

# Structures and Physical Properties of Rigid Polyurethane Foam Prepared with Rosin-Based Polyol

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**ABSTRACT:** Rosin-based polyester polyols were synthesized from a rosin–maleic anhydride adduct, diethylene glycol, and ethylene glycol with and without adding adipic acid and phthalic anhydride, in the presence of catalyst. Rigid polyurethane (PU) foams were prepared with these rosin-based polyols and compared with foam made with an industrial polyester Daltolac™ P744. The experimental results show that the foaming behavior for the foams prepared from such rosin-based polyols is similar to that of industrial products, but their 10% compression strength, both parallel and vertical to foaming rise direction, is higher and the dimensional stability at 100 and –30°C is similar or somewhat better than that of a comparable system. Furthermore, the rosin-modified PU foams exhibit even lower thermal conductivity and much higher activation energies during the pyrolysis process. All these unique physical properties of the rosin-modified rigid PU foams were correlated to the structures of these PU foams. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 598–604, 2002; DOI 10.1002/app.10312

## INTRODUCTION

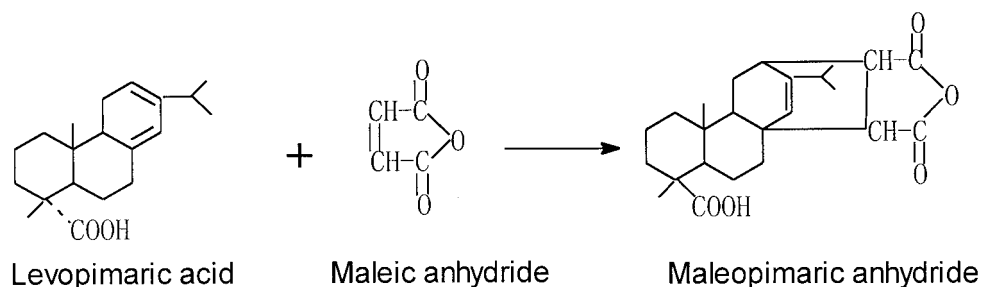
Rigid polyurethane (PU) foam has been widely studied and utilized in the appliance and construction industry, because of its excellent and unique combination of thermal insulation and

mechanical properties. Recently, renewable and natural plant products, such as castor oil<sup>1</sup> and rosin,<sup>2</sup> were used to synthesize polyester polyols and as a component from which to prepare rigid PU foams. This is part of an active program to find the most environmentally benign material. It is well known that rosin is a complicated mixture of organic acids consisting of abietic acid and pimaric acid. The levopimaric acid can easily react with maleic anhydride to form maleopimaric anhydride (MPA) by a Diels–Alder reaction:

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It is clear that MPA in this sense is just like the organic acids which are conventionally used to react with diols to synthesize the polyester polyols currently used by the industry to produce rigid PU foam. Zhang and coworkers<sup>3,4</sup> reported that polyester polyols were synthesized from the reaction of MPA or rosin-maleic anhydride adduct (RMA), which was an adduct of rosin with maleic anhydride containing MPA (which was not purified) with excess of glycols. The rigid PU foams, prepared from such rosin-based polyols, mixed with sucrose-based polyether polyol, exhibited quite good heat resistance. Lu et al.<sup>5</sup> also prepared polyester polyols from RMA and glycols and once again they observed good thermal stability. In the current work, RMA was used to synthesize polyester polyols. These polyols were then used to produce rigid PU foams. The properties of the foam were measured and compared to a standard industrial product.

## EXPERIMENTAL

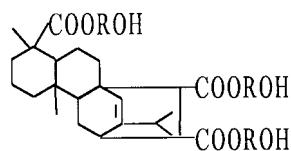
### Rosin-Based Polyester Polyol

RMA containing 67.1 wt % of MPA was kindly provided by Shanghai Nanda Chemical Plant (China). Other chemicals were laboratory reagents supplied by various manufacturers in China. Two kinds of rosin-based polyester polyols were synthesized from RMA, diethylene glycol (DG) and ethylene glycol (EG) with or without

adding adipic acid (AA) and phthalic anhydride (PA) in the presence of catalyst. Thus, 195.1 g RMA, 21.4 g AA, 12.6 g PA, 312.0 g DG, 44.6 g EG, and 0.84 g catalyst were put into a 1000-ml flask equipped with stirring apparatus, thermometer, fractionator, and nitrogen inlet pipe to synthesize the rosin-based polyol in the range of temperature from 215 to 240°C under nitrogen atmosphere. An amount of 422.8 g of such a polyester polyol was produced. The synthesis process of another rosin-based polyol without containing AA and PA was similar to that of rosin-based polyol including AA and PA, but the formulation was changed (195.1 g RMA, 312.0 g DG, 18.6 g EG, and 0.79 g catalyst). An amount of 354.0 g of this polyester polyol was produced. The structural formula for such polyols is shown in Figure 1.

