Influence of Structure of Hydroxyl-Terminated Maleopimaric Acid Ester on Thermal Stability of Rigid Polyurethane Foams

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SYNOPSIS

A series of hydroxyl-terminated maleopimaric acid esters (HTMAEs) and rigid polyurethane (PU) foams based on these HTMAEs were synthesized using chemically modified natural gum rosin and its derivative maleopimaric acid as raw materials. Thermal stability of these polyols and their corresponding rigid PU foams was studied by a thermogravimetric method and a dimensional stability measurement. It was shown that the thermal stability of the final foams was strongly dependent on the structure of their corresponding polyols. The thermogravimetric analysis curves of these rosin-based rigid PU foams displayed two distinct regions of weight loss. It has been shown that at the initial stage of weight loss the process was dominated by polyol component degradation; the second stage was governed by isocyanate component degradation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Improving the thermal stability of rigid polyurethane (PU) foams is one of the urgent tasks faced by the PU industry.[1-3] It was well known that rigid PU foam is one of the most effective heat insulating materials.[4] However, its maximum long-term use temperature is only about 130°C, which limits the application of this material greatly.

A large amount of research[2,3,5,6] has been done on improving thermal stability of rigid PU foams and some achievements have been obtained. From the point of view of polymer structure, rigid PU foam is a kind of polymer network formed through the crosslinking reaction between polyether and/or polyester polyols and isocyanates. Therefore, its thermal stability depends on the following two aspects: the thermal stability of network chains and the crosslinking density of the network. Many methods have been used to raise the thermal stability of rigid PU foams, of which the following two are most commonly adopted: increasing the degree of crosslinking of rigid PU foams by using polyester or polyether polyols with higher functionality[2] and increasing the dosage of isocyanate together with adding catalysts to trimerize isocyanates.[3] Some problems, however, are raised by using the above two methods. Generally, increasing functionality of polyols leads to an increase in viscosity, that is, deteriorating their processability. High dosage of isocyanate usually leads to foams that are too brittle to use.

Previously, the authors have synthesized rosin polyester polyols and rosin polyester polyol-based rigid PU foams from natural, renewable gum rosin.[7] It was found that this type of rigid polyurethane foam has good mechanical properties. In the present work, a series of hydroxyl-terminated maleopimaric acid esters (HTMAEs) of different structure and rigid PU foams based on these HTMAEs were synthesized, using maleopimaric acid (MPA), a derivative of gum rosin, as the raw material. Their thermal stability was studied by a thermogravimetric method and also a dimensional stability measurement. In addition, rigid PU foams were also synthesized directly from gum rosin and turpentine oil

Table I Physical Properties of Maleopimaric Acid

Appearance	Purity (%)	Melting Point (°C)	Carboxyl Value (mg KOH/g)
White crystals	99.9	224–227	420–422

and their properties were compared with those of the HTMAE-based ones.

EXPERIMENTAL

Materials

Linear hydroxyl-terminated polyether, N210, and sorbitol-based polyether, ZS-635, were supplied by Jinling Petrochemical Co. Polymeric methylene diisocyanate (MDI), MR100, was the product of Japan Polyurethane Co. MPA, whose main physical properties are given in Table I, was synthesized[8] from gum rosin by the authors. Gum rosin is a mixture of rosin acids. The main components of natural gum rosin are abietic acid, neoabietic acid, longiabietic acid, and (s)-pimaric acid.[9] There is an equilibrium existing between these acids. When heated to over 100°C, the equilibrium goes towards forming (s)-pimaric acid. MPA is formed through the Diels–Alder reaction between (s)-pimaric acid and maleic anhydride. This reaction is shown in Scheme 1. All other chemicals were used as supplied.

