, which could be inserted into the reactants to record the change of absorption peaks at all times during the hydroxylation and alcoholization of the rape seed oil. The hydroxyl value and acid value of rape seed oil based polyol was tested according to GB17493.2-87 and GB2895-82, respectively. The viscosity of the polyol was measured by means of a NDJ rotating viscometer at 25°C according to GB1793.1-87. The density and 10% compression strength of the rigid foam was tested according to ISO 845 and ISO 844, respectively. The thermal conductivity was measured by a heat flow instrument HC074 (EKO), whereas the dimensional stability was measured according to ISO 2796.

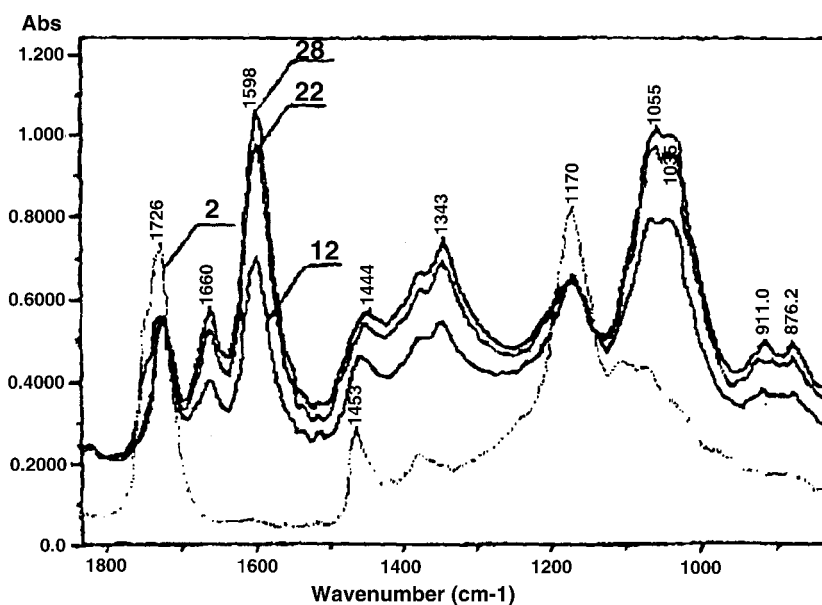
RESULTS AND DISCUSSION

Hydroxylation of Rape Seed Oil

Figure 1 shows the infrared spectra recorded during the reaction of formic acid with hydrogen per-



(a)



(b)

Figure 3 Infrared spectra obtained during the alcoholysis of the hydroxylated rape seed oil.

The hydroxyl value of hydroxylated rape seed oil was measured and found to be around 100 mg KOH/g only, which is not suitable for preparation of rigid PU foam. It was therefore concluded that, to increase the hydroxyl value of the product further, the hydroxylated rape seed oil should be alcoholysed further.

Alcoholysis of the Hydroxylated Rape Seed Oil

Figure 3 shows the infrared spectra during the alcoholysis of the hydroxylated rape seed oil. Spectra 1–6 in Figure 3(a) were obtained every 10 min, whereas spectra 6–28 were recorded every 5 min. Figure 3(b) clearly indicates the variation of

Table II Some Physical Parameters of Hydroxylated Rape Seed Oil, Rape Seed Oil Based Polyol and 'DaltolacTM P744

Polyol	Hydroxyl Value (mg KOH/g)	Acid Value (mg KOH/g)	Viscosity at 25°C (mPa s)
'Daltolac TM P744	360	0.57	650
Hydroxylated rape seed oil	100	< 5	400
Rape seed oil based polyol	367	0.14	1600

absorption peaks measured. The peak at 1660 cm^{-1} for the amide group appears and grows with time. This is due to the reaction of ethanolamine and diethanolamine existing in triethanolamine with the ester group in system to form an amide structure. In addition, the side reaction of the aminolysis of ester group was replaced by a transesterification during the alcoholysis. This results in a decrease in the absorption of the carbonyl group at 1725 and 1170 cm^{-1} and the shift of these peaks, as shown in Figure 3(b). It was also found that the hydroxyl value of the final product increased to 367 mg KOH/g, as listed in Table II. These experimental results confirm that the alcoholysis between the hydroxylated rape seed oil and triethanolamine took place in the reaction system. Table II also lists some physical parameters of the reference polyol (DaltolacTM P744), hydroxylated rape seed oil, and alcoholized hydroxylated rape seed oil; the latter will be referred to as rape seed oil based polyol in the rest of this article.

