

Polyesteramides Used for Hot Melt Adhesives: Synthesis and Effect of Inherent Viscosity on Properties

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Received 3 June 2000; accepted 5 September 2000

ABSTRACT: Polyesteramides, with different inherent viscosities, were synthesized from dimer acid, sebacic acid, ethylenediamine, and diethylene glycolamine. The effect of inherent viscosity of the polyesteramides on their thermal properties, such as melt viscosity, softening point, heat of fusion, glass-transition temperature, and low-temperature flexibility, was studied. The effect of the inherent viscosity on mechanical properties, such as tensile strength, elongation at break, and hardness, and on adhesion properties, such as lap shear strength and T-peel strength, was also investigated. The results show that melt viscosity, tensile strength, and elongation at break increase as the inherent viscosity increases, and that lap shear strength of the polyesteramides also increases with increasing inherent viscosity, whereas softening point, glass-transition temperature, and shore D hardness of the polyesteramides essentially do not change as the inherent viscosity increases within a certain range. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2696–2701, 2001

Key words: inherent viscosity; polyesteramide; dimer acid; hot melt adhesive; synthesis

INTRODUCTION

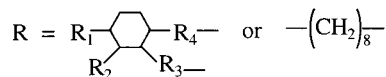
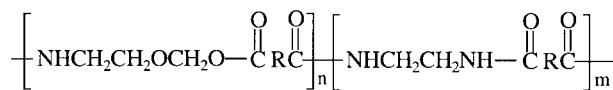
Polyamide is an important class of hot melt adhesive resin. In comparison with ethylene-vinyl acetate copolymer (EVA), which has been popularly used as a hot melt adhesive, it has higher adhesion strength and a wider application temperature range; therefore, its application in hot melt adhesives is becoming increasingly popular.^{1–7} The polyamide synthesized from dimer acid, sebacic acid, ethylenediamine, and diethylene glycolamine, which contains ester groups in its backbone, i.e., polyesteramide, has outstanding properties in all aspects. It has high strength, as polyamide does and, at the same time, has the low-temperature flexibility of the polyester. It has

good adhesion to such adherents as PE, Al, and Pb. Moreover, because this polyesteramide resin has excellent compatibility with various EVA, it can be blended with EVA to prepare many kinds of hot melt adhesives.^{8,9}

The inherent viscosity of the polyesteramides affects their properties to some extent. Several essential properties change greatly as the inherent viscosity varies. It was found in our lab that the relationship between the inherent viscosity of the polyesteramides and their properties is almost the same for polyesteramides synthesized from dimer acid, sebacic acid, ethylenediamine, and diethylene glycolamine at different ratios. Studies on the relationship between the inherent viscosity of the polyesteramides and their basic properties are therefore of crucial importance for synthesizing polyesteramides with excellent properties. In the study detailed in the present article, a range of polyesteramides that have the same molecule chain structure but

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Journal of Applied Polymer Science, Vol. 81, 2696–2701 (2001)
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$$\text{R}_1 + \text{R}_2 + \text{R}_3 + \text{R}_4 = 28\text{carbons}$$

Scheme I Molecule chain structure of polyesteramides.

different inherent viscosities, were synthesized, with different reaction times, from dimer acid, sebacic acid, ethylenediamine, and diethylene glycolamine at specific ratios with suitable softening points and a wide application temperature range. The effect of inherent viscosity on such basic properties as softening point, melt viscosity, tensile strength, elongation at break, shore D hardness, glass-transition temperature, lap shear strength, and T-peel strength was studied.

EXPERIMENTAL

Materials

Dimer acid (UNIDYME-14), with an acid value of 196 mg potassium hydroxide (KOH)/g, was supplied by Union Camp. The contents were as follows: monomer, <1%; dimer, ~96%; and trimer, ~3%. Diethylene glycolamine with a purity of 98% was supplied by J & K (China) Chemical Ltd. Sebacic acid and ethylenediamine of chemical reagent grade were obtained from Beijing Chemical Reagents Shop.