Synthesis of Polyester Polyols from MPA, Rosin, and Turpentine Oil

HTMAE was synthesized by mixing together appropriate amounts of MPA (1 mol), linear alkyl
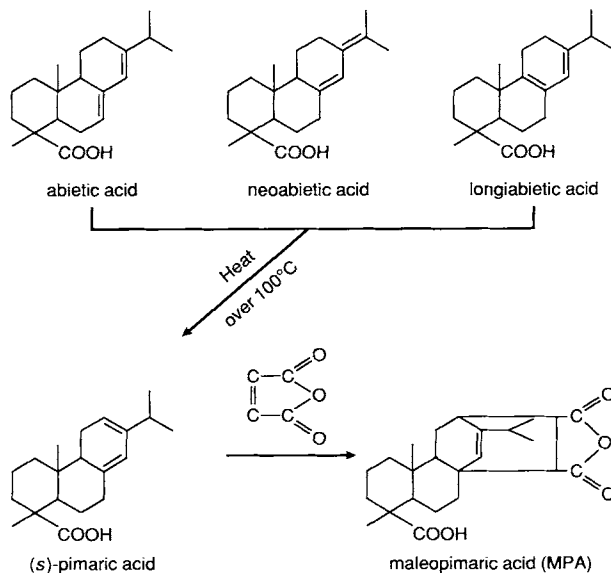
Scheme 1 The synthesis of MPA from gum rosin.

diols (3–15 mol), and catalyst, keeping the system at about 260°C until the carboxyl value was less than 5 mg KOH/g. After washing 2–3 times with distilled water, the product was distilled at a reduced pressure to drive off any unreacted low molecular weight diols and water. The physical properties of HTMAEs synthesized under different conditions are given in Table II. The rosin and turpentine oil based polyester polyols, RPP and TOPP, were prepared directly from gum rosin and turpentine oil in the same way as mentioned above. Their physical properties are also shown in Table II.

Preparation of Rigid PU Foams From HTMAE, RPP, and TOPP

HTMAE or RPP or TOPP was mixed with a certain amount of polyether ZS-635 (at a weight ratio of

Table II Properties of Different Esters of Maleopimaric Acid, Rosin Polyester Polyol (RPP), and Turpentine Oil Polyester Polyol (TOPP)

Sample	Different Esters of MPA				RPP	TOPP
	EG	DEG	TEG	N210		
Hydroxyl value (mg KOH/g)	233.5	164.7	131.6	92.3	400	260
Viscosity[a] (25°C, mPa)	180	68	27	1.5	—	—
Molecular weight[b]	719	1020	1277	1820	420	430

[a] Viscosity for 20% acetone solution.

[b] Calculated from hydroxyl values at the condition when functionality is assumed to be 3. For TOPP, functionality is assumed to be 2.

polyester polyol/ZS-635 of 1), blowing agent $CFCl_3$ (at an amount that gives the final foams an apparent density of about 43 kg/m^3), silicon surfactant, and some mixed tertiary amine and alkali-metal salt catalysts to form the polyol component A. After the polymeric MDI, MR100, was added to polyol component A at an NCO/OH molar ratio of 3.0, the final mixture was strongly stirred at about 1400 rpm for 10 min. The mixture was cast into a metal mold and left at room temperature for about 30 min prior to demolding. All the synthesized rigid PU foams were aged at room temperature for 1 week before being tested.

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 sample weight was about 2 mg.

Deformations of rigid PU foams were measured after they were placed in an oven at 170°C for 48 h. Viscosity testing was performed using a Tonji NDJ-79 type rotary viscometer at 25°C. Molecular weights were measured using a Knaur VPO analyzer.

