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Influence of monofunctional reactants on the physical properties of dimer acid-based polyamides

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Dimer acid-based polyamides were synthesized by condensation polymerization in the absence and presence of monofunctional reactants. Acetic acid, oleic acid and propyl amine were used as monofunctional reactants. The influences of the equivalent percentage (E%) and type of monofunctional reactant on the physical properties of dimer acid-based polyamides such as glass transition temperature (T_g), melting point (T_m), heat of fusion (ΔH), degree of polymerization (DP), number average molecular weight (M_n), and kinematic viscosity were investigated. The molecular weight and viscosity of dimer acid-based polyamides decreased with the increase in equivalent percentage of monofunctional reactant. Differential scanning calorimetry (DSC) studies showed that acetic acid and propyl amine had higher effect on the thermal properties of polyamides than that of oleic acid. In the case of polyamides prepared in the presence of acetic acid, the values of T_g, T_m, and ΔH of the polyamides increased remarkably with the increase in acetic acid content. On the contrary, propyl amine had a decreasing effect on the values of T_g, T_m, and ΔH of the polyamides. Incorporation of oleic acid into the polymer structure had no significant effect on the values of T_g and T_m of the dimer acid-based polyamides.

KEYWORDS: dimer acid; polyamides; differential scanning calorimetry (DSC); synthesis; molecular weight

INTRODUCTION

The polyamides derived from dimer acids gain their distinctive physical properties from the dimer acids used in their production. Dimer acids are well-known and commercially available products and they are obtained by the polymerization of the C_{18}-acids such as oleic and linoleic acids. They are enviromentally friendly chemicals, less expensive, biodegradable, never crystallize, soluble in hydrocarbons, reactive, and they have comparatively high molecular weight (560) but they are liquid at room temperature. In comparison to the well-known nylons, dimer acid-based polyamides are more soluble in lower alcohols and more flexible. In addition, they have lower melting points and lower average molecular weights, and a greater compatibility with other resins and modifiers. Therefore, these polyamides find a wide variety of important applications. They are widely used in printing inks as binder components, as varnishes in organic solvents and heat-seal coatings.[1–5]

Dimer acid formation from two unsaturated fatty acids is shown in Scheme 1.[6] The fatty acid in the dimer acid is the major constituent. The character D in HOOC-D-COOH (Scheme 1) represents the C_{34}-divalent hydrocarbon radical. The reaction product of the dimer acid and the diamine is frequently represented by HO[OC-D-CONH-R-NH]$_n$H. The properties of polyamides are modified by using various difunctional or monofunctional reactants.[1]

Various formulations and synthesis techniques for dimer acid-based polyamides have been described in previous literature.[7–10]

Fan *et al.*[7] synthesized a series of polyamides from different soy-based dimer acids and diamines by condensation polymerization, and investigated the influences of aromatic and aliphatic diamines on the physical properties of the polyamides. They found that polyamides with an aromatic segment exhibited better thermal performance than those with aliphatic segments.

In another work, Fan *et al.*[8] investigated the thermal and swelling behavior of soy-based polyamides prepared in the presence and absence of α-aminoacid (L-tyrosine). They reported that the glass transition temperature (T_g), melting temperature (T_m), heat of fusion (ΔH), and crystallinity of the copolyamides were remarkably decreased as the content of L-tyrosine was increased.

Deng *et al.*[9] reported the preparation of fatty polyamides in the presence of a series of amino acids such as L-tyrosine, L-phenylalanine, and L-glutamic acids and they studied the effects of the functional groups on the physical properties of the soy-based polyamides. They found that the introduction of amino acid into the polyamide backbone significantly decreased the T_g and T_m values of the polyamides.