Preparation of Polyesteramides

To a four-necked 2000-mL flask equipped with stirring system, condenser, nitrogen gas inlet, and thermometer, 1050 g (1.8 mol) dimer acid, 41.0 g (0.20 mol) sebacic acid, 65.8 g (0.63 mol) diethylene glycolamine, and 87.7 g (1.46 mol) ethylenediamine were added. The reaction was carried out with stirring under nitrogen. First, the reactants were heated to 200–250°C in 2 h with the water formed in the system removed by refluxing. Then, the reaction was carried out at the above temperature for an additional 2 h. Finally, the reaction was conducted under constant vacuum (pressure <1 mmHg) at 200–250°C. A series of polyesteramides of different molecular weights were obtained with different times of reaction under vacuum.

Measurements

Infrared (IR) spectra were obtained using a NICOLET-205 IR Spectrometer. The inherent viscosity at 30°C, in *m*-cresol at a concentration of 1 g/dL, was measured using a Ubbelohde viscometer in accordance with GB12006.1-89. Softening point was determined in accordance with ASTM E-28 with a heating rate of 5°C/min. The glass-transition temperature (T_g) was determined using a Perkin-Elmer DSC7 with heating and cooling rates of 10°C/min. Melt viscosity was measured using a Brookfield Thermosel (Brookfield Engineering Laboratories), in accordance with ASTM D3226. Tensile strength of the compression-molded sheet was measured in accordance with ASTM D638 with a crosshead speed of 50 mm/min. The shore D hardness was determined in accordance with GB2411. Low-temperature

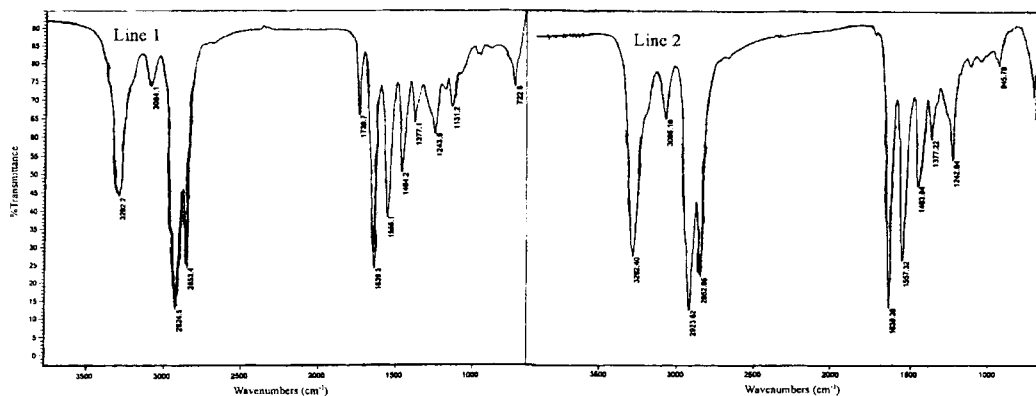


Figure 1 IR spectra of polyesteramides (line 1) and polyamides (line 2)

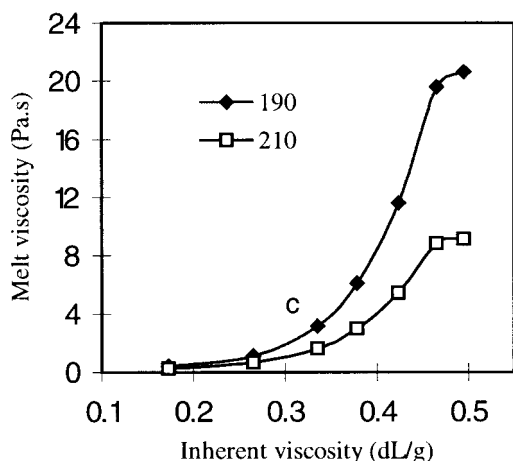


Figure 2 Effect of inherent viscosity on melt viscosity. (190 and 210 mean that test temperatures are 190°C and 210°C, respectively.)

flexibility was determined in accordance with ASTM D3111-76, with a 3.2-mm-diameter test rod, and was based on the lowest temperature at which 80% of samples would not break.

Adhesion strengths of the polyesteramides used as hot melt adhesives were measured as follows. Aluminum was chosen as the adherent, and its surface was treated with 20 wt % $\text{Na}_2\text{SiO}_3/\text{H}_2\text{O}$ solution, with 2% emulsifier OP added, was heated to 70°C. Aluminum was dipped into it for 5 min and was then washed with distilled water and dried.

