# Non-reactive polyamides from $C_{36}$ dimer acids: preparation and properties*

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Non-reactive polyamides were prepared by reacting a mixture comprising polymeric fatty acids, diamines such as ethylenediamine and hexamethylenediamine and an aliphatic monobasic acid or amine, to obtain a product of the desired extent of reaction, degree of polymerization, number average molecular weight, viscosity and softening point. The polymeric fatty acids used were of four types: imported acids; 97/3, 83/17 and 75/25 dimer/trimer mixtures, Empol 1010, 1018 and 1024 respectively and indigenous dimer acids. The indigenous acids were prepared in the authors' institute and comprised mixtures of monomer, dimer and trimer acids. In all the polyamides prepared, the extent of reaction was ~96%, the degree of polymerization ranged from 5–14, the number average molecular weight ranged from 1423–11 848, the viscosity of 35% solution in butanol/toluene 1:1, v/v, 19–147 s at 25°C (Ford Cup No. 4) and the softening point was 94.5–115°C. Most of these polyamides have properties comparable to the commercially available polyamides used in flexographic inks, adhesives and over-print varnishes.

**(Keywords: polyamides; synthesis; dimer acids)**

## INTRODUCTION

Fatty polyamides can be broadly classified into two categories: non-reactive and reactive. The non-reactive polyamides have a far lesser number of primary and secondary amine groups to react with epoxy resins compared to the reactive ones. These polyamides also differ in their properties and therefore in their end uses. Non-reactive polyamides are mostly solids and are used in the printing ink industry, mainly for flexographic and rotogravure inks, where hardness and solvent release is required. They are also used in over-print varnishes, adhesives and heat-seal coatings. Reactive polyamides are liquid in nature and are used in the surface coatings and adhesives industry[1].

The raw materials for the non-reactive polyamides described in this paper have to be polymeric fatty acids and diamines because the flexographic inks presently in use are applied to polypropylene films, which in turn require temperatures of 105–115°C and should resist blocking or sticking together.

Faulkenburg *et al.* have reported[2] the preparation of a series of polyamides from polymeric fatty acids and difunctional and polyfunctional amines. The polymeric fatty acids used in these preparations were not distilled and purified. Cowan *et al.*[3,4] have prepared polyamides from ethylenediamine and polymeric fatty acids called 'Norelac' which are suitable for use in the protective coating and packaging industries. There are a large number of patents[5–8] on the preparation of polyamides with varied properties.

The present work, which has been patented as per notification in the Gazette of India Part III Section 2, reports (a) the preparation of a series of polyamides for use in the flexographic ink industry with $C_{36}$ dimer acids and ethylenediamine; (b) calculation of the extent of the polyamidation reaction ($p$) and degree of polymerization ($DP$) and number average molecular weight ($M_n$), by using the end group titration method; and (c) estimation of the viscosity and softening point of the polyamides.

## EXPERIMENTAL

### *Materials*

Dimer acids were imported from Emery Industries Inc., USA (Empol 1010, 1018 and 1024 comprising 97/3, 83/17 and 75/25 dimer/trimer acids respectively). Indigenous dimer acids[9,10] were obtained from the authors' institute and comprised 14–35% monomeric acids, 45–50% dimeric and 20–36% trimeric and polymeric acids.

Ethylenediamine and hexamethylene diamine, 98% pure, laboratory reagent grade, were obtained from Indian Drugs and Pharmaceuticals Ltd, Hyderabad. Ethylenediamine was distilled and used, whenever necessary (BP 116°C under atmospheric pressure).

Stearic acid, commercial grade 80% pure, and oleic acid, commercial grade 60% pure, were obtained from Godrej Soaps Pvt. Ltd, Bombay, India.

Safflower and castor oils were purchased from Sanjiv Kumar Dhanji Oil Mills, Hyderabad, India and the total fatty acids from these oils were prepared in the laboratory. Dehydrated castor oil fatty acids[11,12] containing about 50% conjugated acids were obtained from the authors' institute. Coconut amine was purchased from Godrej Soaps Pvt. Ltd, Bombay, India.