Vedanayagam and Kale[10] prepared non-reactive fatty polyamides from dimer acids, diamines and an aliphatic monoacid or monoamine, and they reported the acid value (AV), amine value (AmV), degree of polymerization (DP),

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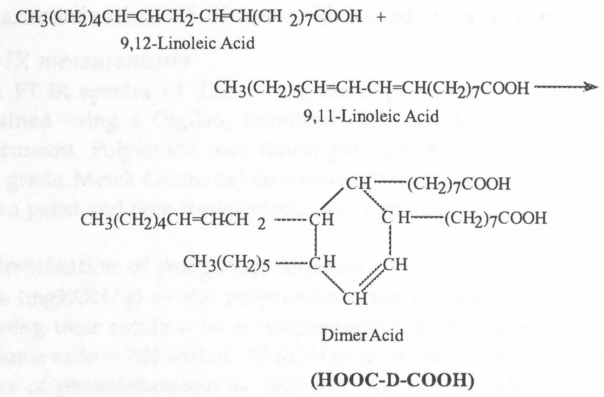

Scheme 1. Dimer acid preparation from 9,12- and 9,11-linoleic acid.

extent of reaction (p), number average molecular weight (M_n), viscosity and softening point of the fatty polyamides.

Preparation of dimer acid-based polyamides containing monofunctional reactants have also been reported in a series of patents and their solubility has been investigated due to their commercial importance.[11–13] However, thermal properties and kinematic viscosity values of the monoacid- or monoamine-containing dimer acid-based polyamides have not been reported in the literature. This study can provide both scientific and commercial benefit for thermal and various physical properties of dimer acid-based polyamides.

In the present study, a series of dimer acid-based polyamides were synthesized in the presence of different equivalent percentages (E%) of monofunctional reactants such as acetic acid, oleic acid, and propyl amine in order to modify the physical properties of the polymer. A thorough investigation was carried out to determine how the incorporation of monofunctional reactants affects the physical properties of the dimer acid-based polyamides. Physical properties investigated were values of T_g and T_m, crystallinity, AV, AmV, DP, M_n, and kinematic viscosity.

EXPERIMENTAL

Materials

Dimer acid (Pripol 1013), a yellowish transparent liquid, with an AV of 196 mg KOH/g was supplied by the Uniqema, and its purity was as follows: monomer <0.2%; 95–98% dimer; 2–4% trimer. Extra pure ethylenediamine and propyl amine were obtained from Merck. Pure oleic acid was obtained from Riedel-de-Haen. Glacial acetic acid was a Carlo Erba product. Reagent grade isopropyl alcohol, toluene, and methanol were used as solvents.

Synthesis of dimer acid-based polyamides

Dimer acid-based polyamides were synthesized via condensation polymerization. In addition to difunctional monomers of dimer acid and ethylenediamine, acetic acid and oleic acid were used as monoacids, and propyl amine as a monoamine. The ratio of total acid equivalents to total amine equivalents was kept approximately at 1 in all polymerization reactions and the equivalent percentage of the monoacid and monoamine were varied according to the total acid and total amine equivalents, respectively. The equivalent ratios of dimer acid to monoacid were chosen as 90:10, 80:20, and 65:35 and in the same manner, the equivalent ratios of ethylenediamine to propyl amine were chosen as 90:10, 80:20, and 65:35, respectively.

An example of dimer acid-based polyamide preparation is as follows: a reaction mixture consisting of dimer acid (80 E% of the total acid equivalent) and acetic acid (20 E% of the total acid equivalent) was placed into a 500 ml five-necked reactor equipped with a thermometer, mechanical stirrer, a Dean–Stark apparatus, a dropping funnel and a nitrogen inlet. The reaction system used in the polymerization reactions is illustrated in Fig. 1. The reactants were heated slowly to 50°C with stirring under nitrogen atmosphere to avoid any volatilization of employed reactants. At this temperature, ethylenediamine equivalent to total acid equivalent was added by using a dropping funnel over a period of 10 min. After the addition of ethylenediamine, the mixture was heated gradually to 140°C within 1 hr, then this temperature was kept for a further 1 hr, and after the temperature was raised to 200°C. When the completion of the polymerization was confirmed by AVs and AmVs less than about 10, a vacuum was applied to the reaction mixture for 30 min in order to remove the remaining volatile components. Three series of dimer acid-based polyamides with different monofunctional reactant at various equivalent percentages were synthesized according to typical synthesis procedure given above.