### Rigid PU Foam

An industrial polyester polyol (Daltolac™ P744) and isocyanate (Suprasec™ 2085; functionality of NCO: 2.85; NCO content: 30.2 wt %) were manufactured by Huntsman Polyurethanes. (Daltolac and Suprasec are trademarks of Huntsman ICI Chemicals LLC.) Other chemicals were provided by various manufacturers. 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 profile of the foaming system, approximately 35 g of total formulation was mixed in a 500-ml beaker and allowed to react and expand in the beaker while the reaction profile was measured. To make foam for the measurement of physical properties, 420 g of total formulation was mixed in a 600-ml beaker and the mixture was then quickly poured into an open mold (200 × 200 × 300 mm).



**Figure 1** Structure formula of rosin-based polyols.

**Table I Chemical Systems and Formula for Rigid PU Foams**

Raw Material	Trade Name	wt Part
Polyester polyol	<sup>a</sup>	100.00
Surfactant	B8423	2.37
Catalyst of trimerization	LB	2.50
Foaming catalyst	SFC	0.65
Flame retardant	TCP	11.89
Foaming agent	Water	1.19
Foaming agent	141b	29.00
Isocyanate	'Suprasec <sup>TM</sup> 2085	<sup>b</sup>

<sup>a</sup>Daltolac<sup>TM</sup> P744 or rosin-based polyester polyol.

<sup>b</sup>[NCO]/[OH] = 2.27.

### Characterization and Physical Property Measurements

The hydroxyl value and acid value for rosin-based polyols were tested according to GB 7193.2-87 and GB 2895-82, respectively. The viscosity of rosin-based polyols was measured by means of a NDJ rotating viscometer at 25°C according to GB 7193.1-87 and the water content in rosin-based polyols was tested with Karl-Fisher titration. A Nicolet 5SXC FTIR spectrometer was employed to characterize the rigid PU foams. The core density, 10% compression strength, and dimensional stability for rigid PU foams were tested according to ISO 845, ISO 844, and ISO 2796, respectively. The thermal conductivity of PU foams was measured by heat flow instrument HC074 (EKO). For investigating with a scanning electron microscope (Stereoscan 250 MK3, Cambridge), the PU foam was first cut parallel to the foaming rise and then vertical to the foaming rise, respectively. Then, the surface of the specimen was coated with gold

vapor before examining. The heat resistance of foams was measured by DuPont 1090 thermogravimetric analyzer (TGA) at a heating rate of 20°C/min.

## RESULTS AND DISCUSSION

### Rosin-Based Polyester Polyol

Table II shows the main physical parameters and the foaming behavior of the two kinds of rosin-based polyester polyols synthesized (for simplicity, they were designated as RP-1 and RP-2, respectively), which are compared with those of industrial polyester polyol (Daltolac<sup>TM</sup> P744) used to prepare rigid PU foam in Europe. It is clear that the hydroxyl value, acid value, and water content for RP-1 and RP-2 are similar to those of Daltolac<sup>TM</sup> P744, but their viscosities are much higher than those of Daltolac<sup>TM</sup> P744 and may be attributed to the large phenanthrene nucleus existing in the rosin, giving rise to steric hindrance during the flow process. However, it should be pointed out that although the viscosity of such polyols is high, they are still suitable to make rigid foams, as the viscosity is < 6000 mPa s, which is a commonly accepted upper limit used in the PU industry. Table II also shows that the foaming reaction rate of these rosin-based polyester polyols is slightly faster than that of Daltolac<sup>TM</sup> P744. The increased reactivity for RP-1 and RP-2 could be due to the presence of primary hydroxyl groups at the end of the macromolecular chains (see Fig. 1) or alternatively could reflect an enhanced miscibility with the isocyanate. Although a difference in the foaming behavior between the polyol systems studied was observed,

**Table II Some Physical Parameters and Foaming Behavior of Cup Foam for Rosin-Based Polyester Polyols and Daltolac<sup>TM</sup> P744**

Polyol	Physical Parameter				Foaming Behavior/Time				
	Hydroxyl Value (mg KOH/g)	Acid Value (mg KOH/g)	Water Content (%)	Viscosity at 25°C (m Pa s)	Cream (s)	Full Cup (s)	String (s)	Tack Free (s)	End of Rise (s)
Daltolac <sup>TM</sup> P744	360	0.57	0.05	650	25	35	36	40	50
RP-1 <sup>a</sup>	377	0.67	0.06	5500	20	29	30	35	45
RP-2 <sup>b</sup>	392	0.53	0.12	4500	21	29	30	35	45

<sup>a</sup>Rosin-based polyol synthesized with adding AA and PA.