The polyesteramide adhesive films were obtained by compression molding. The adhesion joint was obtained by pressing the film between two pieces of treated aluminum adherent at a temperature of 180°C and pressure of 35 kPa for 15 min, followed by cooling at room temperature for 1 day. Lap shear strength was determined according to ASTM1002-72 with a crosshead

speed of 20 mm/min. T-peel strength was measured in accordance with GB2791-81 with a cross-head speed of 200 mm/min.

RESULTS AND DISCUSSION

Characterization of Polyesteramides

According to Wheeler and Milun,^{10,11} the polyesteramides synthesized from dimer acid, sebacic acid, ethylenediamine, and diethylene glycolamine may be expressed as shown in Scheme I.

In Figure 1, line 1 is the IR spectrum of the polyesteramides, and line 2 is the IR spectrum of polyamides synthesized from dimer acid, sebacic acid, and ethylenediamine. Comparison of line 1 with line 2 shows that line 1 has obvious ester group absorption at 1740 cm^{-1} , demonstrating that the products are polyesteramides.

Effect of Inherent Viscosity on Thermal Properties

Melt Viscosity and Softening Point

Melt viscosity and softening point are two properties of great importance for the polyesteramide, which significantly affect the application of the resulting hot melt adhesives. Figure 2 shows the effect of inherent viscosity of polyesteramides on their melt viscosity at different temperatures. The softening points of the polyesteramides with different inherent viscosities are listed in Table I. Softening point varies within a narrow range of 117–120°C when inherent viscosity varies within 0.173–0.495, indicating that the molecular weight has little effect on softening point (Table I). The softening point of polyesteramides is determined by the chemical structure of their molecule chains, e.g., the contents of the ester group and the amide group.

Table I Effect of Inherent Viscosity on Softening Point, Heat of Fusion, T_g , and Low-Temperature Flexibility

Properties	Sample no.						
	1	2	3	4	5	6	7
Inherent viscosity (dL/g)	0.173	0.265	0.335	0.378	0.423	0.465	0.495
Softening point (°C)	117	118	119	118	118	120	120
Heat of fusion (J/g)	15.6	15.7	15.6	17.0	15.6	14.9	14.6
T_g (°C)	-26.6	-23.9	-23.0	-22.4	-23.6	-22.3	-23.6
Low-temperature flexibility (°C)	-15	-17	-19	-19	-20	-21	-19

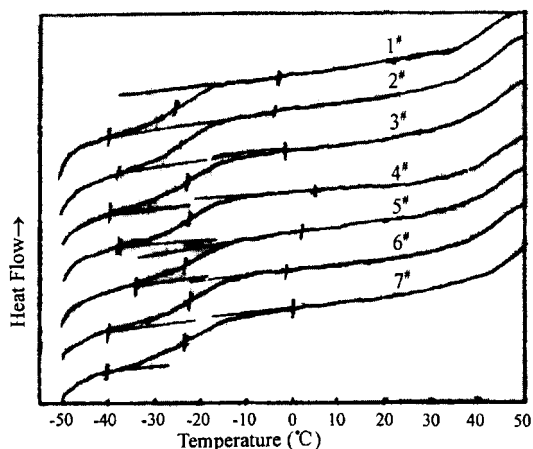


Figure 3 Differential scanning calorimetry thermograms of polyesteramides with different inherent viscosities for T_g .

Heat of Fusion and T_g

Figures 3 and 4 are differential scanning calorimetry (DSC) thermograms of the polyesteramides with different inherent viscosities. Figure 3 shows glass transition, and Figure 4 shows heat of fusion. Figure 3 shows that all polyesteramides have an obvious glass transition at $\sim -20^\circ\text{C}$. Figure 4 shows that all polyesteramides exhibit obvious heat absorption at $30\text{--}120^\circ\text{C}$. This property results from the hydrocarbon ring and the long hydrocarbon chain of dimer acid, such as *R2* and *R4*, shown in Scheme I, which can crystallize under certain circumstances, and the hydrogen bond resulting from the amide group of polyesteramide molecules.

The T_g and heat of fusion are also listed in Table I, which were calculated from the thermograms displayed in Figures 3 and 4, respectively. Table I shows that T_g and heat of fusion essentially keep constant with increasing inherent viscosity, which indicates that T_g and heat of fusion are determined by the chemical structure of the polyesteramide molecule chains and are not affected by molecular weight.