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Perchloric acid 0.1 N and alcoholic potassium hydroxide 0.1 N were used. Bromophenol blue was used as indicator for the determination of amine value. Phenolphthalein was used as indicator for the determination of acid value. n-Butanol, toluene, xylene, chloroform (laboratory reagent grade) and ethanol (distilled over potassium hydroxide) were used.

### *Method*

Polyamide resins were prepared with four different types of dimer/trimer acid mixtures as shown in *Tables 1* to *4*. A typical example is as follows. A reaction mixture consisting of known amounts of dimer acids (97% dimer and 3% trimer) and commercial stearic acid was charged into a 1 l, metallic reactor made of 316 stainless steel and equipped with a thermowell, mechanical stirrer, a Dean and Stark apparatus, a dropping funnel and a nitrogen inlet and was heated electrically. The mixture was stirred and heated in a stream of nitrogen (120–140°C). At this temperature aqueous ethylenediamine (70%, v/v), equivalent to the amount of dimer/trimer mixture and required weight of monobasic acid, was added dropwise over a period of 45 to 90 min. After completion of amine addition, the mixture was heated gradually to 190°C

**Table 1** Effect of change in mole ratio of reactants

| Serial no. | Polymeric fatty acids Empol 1010 (dimer/trimer wt ratio) | Diamine | Ratio acid/amine (equivalent wt ratio) | Acid value (mg KOH g$^{-1}$) | Amine value (mg KOH g$^{-1}$) | Viscosity (s) | Softening point (°C) | Extent of reaction, $p$ | Degree of polymerization, *DP* | Number Average molecular weight, $M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 97/3 | Ethylene diamine | 1:0.85 | 35.1 | 1.1 | 21 | 105 | 0.91 | 5.6 | 1647 |
| 2 | 97/3 | Ethyelene diamine | 1:1 | 6.1 | 3.5 | 147 | 114 | 0.97 | 40.3 | 11 848 |
| 3 | 97/3 | Ethylene diamine | 1:1.25 | 4.2 | 37.0 | 24.5 | 97.5 | 0.89 | 5.1 | 1485 |

**Table 2** Effect of different types of additional reactant

| Serial no. | Polymeric fatty acids, Empol 1010 (dimer/trimer wt. ratio) | Additive | Additive[a] (wt%) | Viscosity (s) | Softening point (°C) | Extent of reaction, $p$ | Degree of polymerization, *DP* | Number average molecular weight, $M_n$ | Acid value (mg KOH g$^{-1}$) | Amine value (mg KOH g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 97/3 | Commercial stearic acid | 9.8 | 33 | 115 | 0.97 | 8.5 | 2499 | 7.6 | 3.8 |
| 2 | 97/3 | Commercial oleic acid | 9.5 | 27 | 113.8 | 0.97 | 8.8 | 2587 | 7.6 | 3.8 |
| 3 | 97/3 | Total fatty matter of castor oil | 9.4 | 39 | 109.3 | 0.97 | 7.75 | 2279 | 5.4 | 5.8 |
| 4 | 97/3 | Total fatty mater of safflower oil | 9.2 | 29 | 110.5 | 0.96 | 8.0 | 2356 | 4.2 | 12.4 |
| 5 | 97/3 | DCO fatty acids | 9.0 | 45 | 111.2 | 0.97 | 9.0 | 2646 | 8.8 | 3.0 |
| 6 | 97/3 | Coconut amine | 10.02 | 28 | 104.5 | 0.96 | 8.2 | 2409 | 9.5 | 3.9 |

[a] Experiments were carried out with 2.5 to 15% of the above-mentioned additives, but only properties of products with 9–10% additive are reported here

