Migration of some plasticizers through cured novolac epoxy resin-polyamide hardener systems

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Received 2 September 1997; accepted 19 February 1998

Four esters based on a homologous series of aliphatic acids and butanol have been synthesized and their structures have been confirmed with the help of IR, NMR and molecular weight. The diffusion coefficients (D) of these plasticizers to cured novolac epoxy resin sheets have been determined with the help of their migration at infinite time (M_u) and Fick’s Second Law. The data indicate that D as well as M_u decrease as the molecular weight increases from P-2 to P-5. Further, the calculated concentration profiles of these plasticizers at various depths of plane sheets of novolac epoxy resin have been calculated and compared with a commercial plasticizer, dioctyl adipate generally used in composite propellants.

Composite propellants are inhibited with novolac epoxy resins\(^1\) either by casting technique\(^2\) or filament winding technique\(^3\). Similar to nitroglycerine (NG) migration in double-base (DB) and composite modified double-base (CMDB) propellants, the phenomenon of migration of plasticizers from composite propellants to inhibitors has recently been reported\(^4,5\). The literature dealing with migration suggests that a low plasticizer migration towards inhibitor is beneficial to the adhesive bond between propellant and inhibitor\(^5,7\) but excessive migration leads to several problems such as separation of bond between propellant and inhibitor, deterioration in their mechanical properties and coning during combustion\(^8,9\).

The kinetics of migration of NG to unsaturated polyesters and chloropolyesters has recently been studied by Agrawal et al.\(^10-13\) Similarly, an attempt has also been made to study the kinetics of diethyl phthalate (DEP) migration to cured novolac epoxy resin\(^5\).

A literature survey shows that the kinetics of migration of esters (plasticizers) based on different chain length aliphatic acids and butanol to cured novolac epoxy resin has not yet been reported. The object of this study is to synthesize various plasticizers, based on aliphatic acids of different chain lengths such as succinic acid, adipic acid, suberic acid and sebacic acid (not commercially available), to establish their structures using IR and NMR and to derive the kinetics of migration of these plasticizers into a cured novolac epoxy resin. Similarly, a commercially available plasticizer, dioctyl adipate (DOA), one of the ingredients for composite propellants, has also been studied for comparison.

Materials and Methods

Materials used for the present work and their sources of supply are

<table>
<thead>
<tr>
<th>Materials</th>
<th>Source of Supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic acid, AR</td>
<td>M/s Loba Chemicals, Bombay, India</td>
</tr>
<tr>
<td>Adipic acid, AR</td>
<td>M/s Merk Ltd., Bombay, India</td>
</tr>
<tr>
<td>Suberic acid, AR</td>
<td>M/s Fluka Chemicals AG, Switzerland</td>
</tr>
<tr>
<td>Sebacic acid, AR</td>
<td>M/s Koch-Light Laboratories Ltd., England</td>
</tr>
<tr>
<td>Butanol, AR</td>
<td>M/s Thomas Baker Chemicals Pvt. Ltd., Bombay, India</td>
</tr>
<tr>
<td>p-toluene sulphonic acid (P-TSA)</td>
<td>M/s E Merk, Bombay, India</td>
</tr>
<tr>
<td>Novolac epoxy resin (Dobeckot E-4)</td>
<td>Dr. Beck &amp; Co., Pune, India</td>
</tr>
<tr>
<td>Polyamide hardener (EH-411)</td>
<td>Dr. Beck &amp; Co., Pune, India</td>
</tr>
<tr>
<td>Diocetyl adipate (DOA), L.R.</td>
<td>From trade.</td>
</tr>
</tbody>
</table>

\*For correspondence
Methods.

Synthesis of plasticizers—A typical synthesis of dibutyl adipate is as follows:

Adipic acid, 0.5 mol and butanol 1.0 mol were placed in a 4-necked round bottom flask equipped with a stirrer, thermometer, condenser and nitrogen gas bubbler. In order to ensure completeness of the reaction and get better yields, 30% excess butanol was taken. The contents were initially refluxed for 5 h in the presence of 0.01 mol of p-toluene sulphonic acid (p-TSA) and the liberated water was removed by a Dean Stark's tube till acid value comes down to 4 ± 0.5. The excess of butanol was removed by distillation. The resulting plasticizer was cooled and washed with distilled water till it was free from sulphate ions. The water was finally removed by distillation under reduced pressure at about 80°C. The resultant plasticizer was designated as P-4 (where P stands for plasticizer and 4 stands for the number of CH$_2$ groups in the acid).