Low-Temperature Flexibility

Low-temperature flexibility as described in this article is measured according to ASTM-3111D, an important industry test method used for hot melt adhesives. Compared with ordinary polyamides, polyesteramides have excellent low-temperature flexibility due to the flexible ester group in their backbones, which contributes to their excellent

adhesion properties at low temperatures. Table I shows that low-temperature flexibility is better with increasing inherent viscosity within the range of 0.173–0.335. However, when the inherent viscosity varies within 0.335–0.495, a plateau in low-temperature flexibility is reached.

Effect of Inherent Viscosity on Mechanical Properties

The mechanical properties of polyesteramides have a significant effect on the adhesion properties of the resulting hot-melt adhesives. Table II lists shore D hardness of the polyesteramides with different inherent viscosities, which shows that shore D hardness increases with increasing inherent viscosity.

Figure 5 shows that the tensile strength of the polyesteramides increases slowly when the inherent viscosity is $<0.265\text{ dL/g}$. When the inherent viscosity is $<0.265\text{ dL/g}$, the molecular weight of the polyesteramide is very low, and the tensile strength is primarily determined by the crystallization resulting from the long hydrocarbon chain and hydrogen bonds resulting from amide groups and ester groups. As inherent viscosity increases from 0.265 dL/g to 0.465 dL/g , the molecular weight becomes an important factor that apparently improves the tensile strength. Therefore, tensile strength increases significantly when the inherent viscosity increases from 0.265 dL/g to 0.465 dL/g . When the inherent viscosity is $>0.465\text{ dL/g}$, the molecular weight of the polyesteramide is so high that it can no longer improve the tensile strength. Thus, the tensile strength

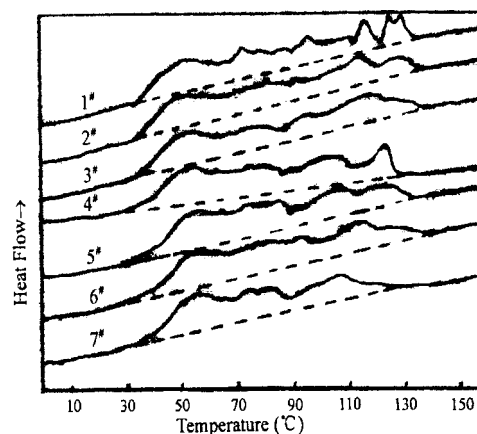


Figure 4 Differential scanning calorimetry thermograms of polyesteramides with different inherent viscosities for heat of fusion

Table II Shore D Hardness of Polyesteramides With Different Inherent Viscosities

	Sample no.						
	1	2	3	4	5	6	7
Inherent viscosity (dL/g)	0.173	0.265	0.335	0.378	0.423	0.465	0.495
Shore D hardness	<20	23	24	23	25	26	26

increases slowly when the inherent viscosity is 0.465–0.495dL/g.

Figure 6 shows the elongation at break of polyesteramides with different inherent viscosities. As inherent viscosity increases from 0.265 to 0.378, there is a sharp increase in elongation at break, but there is a plateau in elongation at break when inherent viscosity is beyond 0.378.

Effect of Inherent Viscosity on Adhesion Strength

Lap Shear Strength

The effect of inherent viscosity on lap shear strength is shown in Figure 7. At either 23°C or 60°C, lap shear strength increases apparently when the inherent viscosity is <0.378dL/g, but increases slowly when the inherent viscosity is 0.378–0.495dL/g. Figures 5 and 7 indicate that molecular weight has the same effect on the lap shear strength as on tensile strength, suggesting that the lap shear strength of the polyesteramide increases with increasing tensile strength. Temperature has a significant effect on the lap shear strength of all samples. Lap shear strength decreases to one-half when the temperature rises from 23°C to 60°C.

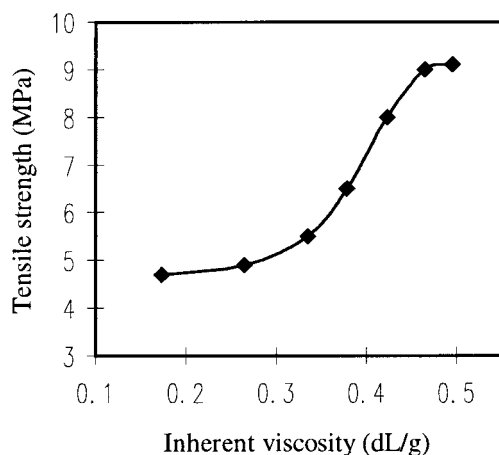


Figure 5 Effect of inherent viscosity on tensile strength.