RESULTS AND DISCUSSION

Thermal Stability of Polyols with Different Structures

Rigid PU foams are actually polymer networks formed through the reaction of polyols and isocyanates. The network chains are primarily composed of
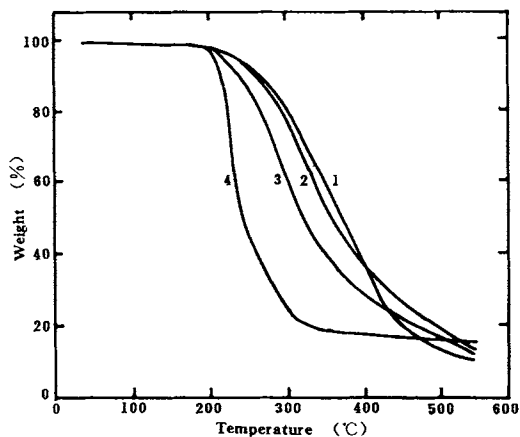
Figure 1 TGA curves of different polyols: (1) diethylene glycol ester of MPA; (2) diethylene glycol ester of maleopimarified gum rosin; (3) diethylene glycol ester of turpentine oil; (4) sorbitol based polyether, ZS-635.
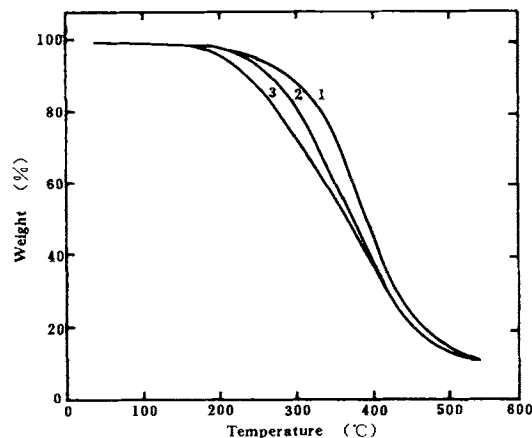
Figure 2 TGA curves of different esters of MPA: (1) ethylene glycol ester; (2) diethylene glycol ester; (3) triethylene glycol ester.

polyol components. Therefore, the thermal stability of polyols plays a very important role in thermal stability of the final material. The thermogravimetric curves of different polyols were shown in Figures 1 and 2. The thermogravimetric analysis (TGA) curve of the sorbitol-based polyether, ZS-635, is also presented in Figure 1. Following the esterification of MPA, a complicated mixture of HTHMEs will be formed. The basic formula of these HTMAE is illustrated in Scheme 2.

However, in some cases, especially when HTMAE is synthesized at high MPA concentration, the numbers of the terminal hydroxyl groups might be less than 1 because of the possible reaction between the hydroxyl groups of incompletely esterified MPA and the remaining carboxyl groups or carboxyl groups of other MPA molecules.

The difference between RPP and HTMAE is that RPP contains about 85% HTMAE as well as 10% mono-rosin acid ester and about 5% nonester components.[7-9] TOPP is a complex mixture, of which pinene-based polyester polyols comprise the main part.[8,9] Figure 1 clearly shows that polyesters are
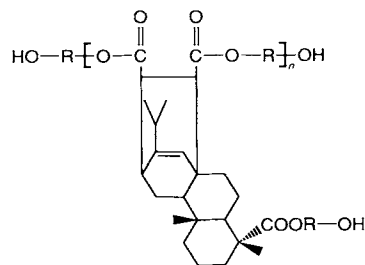
Scheme 2 The chemical structure of HTMAE.

more thermally stable than the polyether, due to the high bond energy of ester, about 12.14 kJ/mol, compared to that of ether, about 4.19 kJ/mol. The comparison of TGA curves 1, 2, and 3 in Figure 1 shows that HTMAE is the best polyol in terms of thermal stability, followed by RPP and TOPP. The existence of a thermally stable group, the triple ring structure, may be the reason for the better thermal stability of HTMAE and RPP compared to TOPP. With about 10% mono-resin acid ester and 5% nonester component, RPP contains fewer triple rings than HTMAE, resulting in its slightly lower thermal stability compared to HTMAE. The effect of the molecular weight of the diols used in the preparation of HTMAEs is illustrated in Figure 2 where three esters of MPA, ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) esters of MPA are compared. Differences in thermal stability appear for the different esters of MPA, with the smaller diol ester of MPA giving the higher thermal stability.