**Table 3** Effect of trifunctional acid

| Serial no. | Polymeric fatty acids (dimer/trimer wt. ratio) | Additive (wt%) | Acid value (mg KOH g$^{-1}$) | Amine value (mg KOH g$^{-1}$) | Viscosity (s) | Softening point (°C) | Extent of reaction, $p$ | Degree of polymerization, *DP* | Number average molecular weight, $M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| | | Commercial stearic acid | | | | | | | |
| | Empol 1018 | | | | | | | | |
| 1 | 83/17 | 8.3 | 9.0 | 4.0 | 49 | 110 | 0.96 | 11.9 | 3715 |
| 2 | 83/17 | 12.4 | 9.8 | 3.4 | 31 | 107.5 | 0.96 | 8.4 | 2635 |
| 3 | 83/17 | 17.4 | 11.6 | 7.1 | 24 | 105 | 0.95 | 5.9 | 1841 |
| | Empol 1024 | | | | | | | | |
| 4 | 75/25 | 8.2 | 7.0 | 6.0 | 45.5 | 109.0 | 0.97 | 14.0 | 4476 |
| 5 | 75/25 | 10.6 | 9.4 | 4.0 | 32.5 | 106.6 | 0.96 | 10.7 | 3413 |
| 6 | 75/25 | 19.2 | 8.9 | 4.8 | 23.5 | 113.5 | 0.96 | 6.1 | 1952 |
| 7 | 75/25 | 25.6 | 9.9 | 4.7 | 21.5 | 109.5 | 0.96 | 4.8 | 1423 |

**Table 4** Properties of polyamides with indigenous acids

| Serial no. | Indigenous acids (monomer, dimer, trimer approx. wt%) | | | Diamine | Acid value (mg KOH $g^{-1}$) | Amine value (mg KOH $g^{-1}$) | Viscosity (s) | Softening point (°C) |
|---|---|---|---|---|---|---|---|---|
| 1 | 21 | 48 | 31 | Ethylenediamine + additive (oleic acid) | 9.6 | 10.0 | 40.6 | 109.6 |
| 2 | 24 | 45 | 31 | Ethylenediamine | 10.0 | 5.2 | 26 | 114.0 |
| 3 | 14 | 50 | 36 | Ethylenediamine | 9.2 | 9.9 | 41 | 109.0 |
| 4 | 14 | 50 | 36 | Ethylenediamine | 7.4 | 8.1 | 41 | 114.5 |
| 5 | 35 | 45 | 20 | Ethylenediamine | 8.0 | 9.1 | 19 | 108.5 |
| 6 | 35 | 45 | 20 | Hexamethylenediamine | 6.2 | 8.9 | 22.6 | 94.4 |
| 7 | 35 | 45 | 20 | Hexamethylenediamine + additive (adipic acid) | 4.7 | 7.3 | 27 | 113.5 |

during which time the by-product water distilled out. The temperature was raised to 200°C under reduced pressure of about 15–20 mm Hg and held there for 10–15 min. The vacuum was then broken with nitrogen and the product was removed from the reactor under nitrogen and cooled. An amber-coloured, brittle solid resin was obtained. The scheme of preparation is given in *Figure 1*.

### *Characterization of the polyamides*

*Determination of acid value: ASTM No. D 2896-73.* 3–5 g of the polyamide was taken in 50 ml of a solvent mixture of toluene/butanol or xylene/butanol (1:1, v/v) in a beaker. The mixture was heated on a water bath for 15–20 min until the polyamide was completely dissolved. The solution was then cooled and the acid groups were titrated against standardized alcoholic potassium hydroxide with phenolphthalein as indicator.

*Determination of amine value: ASTM No. D2896-73.* The procedure was the same as that for the acid value except that the amino end groups were titrated with a standard solution of perchloric acid with bromophenol blue as indicator.

*Determination of viscosity.* The ASTM No. D 1200-70 was followed. A 35% w/w solution of the polyamide dissolved in butanol:toluene 1:1, v/v was used to determine the viscosity using Ford Cup No. 4 at 25°C.

*Determination of softening point.* The ASTM No. E 2858 T was followed.

