

Influence of the Composition of Rosin-Based Rigid Polyurethane Foams on Their Thermal Stability

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SYNOPSIS

A series of rosin-based rigid polyurethane foams of different composition were synthesized directly from chemically modified gum rosin. The effect of the composition of these rosin-based rigid polyurethane foams on their thermal stability and compression strength was measured. It was shown that the onset temperature of weight loss and the dimensional stability at high temperature increased with increase of the molar ratio of NCO/OH. The TGA data further confirmed that the second stage weight loss in the two-stage weight loss process of these polyurethane foams was governed by thermal degradation of the isocyanate component. Although density had no significant influence on the TGA curves of the rosin-based rigid polyurethane foams, it had great influence on the dimensional stability at high temperature and compression strength of the foams. It has been shown that the inclusion of rosin in rigid polyurethane foams increases the strength and thermal stability compared with that of polyether-based ones. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article,¹ the authors synthesized a variety of polyester polyols from maleopimaric acid, a derivative of gum rosin, as well as from chemically modified rosin and turpentine oil. A series of rigid polyurethane foams with rosin and turpentine oil structural units were synthesized from these polyols and their thermal stability was studied. It was shown that the structures of the polyols have a strong influence on their thermal stability and on that of the final foams, with polyols from pure maleopimaric acid and low molecular weight diols displaying better thermal stability. Lower molecular weight hydroxyl-terminated maleopimaric acid ester, however, generally possessed high viscosity, i.e., poor processibility. The rigid polyurethane foams synthesized directly from gum rosin also exhibited better thermal stability than those based on polyether polyols.^{1,2} It

is of more practical value to synthesize rigid polyurethane foams directly from gum rosin rather than from pure maleopimaric acid, because of the more ready availability and lower cost of the gum rosin.^{3,4} In this article, hydroxyl-terminated rosin polyester polyol (RPP) was synthesized directly from the reaction of rosin, maleic anhydride, and ethylene glycol. A series of rosin-based rigid polyurethane foams with different compositions were synthesized based on RPP and their thermal stability and mechanical properties were studied.

EXPERIMENTAL

Materials

Gum rosin was supplied by Huaxing Forest Chemical Co. of China and the sorbitol-based polyether polyols, ZS-635, was supplied by Jinling Petrochemical Co., China. The polymeric MDI, MR-100, was a product of the Japan Polyurethane Co. The silicon surfactant and blowing agent, CFCl₃, were supplied by Bayer and Changsu Blowing Agent Co. of China, respectively.

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Synthesis of RPP and Rosin-based Rigid Polyurethane Foams

Hydroxyl-terminated rosin polyester polyol (RPP) was synthesized as previously described.¹ The difference between RPP and hydroxyl-terminated maleopimaric acid ester, HTMAE, is that RPP contains about 85% HTMAE as well as 10% mono rosin acid ester and about 5% nonester components.¹⁻⁴ The hydroxyl value of the RPP was about 400 mgKOH/g and its viscosity was 5000 mPa-s at 25°C. The rigid polyurethane foams based on the RPP were prepared¹ in the same way as in the previous article. The molar ratio of NCO/OH was 3.0 and the weight ratio of RPP/ZS-635 was 1.0, unless otherwise indicated. The density of the rosin-based rigid polyurethane foams was controlled at about 42 kg/m³ by varying the dosage of the CFCl₃ blowing agent.

Test Methods

Thermal weight loss data were obtained using a Rigaku TAS-100 type DSC-TGA analyzer. The heating rate was 10°C/min and the initial sample weight was about 2 mg.

Deformation of the rigid polyurethane foams was measured after the samples had been placed in an oven at 170°C for 48 h. The samples were initially 100 × 100 × 10 mm. The deformation quoted is the average change in each of these three dimensions after treatment.

The compression strength was measured at room temperature, using an Instron Model 1137 tester, according to the ISO844-1978 standard. This test was carried out in the direction perpendicular to foam rise and at a constant crosshead speed of 3 mm/min.

RESULTS AND DISCUSSION

The Influence of Molar Ratio of NCO/OH on the Properties of the Final Foams

These rigid polyurethane foams are composed of crosslinked polymer networks formed by the reaction of polyols and polymeric isocyanates. In addition to reacting with the hydroxyl groups of polyols, excess isocyanate may not only react with the active hydrogens of the urethane linkages, leading to the formation of allophanates, but also may be trimerized by the effect of catalysts to form polyisocyanurate structures. Therefore, the molar ratio of NCO/OH is expected to play an important part in

determining the structure and properties of these rigid polyurethane foams.