Due to low reactivity and strong spatial barriers, the esterification of MPA usually needs harsh conditions.[7-9] To speed up the reaction, a common method is to increase the amount of diol used, which may have some effect on structure and properties of the final products. To investigate this influence, three samples of DEG esters of MPA were synthesized at the DEG/MPA molar ratios of 3 : 1, 6 : 1, and 15 : 1, respectively. Their hydroxyl values and molecular weights measured by vapor pressure osmometry are given in Table III and their TGA curves are shown in Figure 3. Table III indicates that HTMAE synthesized at higher DEG/MPA ratios has a higher hydroxyl value and a smaller molecular weight, but this effect can be neglected when the DEG/MPA ratio is larger than 6 : 1. It can be imagined that the hydroxyl groups of the esterified MPA may be less likely to react with the carboxyl groups of the incompletely esterified MPA at higher molar ratio of DEG/MPA. Therefore, HTMAE synthesized at lower molar ratio of DEG/MPA tends to
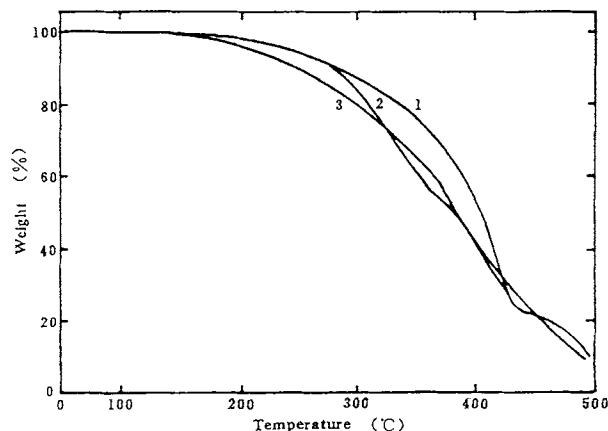
Figure 3   TGA curves of HTMAEs synthesized at different molar ratios of DEG/MPA: (1) 3 : 1; (2) 6 : 1; (3) 15 : 1.

have larger molecular weight, which is more thermally stable (Fig. 3) due possibly to its higher content of triple ring structure.

Thermal Stability of Rigid PU Foams Based on Different HTMAEs

A series of rosin-type rigid PU forms were synthesized based on the different esters of MPA mentioned above. Their physical properties and TGA curves are presented in Table IV and Figure 4, respectively. The TGA curves in Figure 4 display two distinct regions of weight loss that are similar to the TGA curves of segmented PUs.[10] Differences in stability are observed for rigid PU foams based on different esters of MPA, with shorter diol chain length giving higher stability, which is in line with the order of stability shown in Figure 2, suggesting thermally stable polyols resulting in rigid PU foams with better thermal stability.

Table III   Hydroxyl Values and Molecular Weights of HTMAEs Synthesized at Different Mole Ratios of DEG/MPA

DEG/MPA (Molar Ratio)	Hydroxyl Value (mg KOH/g)	Molecular Weight (by VPO)
3 : 1	102.9	947
6 : 1	164.7	827
15 : 1	174.4	859

Table IV   Thermal Stability of Rosin-Type Rigid PU Foams Based on Different MPA Esters

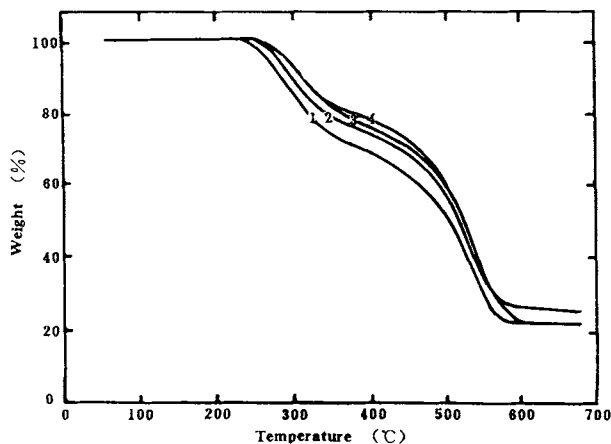| HTMAE | Different MPA Esters | | | |
	EG	DEG	TEG	N210
Deformation (%, 170°C, 48 h)	2.79	3.42	4.21	6.86
T_{ON} (°C)	250.6	252.5	247.6	234.9
$\bar{W}_1$ (wt %)	20.4	20.3	22.1	25.4
$\bar{W}_2$ (wt %)	62.0	61.5	53.4	54.9
$\bar{W}_{OII}$ (wt %)	20.5	21.7	22.3	28.5
$\bar{W}_{NCO}$ (wt %)	70.2	68.5	68.1	61.2

Figure 4 TGA curves of rigid PU foams based on different esters of MPA: (1) N210 polyether ester of MPA; (2) TEG ester of MPA; (3) DEG ester of MPA; (4) EG ester of MPA.