<sup>b</sup>Rosin-based polyol synthesized without adding AA and PA.

they are all in the range of operation conditions for making rigid PU foam.

**Rigid Polyurethane Foam**

A series of physical properties of rigid PU block foams prepared with rosin-based polyester polyols and Daltolac™ P744, respectively, were measured, as listed in Table III. Table III shows that the 10% compression strength in both the parallel and the vertical to foaming rise direction for the rigid foams prepared from RP-1 and RP-2 is higher than that of foam made with Daltolac™ P744 and the thermal conductivity of rosin-modified PU foams decreases appreciably compared with that of the control formulation. Table III also indicates that 10% compression strength in both directions for RP-1 foam is higher than that of RP-2 foam. In this case, it seems that some more flexible segments composed of adipic acid existed in the PU matrix to enhance the toughness of PU foam, giving rise to even better mechanical properties. Furthermore, it is found that the dimensional stability of RP-1 and RP-2 foam systems is similar or somewhat better than that of the control system, especially at high or low temperature (100 and -30°C). All these experimental results indicate that the rigid phenanthrene nucleus of the rosin not only enhances the mechanical properties but improves some general important physical properties for the PU foams as well.

In general, the physical properties of PU foam not only depend on the rigidity of the polymer matrix, but are also related to the cellular structures of the foam. Thus, it is of interest to observe the fracture of the foam specimen by using scanning electron microscopy (SEM). Figure 2 shows the micrographs of the fracture surfaces for rigid PU foams. It is immediately obvious that the foams made with the rosin-based polyols show a high degree of orientation, the cells being stretched in the direction of foam rise. For RP1, the two cell dimensions are 540 μm in the rise direction and 240 μm orthogonal to rise. For RP2, it is 530 and 230 μm, respectively. This is a common phenomenon in PU foam and is caused by the build up of crosslinking structure in the polymer matrix at an early stage in the foam expansion process. In comparison, the control formulation based on Daltolac™ P744 has also exhibited the anisotropic cells, 350 and 764 μm.

These orientation effects can have a dramatic impact on the physical properties. The compression strength is always higher along the long axis