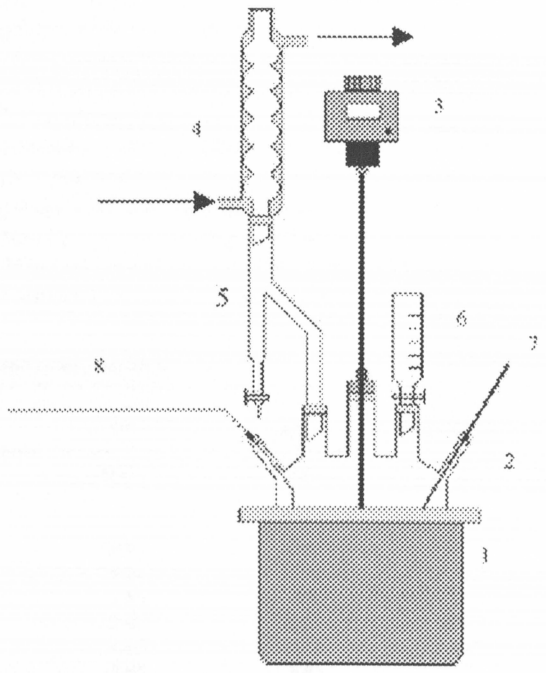

Figure 1. Reaction system. (1) Heating mantle, (2) reactor, (3) mechanical stirrer, (4) condenser, (5) Dean–Stark apparatus, (6) dropping funnel, (7) thermometer, (8) nitrogen inlet.

Characterization of dimer acid-based polyamides

FT-IR measurements

The FT-IR spectra of dimer acid-based polyamides were obtained using a Digilab, Excalibur-FTS 3000 MX model instrument. Polyamide was thoroughly ground with KBr (IR, grade, Merck-Germany) (at a ratio of 1:200) and pressed into a pellet and then the spectrum was recorded.

Determination of end group contents

AVs (mgKOH/g) of the polyamides were determined by titrating their solution in an isopropanol/toluene mixture (volume ratio = 1:1) with 0.1 N KOH in methanol in the presence of phenolphthalein as indicator. AmVs (mgKOH/g) were determined by titrating their solution in an isopropanol/toluene mixture (volume ratio=1:1) with freshly standardized 0.1 N HCl in isopropanol by using bromcresol green solution as indicator.

Determination of number average molecular weight (M_n) and number average degree of polymerization (DP_n)

The M_n values of the dimer acid-based polyamides given in Table 1 were calculated from the following equation when equivalent ratio of dimer acid to ethylenediamine was 1.[14]

$$M_n = (2 \times 56{,}100)/(\text{acid value} + \text{amine value}) \quad (1)$$

The M_n value can also be calculated by using the number average degree of polymerization (DP_n). In the case of the equivalent ratio of the dimer acid/ethylenediamine being 1, the DP_n value can be calculated using eqn (2):

$$DP_n = 1/(1 - p) \quad (2)$$

where p is the extent of the reaction which is determined from end group analysis. Multiplication of DP_n by the molecular weight of repeating unit of the polymer gives the M_n value.[15]

However, the following equation is used to calculate the DP_n when a monofunctional reactant is used in addition to a diacid and diamine during the polyamide preparation,

$$DP = 1 + r/(1 + r - 2rp) \quad (3)$$

where $r = N_A/(N_A + 2N_B)$, N_A is the amount of acid or amine equivalents and N_B is half the monofunctional reactant, and p is the extent of the reaction.

The M_n values of all polyamides given in Table 1 were obtained by the multiplication of the DP by the molecular weight of the repeating unit of the polymer.[10,15]

Determination of viscosity

Kinematic viscosity values for 35 wt% solutions of dimer acid-based polyamides in *n*-propanol were determined using a Setavis Kinematic Viscometer at 30°C.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a Mettler-Toledo 822^e instrument at a heating rate of 10°C/min under nitrogen atmosphere to obtain the T_g and T_m values.