The weight fraction of polyol component, $\bar{W}_{OH}$, and isocyanate component, $\bar{W}_{NCO}$, in rigid PU foams were plotted against the amount of weight loss in the first and second stages in TGA curves $\bar{W}_1$ and $\bar{W}_2$, respectively, as shown in Figure 5(a,b). They show two straight lines with fairly good correlation coefficients, suggesting that at the initial stages of the weight loss the process was governed by polyol component degradation, and the second weight loss stage was dominated by the isocyanate component degradation, which is different from the case of segmented PUs.[10] In our PU system, in addition to the isocyanate, which was added at a molar ratio of NCO/OH of 3, some isocyanate trimerization catalysts were used. Therefore, it can be expected that some of the isocyanate was trimerized to form isocyanurates, causing isocyanate components to be degraded at higher temperature.[3]

The effect of the molecular weight of HTMAEs on the onset temperature, T_{ON}, of the weight loss process and deformation of rigid PU foams at high temperature are displayed in Figure 6(a,b), with lower molecular weight of HTMAE giving higher T_{ON} and lower deformation, that is, better thermal stability, which is in line with the order of thermal stability of the different HTMAEs in Figure 2. With relatively low linear alkyl C — C chain content and higher MPA content, low molecular weight HTMAE is more thermally stable. Furthermore, rigid PU foams based on low molecular weight HTMAE usually possess higher crosslinking density.

It is not difficult to see from Figures 2 and 6 that small diols, such as EG, should be used to synthesize HTMAE in order to prepare rigid PU foams with

better thermal stability. This kind of HTMAE, however, generally possesses higher viscosity, that is, poor processibility. The relationship between molecular weight of HTMAE and its viscosity is presented in Figure 7. The viscosity of HTMAE decreases rapidly with increase in its molecular weight (Fig. 7).

To investigate the effect of the molar ratio of DEG/MPA at which HTMAEs were synthesized on thermal stability of their corresponding rigid PU foams, three samples of rigid PU foams were prepared using the HTMAEs synthesized at the DEG/MPA molar ratios of 3 : 1, 6 : 1, and 15 : 1. The TGA curves are showed in Figure 8. No significant effect
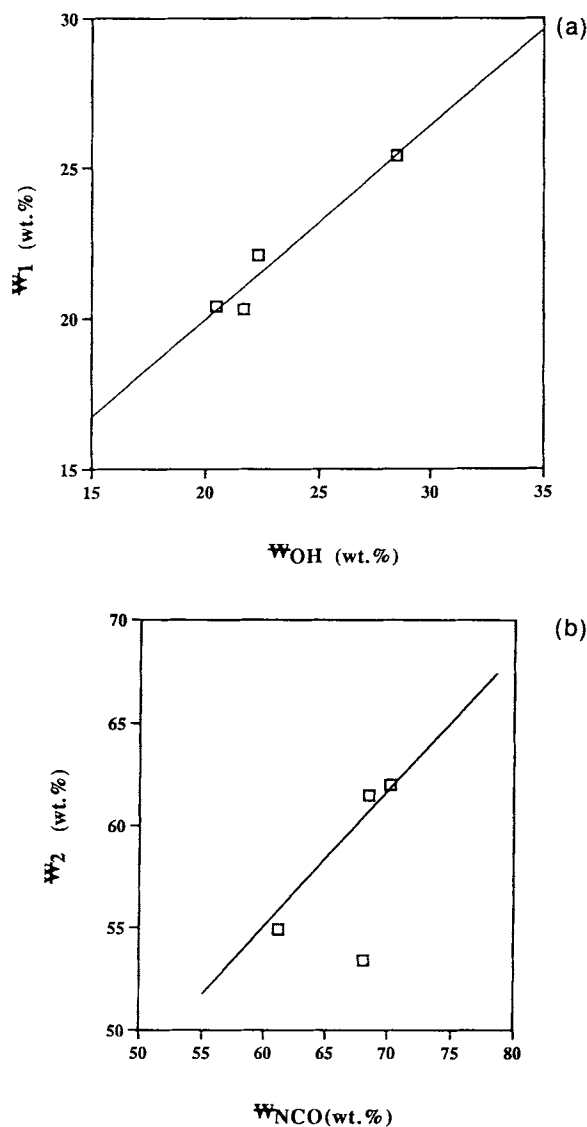