Rigid Polyurethane Foam

The rape seed oil based polyol was used to prepare rigid PU foam according to the formulation given in Table I. Table III shows the foaming behavior of this polyol compared with the reference polyol and indicates that the rape seed oil based polyol could be used as a polyol in the preparation of rigid PU foam, but the reactivity of such a polyol is lower than that of the reference foam. In general, the cream time, full cup time,

and end of rise time can be related to the rate of expansion, principally an exotherm effect, whereas the string time and tack free time can be used to characterize the gelation rate. Table III indicates that both the rate of expansion and the gelation of the rape seed oil based polyol are slower than those of the reference polyol. These phenomena could be attributed to the secondary hydroxyl groups existing in the rape seed oil based polyol, giving rise to strong steric hindrance, while the reference polyol DaltolacTM P744 contains primary hydroxy groups.

The physical properties of the rigid PU foam made from the rape seed oil based polyol were measured and are shown in Table IV. The experimental data reveal that the 10% compression strength of the foam made from the rape seed oil based polyol is lower than that of the reference foam, although its density is high. The other physical properties of the foam made from the rape seed oil based polyol are similar to those of DaltolacTM P744 based foam. Thus, the rape seed oil based polyol could be used to make rigid polyurethane foam, if the formulation is adjusted carefully. The storage life of the polyol was measured and compared to industry standard polyols, which is normally more than 12 months. However, the rape seed based polyol began to solidify after 1 month. This behavior may be related to the strong hydrogen bonding and/or the crystallization in the system and should be studied further.

Table III Foaming Behavior of the Polyol Based on Rape Seed Oil and 'DaltolacTM P744

Polyol	Cream Time (s)	Full Cup Time (s)	String Time (s)	Tack Free Time (s)	End of Rise Time (s)
'Daltolac TM P744	25	35	36	40	50
Rape seed oil based polyol	24	49	64	122	152

Table IV Some Physical Properties of Rigid PU Foams

Polyol	10% Compression Strength (kPa)				Dimensional Stability ^a								
	Core Density (kg/m ³)	Parallel to Foam Rise Direction	Vertical to Foam Rise Direction	Thermal Conductivity (mW/mK)	100°C			70°C, RH 100%			30°C		
					L	W	H	L	W	H	L	W	H
Daltolac™ P744	36.1	184.4	49.0	24.2	2.03	1.35	-0.60	-0.81	1.41	0.03	0.59	-0.03	0.63
Rape seed oil based polyol	40.8	178	52.3	25.0	1.79	1.26	1.0	-0.86	-0.72	-1.26	1.75	0.96	1.68

^a W, L, and T, wide, long, and thick direction of foam, respectively. RH, relative humidity.

In conclusion, the polyol based on rape seed oil could be used as one of the raw materials for preparing rigid polyurethane foams after hydroxylation of the double bonds and alcoholysis of the hydroxylated rape seed oil. The modification of the storage life and the reactivity of the polyol, however, should be studied further.

REFERENCES

1. The ICI Polyurethanes Book, 2nd ed.; Woods, G., Ed.; Wiley: New York, 1990.
2. Low Density Cellular Plastics Physical Basis of Behaviour, 15th ed.; Hilyard, N. C., Cunningham, A., Eds.; Chapman and Hall: New York, 1994.
3. Baser, S. A.; Khakhar, D.V., Cell Polym 1993, 12 (5), 340.
4. Zhang, Y. D.; Jin, Y.; Liu, Z.; Wang, D.; Chem Ind Forest Prod (Chinese) 1991, 11 (3), 203.
5. Morrison, R. T.; Boyd, R. N. Organic Chemistry, 4th ed.; Allyn and Bacon: Needham Heights, MA, 1983.
6. Dahlke, B.; Hellbardt, S.; Paetow, M.; Zech, W. H. J Am Chem Soc 1995, 72 (3), 349.
7. Horning, E. C., Editor-in-Chief. Organic Synthesis, Collective Vol. III; Wiley: New York, 1955; pp 20–29.