**Table III Some Physical Properties of Rigid PU Foams<sup>a</sup>**

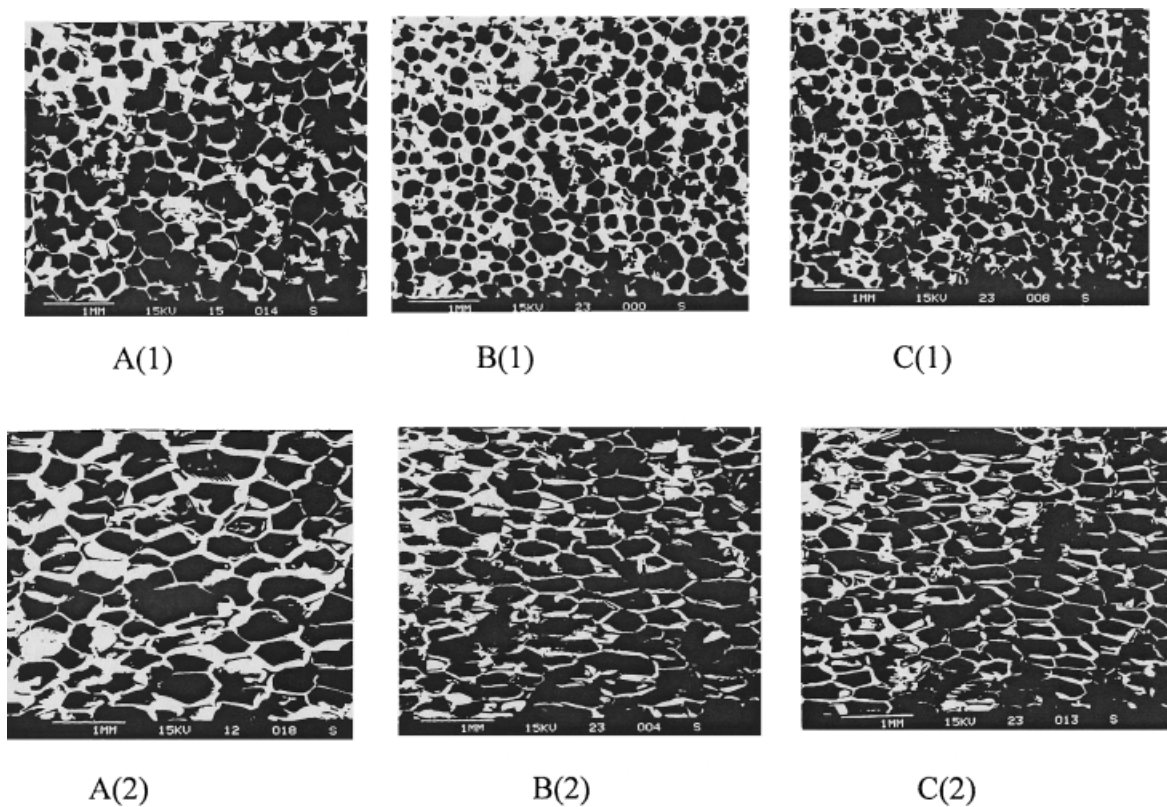
Polyol	Core Density (kg/m <sup>3</sup> )	10% Compression Strength (KPa)		Thermal Conductivity (mW/mK)	Dimensional Stability <sup>b</sup>								
		Parallel to Foam Rise Direction	Vertical to Foam Rise Direction		100°C			70°C, RH 100% <sup>c</sup>			-30°C		
					L	W	H	L	W	H	L	W	H
Daltolac™ P744	36.1	184.4	49.0	24.2	2.03	1.35	-0.60	0.81	1.41	-0.03	-0.59	-0.03	0.63
RP-1	36.8	205.9	94.4	21.5	0.78	0.90	0.19	1.61	1.51	0.41	-0.11	0.08	0.52
RP-2	37.0	197.0	92.9	23.0	2.17	1.53	-0.75	1.70	1.88	0.23	-0.02	-0.07	0.17

<sup>a</sup>All foams were prepared at ambient temperature (22.5°C) and tested after storing at ambient temperature for three days.

<sup>b</sup>W, L, and T, wide, long, and thick direction of foam, respectively.

<sup>c</sup>RH, relative humidity.

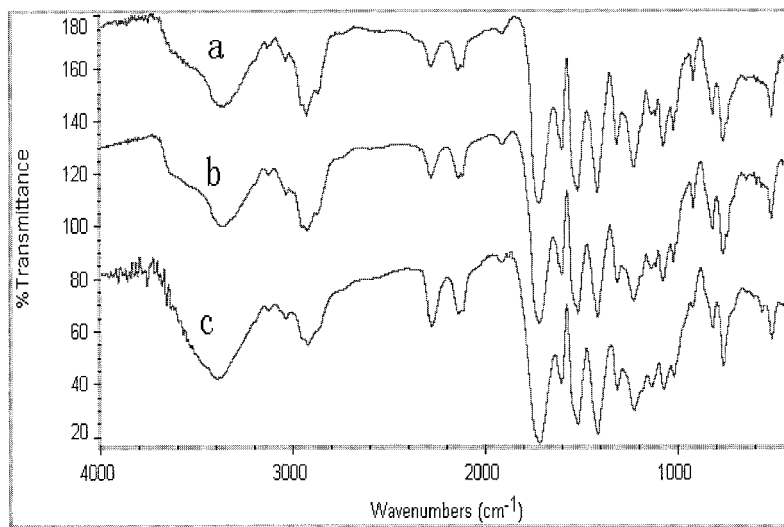




**Figure 2** Scanning electron microphotographs of fracture surfaces of three rigid polyurethane foams at different foaming rise directions. (A) Daltolac™ P744; (B) RP-1, (C) RP-2; (1) vertical to foaming rise direction; (2) parallel to rise direction.

of the cell, as can be seen in all three cases. However, the absolute magnitude, at equivalent density, differs and it can be concluded that there

is an increase in the strength of the foam when the rosin-based polyols are used, particularly RP1.