RESULTS AND DISCUSSION

In this study, dimer acid has the highest weight fraction in the starting materials and the ratio of total acid equivalents to total amine equivalents was kept approximately at 1. Ethylenediamine was used as diamine. Acetic and oleic acids, and propyl amine were used as monoacids and monoamine, respectively. The dimer acid-based polyamides synthesized with different monofunctional reactants were solid and brittle at room temperature for all equivalent percentages of the reactants.

FT-IR studies

The FT-IR spectra of dimer acid-based polyamides with and without monofunctional reactants are shown in Fig. 2. The band due to C=O stretching (amide I) is seen at 1641/1640/1640/1636 cm^{-1}. The band at 1559/1559/1558/1572 cm^{-1} (amide II) is attributed to the streching of N–H bonds.[16–18] The band at 723/722/722/719 cm^{-1} shows the absorptions due to polymethylene groups of the dimer acid.[19] It is known that N–H and O–H absorption bands are seen at the same region, 3100–3600 cm^{-1}, as sharp and broad bands, respectively.[18] The sharp bands at 3297/3296/3294 cm^{-1} seen in the spectra of polyamides without a monofunctional reactant and with acetic and oleic acid, respectively are assigned to N–H groups that are hydrogen bonded to C=O groups. The intensity of non-hydrogen-bonded N–H stretching seen at 3424 cm^{-1} as a broad shoulder in the spectrum of polyamide without a monofunctional reactant diminished with

Table 1. Physical characteristics of polyamides with and without monofunctional reactant

	E%	AV (mg KOH/g)	AmV (mg KOH/g)	DP	M_n	Viscosity (cSt)
Polyamides without monofunctional reactant		4.7	5.3	38.0	11200	251.0
Polyamides with[a]						
Acetic acid	10	5.1	5.9	8.00	2350	112.0
	20	6.2	7.4	4.40	1300	49.0
	35	6.5	4.1	2.85	840	24.0
Oleic acid	10	5.3	6.2	7.90	2320	105.0
	20	5.1	7.5	4.40	1300	44.0
	35	7.0	4.1	2.80	820	32.0
Propyl amine	10	4.6	8.6	7.70	2250	139.0
	20	6.1	4.9	4.50	1330	64.0
	35	8.8	4.8	2.70	800	50.0

[a] Equivalent percentage of monoacid or monoamine was 10, 20, and 35 according to total acid or amine equivalent.

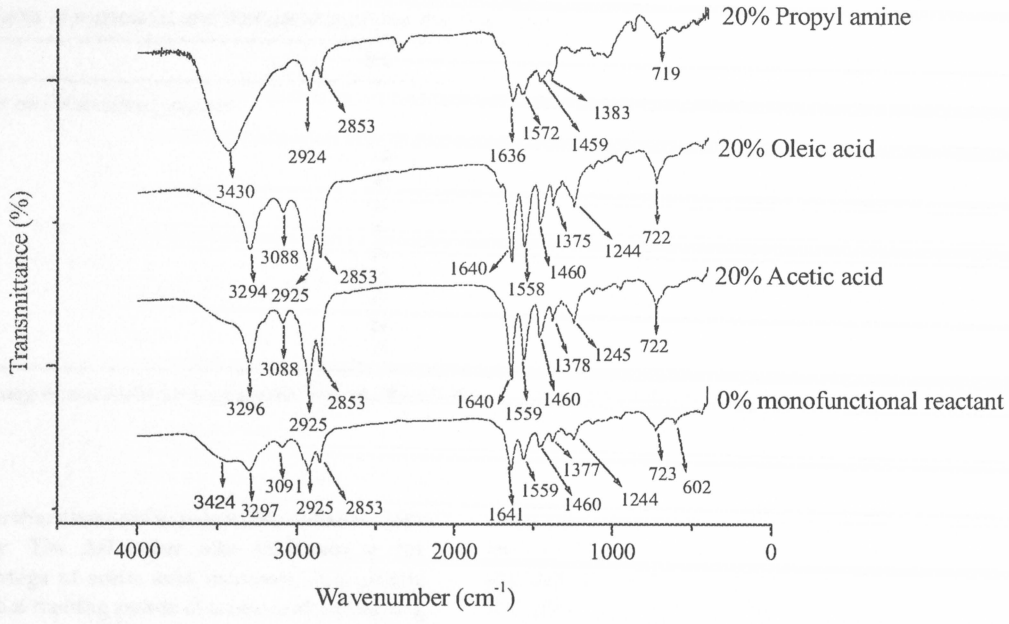

Figure 2. FT-IR of polyamides with (20 E% monoacid or monoamine) and without monofunctional reactant.