The TGA curves of the rosin-based rigid polyurethane foams synthesized at different molar ratios of NCO/OH are shown in Figure 1. All the curves in this figure display two distinct regions of weight loss, which is similar to the TGA curves of segmented polyurethanes⁵ and that of our previous work.¹ It is clear that the amount of weight loss in the first stage decreases with increase in the molar ratio of NCO/OH. It has been shown¹ that the weight loss in the first stage was dominated by the degradation of the polyol components and that in the second stage was governed by the degradation of the isocyanate components. The weight fractions of isocyanate, W_{NCO} , of the rosin-based rigid polyurethane foams are plotted in Figure 2 against the weight loss, W_2 , in the second stages. This shows a linear dependence with a fairly good correlation coefficient, further suggesting that the weight loss in the second stage was governed by the degradation of the isocyanate components.

The onset temperatures of the weight loss of the first stage, T_{ON} , and that of the second stage, $T_{2\text{ON}}$, increase, as expected, with increase of NCO/OH, as shown in Figure 3. This can be attributed to the possibility that at higher NCO/OH molar ratios some of the excess isocyanate reacts with the active hydrogens of urethane linkages, forming allophanates, and, as a result, increases the crosslink densities⁶ of the final foams. In addition, some isocyanate may be trimerized to form the more thermally stable isocyanurate structure.

The dimensional stability of the foams at 170°C also increases with increase of the NCO/OH ratio,

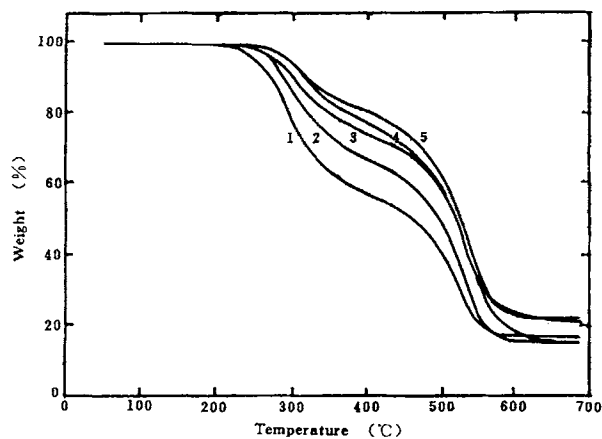


Figure 1 TGA curves of rosin-based rigid polyurethane foams synthesized at different molar ratios of NCO/OH: (1) NCO/OH = 1.2; (2) NCO/OH = 2.0; (3) NCO/OH = 4.0; (4) NCO/OH = 4.0; (5) NCO/OH = 5.0.

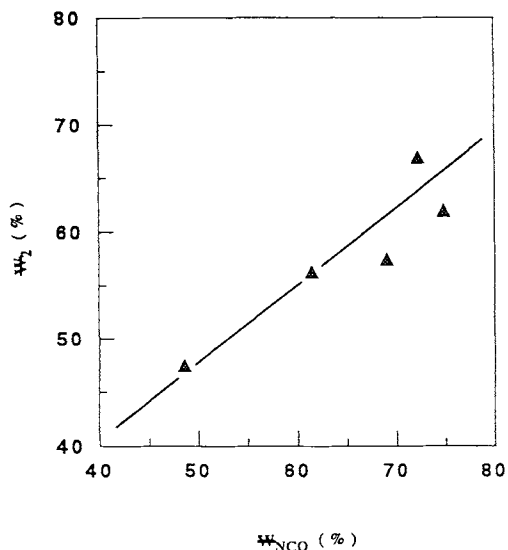


Figure 2 The relationship between the weight fraction, W_{NCO} , of isocyanate in polyurethane foams and the weight loss, W_2 , of the foams in the second stage of the weight loss process.

as shown in Figure 4. This indicates that when the molar ratio of NCO/OH is smaller than 3 the dimensional stability, as well as the compression strength of the foams, increase with increase of the NCO/OH. However, the compression strength deteriorates with further increase in the NCO/OH, while the deformation of the foams at high temperature (170°C) remains constant. This can be attributed to the higher brittleness of the foams with high isocyanurate content and high crosslinking degree at higher molar ratios of NCO/OH.