The plasticizers based on other acids, viz., succinic acid, suberic acid and sebacic acid were also synthesized similarly and designated as P-2, P-6 and P-8 respectively. The details of molar ratios of reactants and acid values are given in Table 1.

Characterization of plasticizers—All the four plasticizers were fully characterized for their physical constants such as refractive index, specific gravity, molecular weight, purity, boiling/distillation range and elemental analysis.

The Infrared (IR) spectra of all plasticizers were recorded on a Perkin-Elmer IR Spectrophotometer, Model 683, by the smear method. $^1$H NMR Spectra were recorded in carbon tetrachloride using JNM-PMX 60 NMR spectrometer and tetramethylsilane (TMS) as the internal standard.

The elemental analysis were carried out on Carlo-Erba Elemental Analyser, Model EH 1108.

The purity of all the plasticizers was confirmed by High Performance Liquid Chromatography (HPLC) using Perkin-Elmer 410-LC Pump, LCI-100 integrator and LC-90 UV detector.

Preparation of specimens

The novolac epoxy resin is originally in the liquid state and specimens of dimensions 50 mm x 50 mm x 2 mm (thickness) were prepared by casting (after mixing with 40/50 parts of polyamide hardener, EH 411) and curing at 25 ± 2°C. All specimens were kept at 25 ± 2°C for a week in order to have the same extent of post-curing before proceeding further.

Plasticizer migration

All specimens were initially weighed and dipped in various plasticizers including DOA in different beakers covered with watch glass and kept at a temperature of 40 ± 2°C in a water jacketted oven. These specimens were removed at an interval of one day, dried with the help of filter paper and the gain in weight was recorded till constant weights were achieved. The plasticizer migration was then calculated by difference in the initial and final weights.

Assumptions

The following assumptions have been made in order to treat the phenomenon of migration of plasticizers mathematically through a thin sheet of cured novolac epoxy resin.

(i) Migration through the sheet of cured novolac epoxy resin is considered uni-directional.

(ii) Plasticizer migration takes place under transient conditions with a constant diffusion Coefficient ($D$).

(iii) The concentration of plasticizer on the faces...
of plane sheet reaches equilibrium as soon as it is immersed in plasticizer.

Mathematical Treatment

The equation for unidirectional diffusion as advanced by 'Fick' through his Second law is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

with initial and boundary conditions such as

$$t=0, \ 0<x<L, \ C=0$$

and

$$t>0, \ x=0, \ x=L, \ C=C_\infty$$

The analytical solution of Eq. (1) for concentration of plasticizer which develop through the sheet of novolac epoxy resin at time $t$ and distance $x$ is given by

$$C_\infty - C_{(t,x)} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin\left(\frac{(2n+1)\pi x}{L}\right) \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{L^2}\right]$$

where $C_{(t,x)}$ is the concentration of plasticizer migrated at time $t$ and distance $x$, $C_\infty$ is the concentration of plasticizer migrated at the time of equilibrium, $D$ is the diffusion coefficient and $L$ is the thickness of sheet.

The amount of plasticizer which migrate to the sheet at time $t$ is given by

$$M_t = M_\infty - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{L^2}\right]$$

where $M_t$ is the migration of plasticizer at time $t$ and $M_\infty$ is the migration of plasticizer at infinite time.

If we consider migration for short periods, Eq.(3) becomes

$$M_t = \frac{4}{\pi} \left[\frac{D \cdot t}{L}\right]^{1/2}$$

which, in fact, is used for the calculation of $D$.

Derivation of kinetics and concentration profiles

The plots of % plasticizer migration for plasticizers P-2, P-4, P-6, and P-8 for Composition-2 and Composition-3 against $(time)^{1/2}$ are straight lines for short time intervals and are shown in Figs. 1a and 1b. The diffusion coefficients ($D$) were calculated using the slopes of these straight lines, $M_\infty$ and Eq.(4). Further, plasticizer migration at different time intervals was calculated with the help of Eq. (3), $D$ and $M_\infty$ whereas the profiles of concentration of plasticizers were calculated with the help of Eq.(2).