## RESULTS AND DISCUSSION

It is observed from *Table 1* that with a 1:1 ratio of acid/amine, the viscosity of the product is high (147 s) accompanied by a high degree of polymerization (40.3) and molecular weight (11 848). When either excess acid or amine is used, there is a drastic decrease in all three parameters (20–25 s, 5–6 and <2000, respectively). The amine or acid value is high depending on which of them is taken in excess. These results are in accordance with the literature, where it is stated that the reaction of two difunctional monomers in stoichiometric amounts can produce a high molecular weight polymer (~25 000) and the depression of molecular weight is brought about by non-equivalence of reactants caused by imbalance in the stoichiometric proportions[1]. When equivalent weights of the dimer acid and the diamine are used the degree of polymerization is calculated using the formula[13]:

$$DP = \frac{1}{1-p} \qquad (1)$$

where $p$ is the extent of reaction which is calculated from the end-group analysis. When there is non-equivalency in the weights of the reactants, equation (2) is used to calculate $DP$. The number average molecular weight is obtained as a product of $DP$ and the weight of the repeating unit.

### *Effect of addition of a monomeric reactant*

It is observed from *Table 2* that when 9–10 wt% (based on the weight of dimer acids) of a monomeric reactant is added, there is again a depression in viscosity, degree of polymerization and molecular weight of the polyamide. The following equation is used to calculate $DP$ when a monomeric reactant is used, in addition to

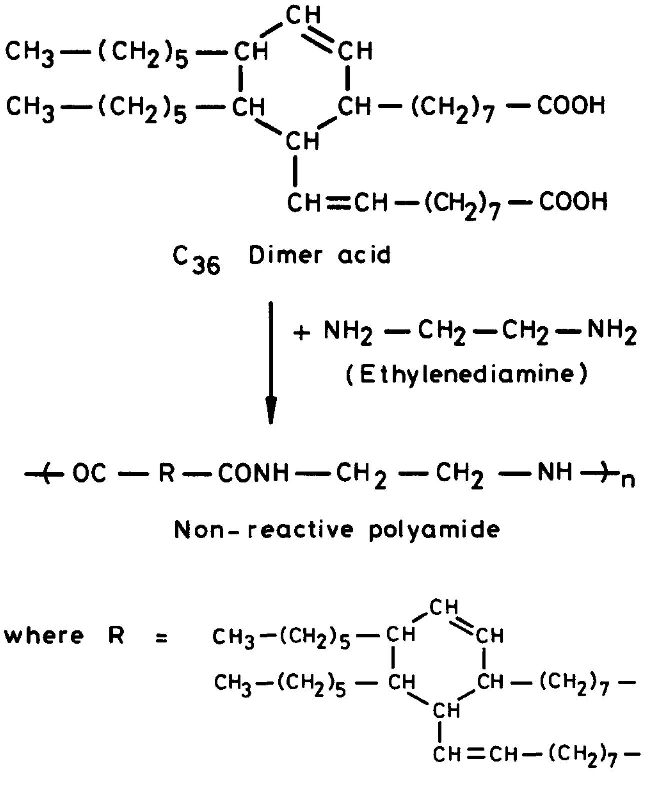

**Figure 1** Scheme for the preparation of non-reactive polyamide

the two difunctional units, or when there is an excess reactant (diamine or diacid)[1]:

$$DP = \frac{1 + r}{2r(1 - p) + 1 - r} \qquad (2)$$

where $r = N_A/(N_A + 2N_B)$ where $N_A$ is the number of acid equivalents and $N_B$ is half the excess reactant or the monomeric reactant, as the case may be, and $p$ is the extent of reaction taken from the end-group analysis. Hence it is possible to calculate the exact amount of monomeric reactant necessary to obtain a required $DP$ and molecular weight.

Different types of monomer acids were used to study their effect on the properties of the products. It was observed that when different types of monomeric fatty acids, saturated, unsaturated or a mixture of fatty acids such as the total fatty acids of castor or safflower oils or dehydrated castor oil fatty acids, were used as additives, the properties of the polyamides such as acid and amine values, number average molecular weight, viscosity and softening point did not vary much, as detailed in *Table 2*.