The Influence of Density on the Properties of Rosin-based Rigid Polyurethane Foams

The morphology^{6,7} of rigid polyurethane foams can be thought of as a continuous polyurethane chain matrix with dispersed closed cells, filled with a CFC_3 blowing agent. Thus, the thickness of the cell walls in the foams is strongly dependent on the foam density. Generally, foams of high density possess thicker cell walls and, consequently, exhibit higher strength, as well as better dimensional stability. In terms of economics, however, the density of rigid polyurethane foams should be as low as possible without lowering their physical performance.

The effect of density of the rosin-based rigid polyurethane foams on their dimensional stability at 170°C and their strength are presented in Figure 5. The compression strength shows a sigmoidal variation with density. A rapid increase in the

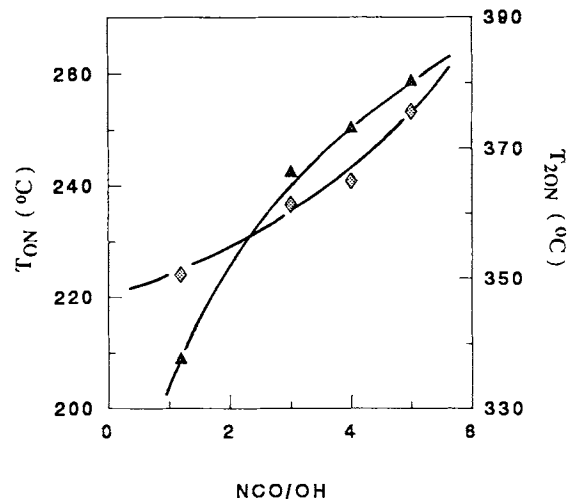


Figure 3 The influence of NCO/OH on the onset temperatures of the first and second stages, T_{ON} and T_{2ON} , of the weight loss process of rosin-based rigid polyurethane foams: (Δ) T_{ON} ($^\circ\text{C}$); (\diamond) T_{2ON} ($^\circ\text{C}$).

compression strength was observed between the densities of 35 and 45 kg/m^3 . The deformation at high temperature decreased rapidly with increase in the foam density. This pattern of behavior may be the result of thicker cell walls for rigid polyurethane foams of higher density, since no significant differences were found for the TGA curves of rosin-based rigid polyurethane foams of different densities. The onset temperatures, T_{ON} , of the weight loss of these

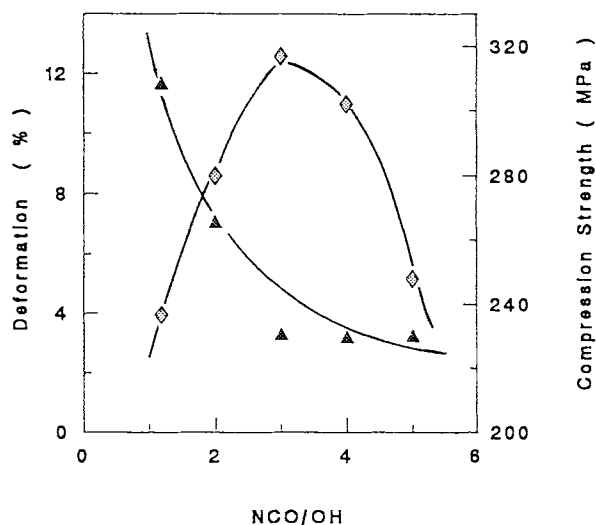


Figure 4 The influence of NCO/OH on the deformation at 170°C and compression strength of the rosin-based rigid polyurethane foams: (Δ) deformation (%); (\diamond) compression strength (MPa).

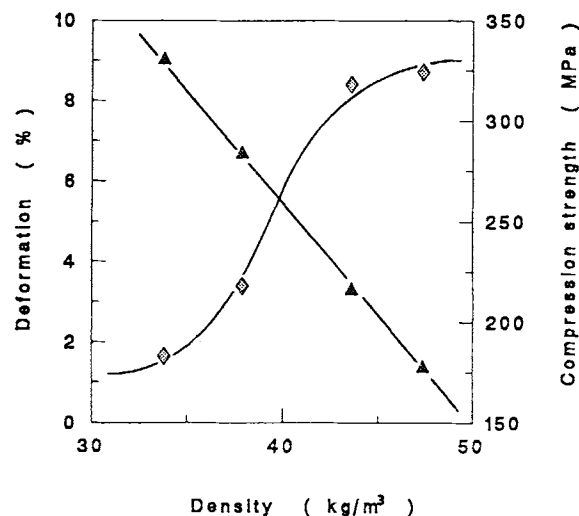


Figure 5 The influence of density of rosin-based rigid polyurethane foams on their compression strength and deformation at 170°C. (Δ) deformation (%); (\diamond) compression strength (MPa).

foams of different densities are nearly the same, as is shown in Figure 6.