monoacid incorporation into the polyamide. However, in the case of propyl amine-containing dimer acid-based polyamide, the sharp hydrogen-bonded N–H stretching band disappeared and instead, a broad band at 3430 cm^{-1} attributed to non-hydrogen-bonded N–H stretching appeared.[16,17]

Influence of monofunctional reactants on AmV, AV, DP, M_n, and viscosity

The AVs and AmVs, DP, M_n, and kinematic viscosity of the polyamides prepared in the presence and absence of a monofunctional reactant are given in Table 1. When dimer acid and ethylenediamine react in a stoichiometrical ratio (1:1), high M_n (11200), high DP (38), and high viscosity (251 cSt) values were obtained compared to those of polyamides containing monofunctional reactants. The decrease in molecular weight and viscosity is due to the use of monofunctional reactants. Molecular weight and viscosity values of the polyamides greatly decrease with increasing equivalent percentage of monoacids or monoamine. Monofunctional reactants behave as chain stoppers and provide low viscosity and low M_n values. The viscosity values of polyamides with acetic acid and oleic acid are nearly the same and they are lower than those of propyl amine-containing polyamides for all identical compositions. The values of DP and M_n of the polyamides with 35 E% of monofunctional reactant are very low. The decrease in molecular weight causes great decreases in viscosity values as can be expected.

Influence of monoacid on the thermal properties of polyamides

Thermal properties of dimer acid-based polyamides prepared in the absence and presence of acetic acid are shown in Fig. 3 and Table 2. The T_g and T_m values of the polyamide without a monofunctional reactant is 69.7 and 103.4°C, respectively. These results are in agreement with the findings of Fan *et al.*[7,8] and the shapes of the DSC thermograms of the polyamides are similar to those reported by Fan *et al.*[7,8]

When the equivalent percentage of acetic acid is 10% of the total acid equivalent, the T_g values of polyamides with acetic acid and without acetic acid are nearly the same and the T_m of polyamides with acetic acid is higher than that of the polyamide without acetic acid. However, the increase of acetic acid content from 10 to 20 E% made no significant effect on the T_g and T_m values of polyamides modified by acetic acid. Interestingly, when the equivalent percentage of acetic acid rose to 35%, the T_g and T_m values of the polyamide increased considerably in comparison to those of the polyamide without acetic acid, and they are approximately

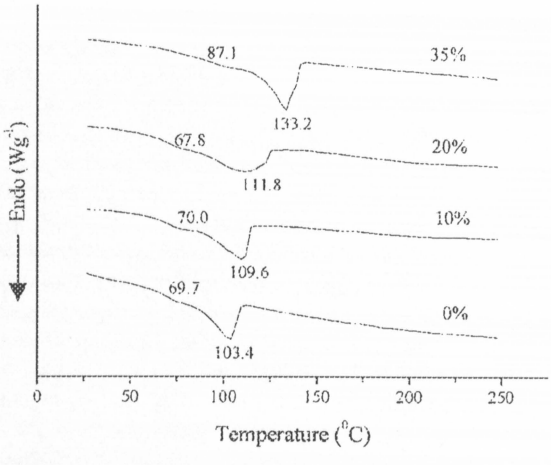

Figure 3. DSC thermograms of polyamides with (10–35 E%) and without (0 E%) acetic acid.