Results and Discussion

Structural aspects

IR spectra of P-4 is shown in Fig.2. It is seen that IR frequency 1725 cm$^{-1}$ corresponding $-\text{C}=\text{O}$ linkage; frequency 2895 cm$^{-1}$ corresponding to $-\text{CH}$ stretching, frequency 720 cm$^{-1}$ corresponding to $-\text{CH}_2$ rocking and frequency 1440 cm$^{-1}$
Table 2—Various physical constants for aliphatic plasticizers

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Physical constants</th>
<th>P-2</th>
<th>P-4</th>
<th>P-6</th>
<th>P-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Refractive index</td>
<td>1.427</td>
<td>1.431</td>
<td>1.435</td>
<td>1.439</td>
</tr>
<tr>
<td></td>
<td>(at 22°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Specific gravity</td>
<td>0.99</td>
<td>0.97</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>(at 25°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Molecular weight</td>
<td>236.9</td>
<td>256.47</td>
<td>292.16</td>
<td>317.02</td>
</tr>
<tr>
<td></td>
<td>Thel. (230)</td>
<td>(230)</td>
<td>(258)</td>
<td>(286)</td>
<td>(314)</td>
</tr>
<tr>
<td>4.</td>
<td>Purity %</td>
<td>98.2</td>
<td>99.3</td>
<td>99.32</td>
<td>98.14</td>
</tr>
<tr>
<td>6.</td>
<td>Elemental analysis</td>
<td>Exp. 64.20</td>
<td>66.11</td>
<td>65.64</td>
<td>70.15</td>
</tr>
<tr>
<td></td>
<td>C%</td>
<td>Cal. (62.61)</td>
<td>(65.12)</td>
<td>(67.1)</td>
<td>(68.80)</td>
</tr>
<tr>
<td></td>
<td>H%</td>
<td>Exp. 9.05</td>
<td>10.26</td>
<td>10.21</td>
<td>11.22</td>
</tr>
<tr>
<td></td>
<td>Cal. (9.56)</td>
<td>(10.08)</td>
<td>(10.49)</td>
<td>(10.83)</td>
<td></td>
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</table>

Table 3—Mechanical properties of novolac epoxy resin cured with polyamide hardener, EH411

<table>
<thead>
<tr>
<th>Composition</th>
<th>Novolac epoxy - E4</th>
<th>Polyamide hardener - EH411</th>
<th>Tensile strength (TS)</th>
<th>Elongation (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>parts</td>
<td>parts</td>
<td>kg/cm²</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>30</td>
<td>201</td>
<td>10.46</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>40</td>
<td>329</td>
<td>8.77</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>50</td>
<td>338</td>
<td>5.22</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>60</td>
<td>264</td>
<td>9.33</td>
</tr>
</tbody>
</table>

Fig. 3—1H NMR spectra of dibutyl adipate (P-4)

Chemical shifts at 0.95, 1.52δ, 2.25δ and 3.97δ indicate the presence of –CH₃, –CH₂–CH₂, –C–CH₂ and –O–CH₃ groups respectively. The chemical shifts in case of other plasticizers, i.e., P-2, P-6 and P-8 are also in the same range and support the presence of above protons in these plasticizers also.

Based on this data, it is inferred that the four plasticizers are extremely pure and the general structure of these plasticizers may be shown as below:

\[
\text{O} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2)_x\text{O}-\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

where \(x = 2, 4, 6 \text{ and } 8\) for succinate, adipate, subarate and sebacate respectively.

**Mechanical properties**

The mechanical properties, i.e., tensile strength (TS) and elongation (E) constitute very important criteria in order to judge the suitability of polymeric materials for inhibition of rocket propellants. A number of novolac epoxy formulations using different percentages of polyamide hardener were made and are depicted in Table 3.
It is seen that the TS increases as % of hardener increases. This is attributed to increase in the extent of crosslinking leading to increase in the TS. It has been extensively reported in the literature\(^ {18,19} \) that TS and E are interrelated in most of the thermosets and if TS increases, E decreases and vice versa. Thus, E decreases from Composition-1 to Composition-3 and TS increases in this order. However, in case of Composition-4, i.e., at 60% hardener level, the mechanism is different and TS decreases as compared to Composition-3 and correspondingly, E increases. This is due to the fact that the polyamide hardeners not only act as curing agents but also act as flexibilizers\(^ {19} \) and that is why, with the increase in its quantity, elongation increases and TS decreases. This is in agreement with the data reported by Agrawal et al\(^ {20} \). An extensive study for evaluation of novolac epoxy resin for inhibition of composite propellants has established that the compositions corresponding to 40/50 parts of polyamide hardener are suitable for the inhibition of composite propellants\(^ 1 \) and\(^ 2 \). Also, the mixing ratios/proportions of polyamide hardeners are not considered as critical as in case of other curing agents/hardeners. Therefore, 40 to 50 part of polyamide hardener is considered optimum\(^ 21 \) and accordingly, Composition-2 and Composition-3 were selected for the study of migration of plasticizers.