Figure 5 (a) The relationship between $\bar{W}_{OH}$ and $\bar{W}_1$ and (b) the relationship between $\bar{W}_{NCO}$ and $\bar{W}_2$.
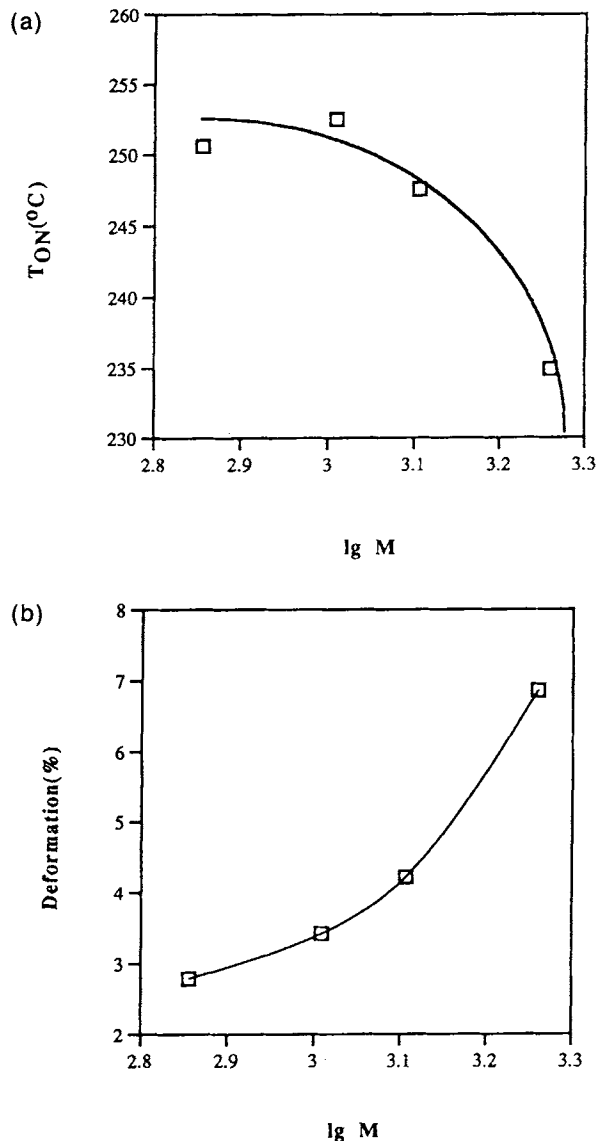
(a)

(b)

Figure 6 (a) The effect of the molecular weight of HTMAEs on the onset temperature, T_{ON}, of weight loss process of rigid PU foams. (b) The effect of the molecular weight of HTMAEs on the deformation of rigid PU foams at high temperature.