Table 2. The effects of monoacid and monoamine on the thermal properties of polyamides

	E%	T_g (°C)	T_m (°C)	ΔH (J/g)
Polyamides without monofunctional reactant		69.7	103.4	15.50
Polyamides with[a]				
Acetic acid	10	70.0	109.6	16.40
	20	67.8	111.8	19.40
	35	87.1	133.2	22.70
Oleic acid	10	67.6	103.8	12.10
	20	64.4	102.4	15.60
	35	62.6	106.7	16.20
Propyl amine	10	67.8	97.6	7.90
	20	61.9	95.5	5.60
	35	59.8	92.1	—

[a] Equivalent percentage of monoacid (or monoamine) was 10, 20, and 35 according to total acid (or amine) equivalent.

17 and 30°C higher than those of the polyamide without acetic acid, respectively. The ΔH value also increases as the equivalent percentage of acetic acid increases. It is clearly seen from Fig. 3 that melting points of acetic acid-containing polyamides increase gradually with the increase in acetic acid content compared to polyamide without acetic acid. The incorporation of acetic acid into the polymer structure affects remarkably the crystallization of the dimer acid-based polyamide and it increases the values of T_g, T_m, and ΔH. Since the density of the amide group in the polyamides increases as the content of acetic acid increases, higher melting points are obtained because of higher probability for the formation of hydrogen bonds. FT-IR spectra of acetic acid-containing polyamides also show the hydrogen-bounded structure.

The influence of oleic acid content on the thermal properties of polyamides is shown in Fig. 4 and Table 2. The T_g values of the dimer acid-based polyamides slightly decrease with an increase in oleic acid content. The T_g values of the polyamides with the contents 10, 20, and 35 E% oleic acid are approximately 2, 5, and 7°C lower than that of the polyamide without oleic acid, respectively. As shown in Table 2 and Fig. 4, T_m of the polyamide with 10 E% oleic acid is almost the same with that of polyamide without oleic acid. In addition, the increase of oleic acid content from 10 to 35 E% did not significantly affect the T_m value of the polyamide. Thus, 35 E% oleic acid incorporation into the dimer acid-based polyamide led to only 3.3°C increase in T_m value of polyamide in comparison to the polyamide without oleic aid. It is observed from Table 2 that 10 E% oleic acid incorporation into the dimer acid-based polyamide decreased slightly the ΔH value in comparison to that of the polyamide without oleic acid. Further increases in oleic acid-incorporation increased the ΔH value approximately to the same value with that of the polyamide without monofunctional acid. As a result, 10 to 35 E% oleic acid incorporation into the dimer acid-based polyamide made no significant effect on T_g, T_m, and ΔH values of the polyamide.

From the thermal analysis results (Table 2), it can be concluded that acetic acid incorporation into the polyamide affected the thermal properties of the polymer more in comparison to oleic acid incorporation. Although the FT-IR spectra of acetic acid- and oleic acid-containing dimer acid-based polyamides are similar, higher T_g and T_m values observed in the case of polyamide with acetic acid can be ascribed to the presence of higher intermolecular forces between the polymer chains and higher crystallinity due to acetic acid which is a short chain monoacid.

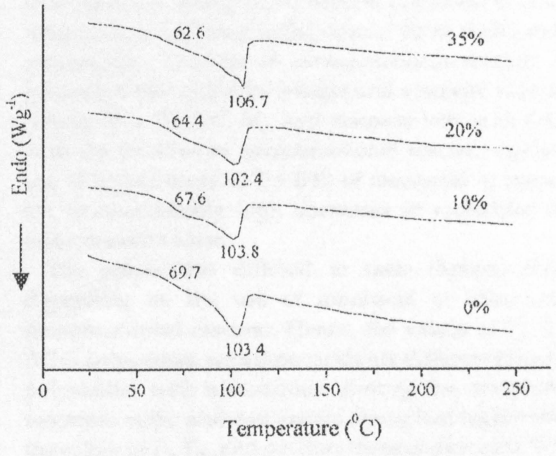

Figure 4. DSC thermograms of polyamides with (10–35 E%) and without (0 E%) oleic acid.