The relationship between deformation at 170°C, α , and the density, d , of the rosin-based rigid polyurethane foams was obtained by a regression analysis of the experimental data:

$$\alpha = 28.49 - 0.574d$$

The correlation coefficient, r , was 0.9998.

The Influence of the Weight Fraction of Rosin Polyester Polyol on the Properties of Rigid Polyurethane Foams

In this article, the rosin-based rigid polyurethane foams were prepared based on a mixed polyols of rosin polyester polyol (RPP) and the sorbitol-based polyether polyol, ZS-635. The effects of the weight ratio of RPP/ZS-635 on the compression strength and deformation at 170°C are shown in Figure 7. Both the compression strength and dimensional stability at 170°C increase with increasing weight ratio of RPP/ZS-635, suggesting that the inclusion of the phenanthrene ring of rosin, which imports both increased thermal stability and toughness, increases the thermal stability as well as the strength of the final foams.

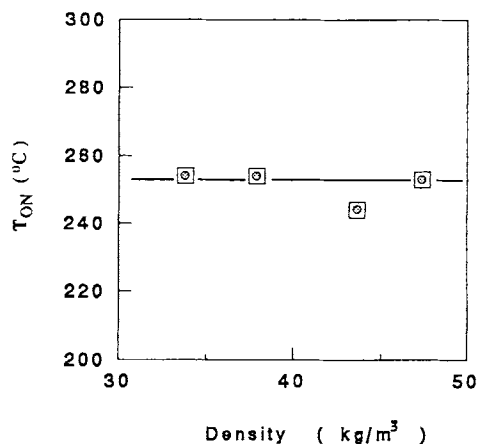


Figure 6 The effect of density of the rosin-based rigid polyurethane foams on their weight loss onset temperatures.

CONCLUSIONS

The composition of rosin-based rigid polyurethane foams has great influence on their physical performances. The degradation onset temperature as well as dimensional stability and compression strength of the foams increase with increase in the molar ratio of NCO/OH. The compression strength, however, deteriorated with further increase in the NCO/OH ratio above 3.0. The TGA

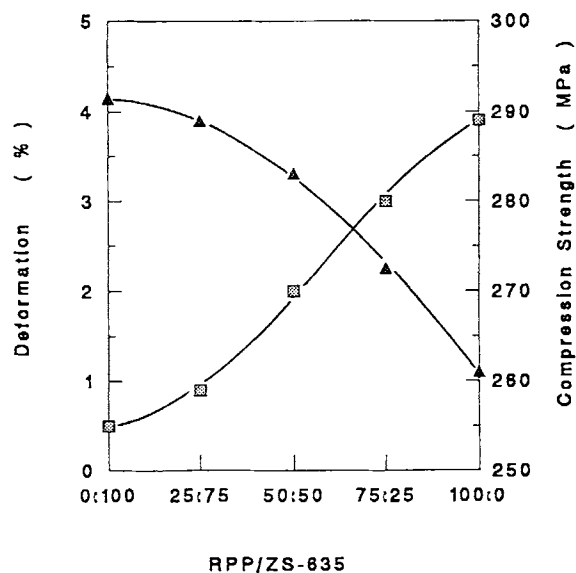


Figure 7 The effect of the weight ratio of rosin polyester polyol (RPP) to sorbitol-based polyether polyol, ZS-635, on deformation and compression strength: (Δ) deformation (%); (\square) compression strength (MPa).

data further confirmed that the second stage weight loss in the two-stage weight loss process of these rosin-based polyurethane foams was governed by the thermal degradation of the isocyanate component. Although foam density had no significant influence on the TGA curves of these rosin-based rigid polyurethane foams, it had great influence on the dimensional stability at high temperature and the compression strength of the foams, suggesting that in addition to thermal stability of the chemical structures of the components of foams the thermal stability of the final foams is strongly dependent on the thickness and strength of the cell walls. The inclusion of the rosin structural units in rigid polyurethane foams increases their thermal stability as well as their strength compared with those based on polyether polyols.

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