was observed for the DEG/MPA ratio on thermal stability of foams, with lower molar ratio of DEG/MPA giving slightly higher thermal stability when DEG/MPA was less than 6 : 1. This seems to be opposite to the order of thermal stability of HTMAE shown in Figure 3. Although HTMAE synthesized at higher molar ratio of DEG/MPA is less thermally stable, it usually has a higher hydroxyl value, that is, higher functionality, that makes the final foams have higher crosslinking densities. In other words,
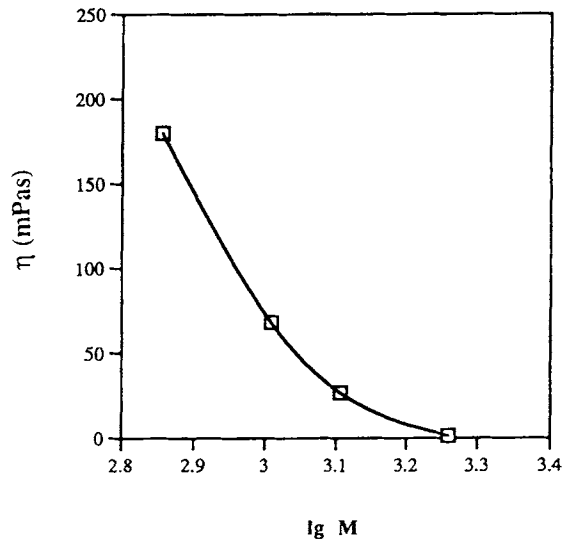

Figure 7 The influence of the molecular weight of HTMAE on its viscosity.

the effect of its lower thermal stability is compensated for by its higher functionality.

Thermal Stability of Rigid PU Foams Based on Different Polyester Polyols

Three samples of rigid PU foams were synthesized based on the DEG esters of MPA, chemically modified gum rosin, and chemically modified turpentine oil. Their onset weight loss temperatures obtained from the TGA curves, together with that of their corresponding polyester polyols, are illustrated in Table V. The rigid PU foams based on DEG ester of MPA possess the best thermal stability, followed
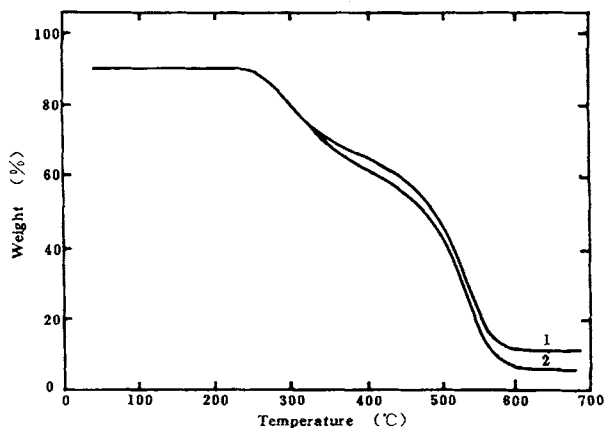

Figure 8 TGA curves of rigid PU foams based on HTMAEs synthesized at different molar ratio of DEG/MPA: (1) 6 : 1 and 15 : 1; (2) 3 : 1.

Table V Onset Temperature, T_{ON1}, of Weight Loss Process of Different Polyols and T_{ON} of Corresponding Rigid PU Foams

Onset Temperature (°C)	DEG Compounds of		
	MPA	Chemically Modified Gum Rosin	Chemically Modified Turpentine Oil
T_{ON1}	212.3	200.0	176.0
T_{ON}	252.5	242.7	226.6

by DEG ester of rosin and turpentine oil, which is in good agreement with the order of thermal stability of their corresponding polyols. This suggests that the thermal stability of monomeric polyols plays a vital part in the thermal stability of the final rigid PU foams.

CONCLUSIONS

It has been shown that HTMAE synthesized from a derivative of natural gum rosin, is more thermally stable than the commonly used polyether polyol and polyester polyol based on turpentine oil. The thermal stability of the final rigid PU foams is dependent on the structure of HTMAEs, with the lower molecular weight diols used in the synthesis of HTMAEs giving higher thermal stability to the final foams. The TGA curves for these rosin-based rigid PU foams display two distinct regions of weight loss. It was shown that at initial stages of the weight loss the process was dominated by the polyol component degradation, whereas the second stage was governed by the isocyanate component degradation.

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