Effect of monoamine on the thermal properties of polyamides

When the equivalent ratio of acid to amine is 1, the effect of propyl amine content was investigated by comparing the thermal properties of polyamide with propyl amine and those of polyamide without propyl amine. As it can be seen from Table 2 and Fig. 5, the decrease in the T_g and T_m values result from the incorporation of propyl amine into the polyamide structure. The T_g values of polyamides with 10, 20, and 35 E% propyl amine are approximately 2, 8, and 10°C lower than that of polyamide without propyl amine, respectively. In addition, propyl amine incorporation into the polyamide decreased the T_m values of the polyamides with the 10, 20, and 35 E% propyl amine incorporation giving values approximately 6, 8, and 11°C lower than that of polyamide without propyl amine, respectively. The decrease in the peak temperatures for melting of propyl amine-containing

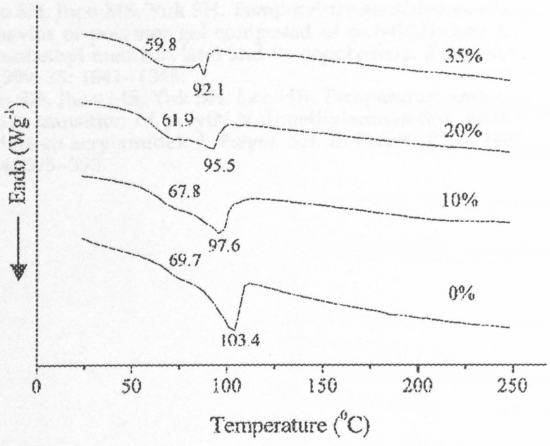

Figure 5. DSC thermograms of polyamides with (10–35 E%) and without (0 E%) propyl amine.

polyamides (Fig. 5) indicate the decline in the crystallinity of the polyamides. When propyl amine content increased to 35 E%, the intensity of peaks for melting of polyamide significantly decreased. Also, the T_g and T_m values of the propyl amine-containing polyamides are lower than those of the polyamides with acetic and oleic acid. Taking the FT-IR spectra into consideration, higher effect of propyl amine incorporation on the thermal properties of polyamide in comparison to monoacid incorporation can be ascribed to the absence or lack of hydrogen bonding. The lower melting temperatures indicate a lower ordered crystalline morphology due to the lower density of amide groups in the polyamide and the lower enthalpy of fusion may also confirm this conclusion.

CONCLUSIONS

Three series of dimer acid-based polyamides were synthesized in the absence and presence of monofunctional reactants such as acetic and oleic acid, and propyl amine. The equivalent percentage of total acid and total amine equivalent was varied according to the content of monoacid or monoamine; thus, it was used in the ratio of 90:10, 80:20, and 65:35, respectively. The use of monofunctional reactant greatly influenced the molecular weight and viscosity values of the polyamides. The DP, M_n, and viscosity values all decreased with the increase in monofunctional reactant content. The use of higher contents (35 E%) of monoacid or monoamine led to considerably high decreases in molecular weights and viscosity values.

The polyamides differed in their thermal properties depending on the use of monoacid or monoamine as monofunctional reactant. Hence, the values of T_g, T_m, and ΔH of polyamides with monoacids are different from those of polyamides with monoamine. Among the monofunctional reactants, acetic acid and propyl amine had higher effects on the values of T_g, T_m, and ΔH than those of oleic acid. While the incorporation of acetic acid into the dimer acid-based polyamide increased the T_g values of the polymer, oleic acid-incorporation slightly decreased them. It can be concluded that the incorporation of short-chain monoacid into the dimer acid-based polyamides imparts higher crystallinity in comparison to that of long-chain monoacid. In addition, the presence of hydrogen bonding between C=O and N–H groups of polymer chains were detected by FT-IR for the polyamide with both monoacid, but it was not the case for polymer with monoamine. The decreasing effect of propyl amine incorporation on the thermal properties of polyamide is higher than that of the long-chain monoacid. Crystallinity of the polyamide decreased with the increase in propyl amine content. Among the monofunctional reactants, oleic acid had no significant effect on the thermal properties of the polyamides. The T_g and T_m values of the polyamides with oleic acid varied within narrow ranges 62.6–67.6°C and 103.8–106.7°C, respectively. These results indicate that the type and content of the monofunctional reactant are important factors affecting the physical properties of dimer acid-based polyamides.

Acknowledgment

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