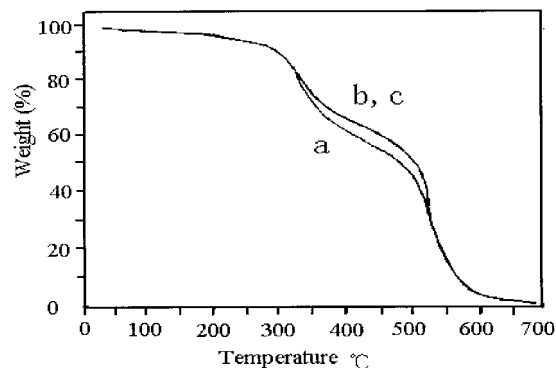


**Figure 3** Infrared spectra for rigid polyurethane foams. (a) Daltolac™ P744; (b) RP-1; (c) RP-2.

A second effect of the orientation is seen in the thermal conductivity. It is well established that the thermal conductivity is related to the effective cell size of the insulating material. The thermal conductivity of the samples in Table III were measured orthogonal to rise; thus, the relevant cell sizes were 350  $\mu\text{m}$  for the control, 240  $\mu\text{m}$  for RP1, and 230  $\mu\text{m}$  for RP2. This sort of change in cell size would be expected to reduce the thermal conductivity by approximately 1 mW/mK,<sup>6</sup> which is indeed in the case for RP2. The greater decrease for RP1 must be attributed to other factors which have not yet been identified.

As shown in Table I, for preparing rigid PU foam there is a catalyst of trimerization and excess of isocyanate for the urethane reaction in the system. Thus, isocyanurate formation can be expected.<sup>7</sup> The occurrence of isocyanurate groups in the foams was observed from FTIR spectra, as shown in Figure 3. It indicates that the absorption peaks at 1410, 1710, and 2270  $\text{cm}^{-1}$  are attributed to the isocyanurate group, the hydrogen-bonded carbonyl group, and the isocyanate group,<sup>8,9</sup> respectively, for all foams studied here. Isocyanurate foams are generally recognized as being superior to rigid PU foams in terms of flammability, dimensional stability, and thermal stability.<sup>10</sup> Table III indicates that the rosin-based foams exhibit better dimensional stability at 100 and  $-30^\circ\text{C}$ , but show a bit poorer dimensional stability under humid conditions ( $70^\circ\text{C}$ , RH 100%) than that of the control system. The excellent dimensional and thermal stability for rosin-based foams must be related to the rigid polymer matrix. The lowering of the dimensional stability at humidity condition for such foams might be attributed to some hydrophilic impurities existing in the natural rosin used to make RMA and polyols.

The thermal stability for all three foams was examined by means of TGA, as shown in Figure 4. This shows that there are two stages in the pyrolysis process for these systems. The temperatures corresponding to maximum rate of weight



**Figure 4** TGA curves of rigid polyurethane foams. (a) Daltolac™ P744; (b) RP-1; (c) RP-2.

loss and the weight loss content in both stages are listed in Table IV. As the isocyanurate content of these systems is calculated and found to be all at around 30 wt %, the first pyrolysis procedure should be related to the urethane group and the second one could be therefore attributed to the isocyanurate groups in the foams. The activation energies of these two decomposition reactions can be calculated according to the Broido method<sup>11</sup>:

$$\ln(1/y) = -(E/R)(1/T) + \text{constant}$$

$$y = (W_t - W_\infty)/(W_0 - W_\infty)$$

where  $W_t$  is the weight at time  $t$ ,  $W_0$  is the weight of initial stage, and  $W_\infty$  is the weight at unlimited time, which is usually equal to zero. All activation energies calculated are also listed in Table IV. It clearly indicates that both values of  $E_1$  and  $E_2$  for the rigid PU foams prepared with rosin-based polyester polyols are higher than that for the industrial one. This is believed to be due to the presence of the phenanthrene nucleus.

In conclusion, the rigid PU foams were prepared with the rosin-based polyols and compared with foam made with an industrial polyester polyol. The foaming behavior of the foams pre-

**Table IV** Pyrolysis Behavior of Rigid PU Foams

Polyol	$T_1$ ( $^\circ\text{C}$ )	$W_1$ (%)	$E_1$ (KJ/mol)	$T_2$ ( $^\circ\text{C}$ )	$W_2$ (%)	$E_2$ (KJ/mol)
Daltolac™ P744	334	38.7	41.8	522	58.1	84.2
RP-1	343	30.5	56.2	521	64.3	111.6
RP-2	340	31.7	56.2	523	63.0	111.6

pared from such rosin-based polyols is similar to that of industrial products. All the physical properties measured for PU foams containing rosin structure are better than those for the industrial foam.

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