T-Peel Strength

Table III shows that T-peel strength reaches its maximum when the inherent viscosity is 0.378–0.423. This is because the molecular weight is rela-

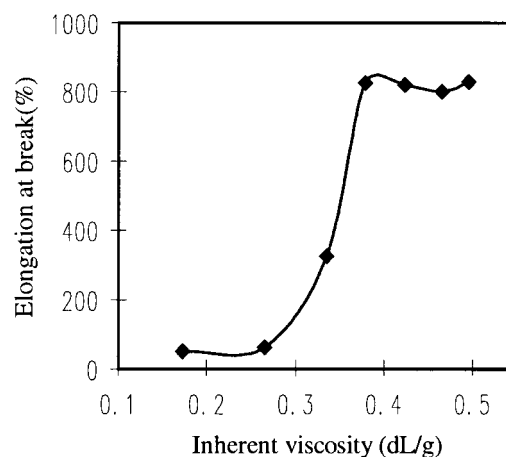


Figure 6 Effect of inherent viscosity on elongation at break.

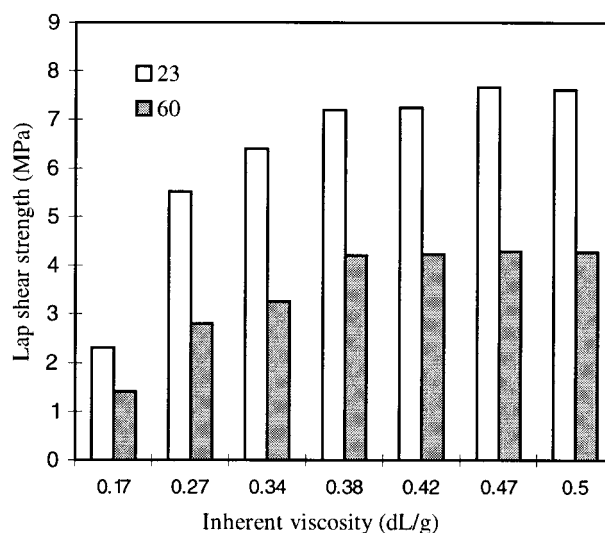


Figure 7 Effect of inherent viscosity on lap shear strength. (23 and 60 mean that test temperatures are 23°C and 60°C, respectively.)

Table III T-Peel Strength of Polyesteramides With Different Inherent Viscosities

Properties	Sample no.						
	1	2	3	4	5	6	7
Inherent viscosity (dL/g)	0.173	0.265	0.335	0.378	0.423	0.465	0.495
T-peel strength thickness ^a (mm)	0.41	1.57	1.97	3.52	4.09	2.60	2.20
	0.28	0.28	0.30	0.30	0.31	0.37	0.38

^a Average thickness of the adhesive between the aluminum adherends.

tively low when inherent viscosity is <0.378, which results in a relatively low tensile strength and elongation at break, as can be seen in Figures 5 and 6. The T-peel strength decreases as the tensile strength and elongation at break decrease. Moreover, during the T-peel strength test, those samples having relatively low tensile strength and elongation at break appear to have brittle cracking, which also decreases the T-peel strength. When the inherent viscosity is >0.465, the relatively high melt viscosity (Fig. 2) results in a higher average thickness of the adhesive between the aluminum adherends, leading to decreasing T-peel strength.

CONCLUSIONS

Polyesteramide is an important class of resin used for hot melt adhesives. Its softening point, melt viscosity, T_g , low-temperature flexibility, lap shear strength, and T-peel strength are of great importance for its application in hot melt adhesives. The range of the inherent viscosity studied in this article is 0.173–0.495, which basically illustrates the effect of the inherent viscosity on the properties of the polyesteramide. The inherent viscosity has little effect on the softening point

and T_g , while it greatly affects the mechanical properties. The inherent viscosity has the same effect on lap shear strength as on tensile strength, and the lap shear strength increases as the tensile strength increases. The polyesteramide has the best properties in all aspects when the inherent viscosity is 0.378–0.465.

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