### *Effect of trifunctional acids*

The same types of polyamides as described above were prepared with two other types of dimer acids, Empol 1018 and Empol 1024, having 17% and 25% of trimer acids respectively (*Table 3*). The structure of the trimer acid is shown in *Figure 2*. When polyfunctional units are used, $DP$ is calculated as follows[13]:

$$DP = \frac{f\left(1 - \rho + \frac{1}{r}\right) + 2\rho}{f\left(1 - \rho + \frac{1}{r} - 2p\right) + 2\rho} \qquad (3)$$

where $f$ is the number of functional units in the branched acid, $\rho$ is the ratio of polyfunctional units to the total number of difunctional and polyfunctional units, $p$ is the extent of reaction and $r$ as described in equation (2). In this case the branched acids are trifunctional, therefore $f = 3$, and $\rho$ can be calculated according to the raw materials used (i.e. the amount of dimer/trimer acids taken for the reaction).

It was found that when no monomeric reactant was added, the product gelled. Therefore here again different calculated amounts of monomeric reactant were added and various products were obtained. The results are given in *Table 3*. In the case of Empol 1018 dimer acids with an increase in the amount of monomeric additive, commercial stearic acid, from 8.3 to 17.4%, the viscosity, the degree of polymerization and the number average molecular weights of the polyamides were found to decrease from 49 to 24 s, 11.9 to 5.9 and 3715 to 1841 respectively. However, in the case of Empol 1024 dimer acids, with an increase in the amount of monomeric acid from 8.2 to 25.6%, the values decreased from 45.5 to 21.5 s, 14 to 4.8 and 4476 to 1423 respectively.

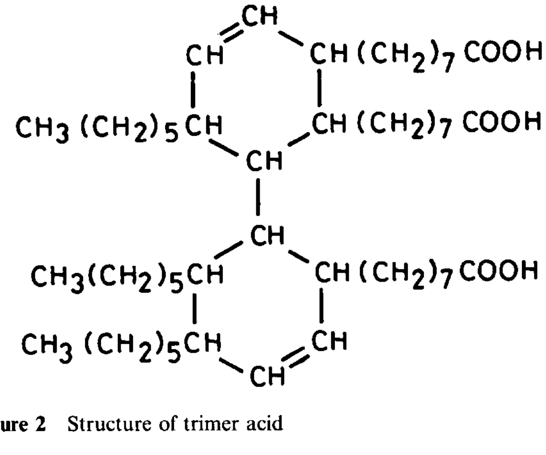

**Figure 2** Structure of trimer acid

### *Experiments with indigenous acids*

These acids comprised 14–35% monomer, 45–50% dimer and 20–36% trimer acids and the properties of the polyamides prepared from them (*Table 4*) differed slightly from the polyamides described earlier. The amine and acid values were below 10 mg KOH g$^{-1}$, viscosity ranged from 19–41 s and the softening point ranged from 94–115°C. The extent of reaction, degree of polymerization and molecular weight could not be calculated, as the exact amounts of monomer, dimer or trimer in the various mixtures were not available.

Commercial, non-reactive polyamides[15] which are used in flexographic inks, adhesives and over-print varnishes have acid and amine values below 7, viscosities of 35% w/w solution of the polyamide in 1:1 v/v, butanol/toluene at 25°C, 30–46 s (Ford cup No. 4) and softening points 110 ± 5°C. It can be seen from *Tables 2–4* that non-reactive polyamides with the above specifications can be obtained from either imported or indigenous dimer acids.

## CONCLUSIONS

Non-reactive polyamides have been prepared from four different types of dimer/trimer acid mixtures: 97/3, 83/17, 75/25 and indigenous acids. In these products the extent of reaction was ~96%, the degree of polymerization ranged from 5 to 40, the number average molecular weight ranged from 1423 to 11 848, viscosity from 19 to 147 s and softening point from 94.5 to 115°C. Most of these polyamides have properties comparable to commercial polyamides (acid and amine value <7 mg KOH g$^{-1}$, viscosity 32–46 s, of 35% solids, in butanol/toluene, 1:1 v/v at 25°C and softening point 110 ± 5°C) which find use in flexographic inks, adhesive and over-print varnish formulations.

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