**Diffusion coefficient and migration of plasticizers**

The diffusion coefficient \( (D) \) and migration of plasticizers at infinite time \( (M_\infty) \) data for Composition-2 and Composition-3 at 40°C are given in Table 4. It is seen from the data that the order for \( D \) for Composite-2 is P-2 > P-4 > P-6 > P-8.

This is attributed to the molecular weights of these plasticizers. The molecular weight data (Table 1) show that molecular weight of P-2, based on shortest chain length acid is 230 whereas molecular weight of P-8, based on longest chain length acid is 314 and molecular weight increases from P-2 to P-8. Thus, the rate of migration of plasticizer P-4 is expected to be lower than P-2 resulting in lower value of \( D \) in case of P-4 as compared to P-2. Similarly, rate of migration of P-6 is expected to be lower than P-4 and that of P-8 is expected to be lower than P-6 by following the same analogy. Thus, as the molecular weight increases from P-2 to P-8, the rate of diffusion, i.e., \( D \) is expected to decrease in this order which is observed experimentally. The diffusion coefficient data for Composition-3 show that the order for \( D \) is similar to that of Composition-2. However, while going from Composition-2 to Composition-3 value of \( D \) decreases and is due to the increase in TS (indicative of crosslink density) in case of Composition-3 (Table 3). The compactness of molecular structure increases in Composition-3 as compared to Composition-2 due to higher TS.

### Table 4—Diffusion coefficient and M data for Composition-2 and Composition-3

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Composition-2</th>
<th>Composition-3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_\infty )</td>
<td>( D \times 10^{-9} )</td>
</tr>
<tr>
<td>P-2</td>
<td>29.3 %</td>
<td>2.749 cm(^2)/s</td>
</tr>
<tr>
<td>P-4</td>
<td>24.1 %</td>
<td>2.182 cm(^2)/s</td>
</tr>
<tr>
<td>P-6</td>
<td>22.1 %</td>
<td>1.700 cm(^2)/s</td>
</tr>
<tr>
<td>P-8</td>
<td>19.5 %</td>
<td>1.525 cm(^2)/s</td>
</tr>
<tr>
<td>DOA</td>
<td>3.5 %</td>
<td>1.169 cm(^2)/s</td>
</tr>
</tbody>
</table>

Fig. 4—Variation of plasticizer migration with time for Composition-2

Fig. 5—Variation of plasticizer migration with time for Composition-3
Consequently, it retards the migration of plasticizer and accordingly, results in lowering of $D$.

The graphical presentation of calculated and experimental plasticizer migrations versus time are shown in Figs 4 and 5. It is clear that most of the calculated values at different time intervals match very closely with the experimental values and thus it proves the validity of the assumptions as well as correctness of $D$ and $M_{oo}$. Similar patterns of close match between the calculated and experimental migrations at different time intervals are observed in case of plasticizers P-2, P-6 and P-8.

Profiles of concentration of plasticizers

The profiles of concentration of plasticizers P-2 to P-8 and DOA which develop in the sheets of Composition-2 and Composition-3 at different time intervals and distances are shown in Figs 6, 7 and 8 respectively.

The concentration profiles show that the concentration at the centre increases with the increase in time. Also, the concentration increases steadily as the distance from the centre to the face increases. A comparison of concentration of plasticizers which develop at the centre of sheet, i.e., L/2 for Composition-2 brings out that the concentration decreases from P-2 to P-8 and is 93.20, 87.56, 79.21 and 74.9% respectively at the end of 50 days. A similar trend is also observed for Composition-3 and concentration of P-2, P-4, P-6 and P-8 at the centre of sheet is 83.29, 83.02, 75.94 and 73.77% respectively after 50 days.

The concentration profiles of DOA, in the sheets of Composition-2 and Composition-3 are shown in Fig. 8. The DOA concentration at the centres of sheets of Composition-2 and Composition-3 is 63.38 and 51.33% respectively after 50 days.

A comparison of $M_{oo}$, diffusion coefficients and concentrations developed at the centres of the
sheets of Composition-2 and Composition-3 for P-2, P-4, P-6, P-8 and DOA suggest that Composition-3 is better than Composition-2 for inhibition of HTPB based composite propellants.

From the structures of DOA and the present series of plasticizers, it is noted that they are all straight chain aliphatic diesters derived from different acids and alcohol. However, DOA, being a higher molecular weight than these plasticizers shows low diffusion coefficient and \( M_\infty \) values.

**Acknowledgement**

The authors acknowledge with thanks the technical assistance rendered by Dr. T. Mukundan, Scientist during the investigation. We are also thankful to the Director, HEMRL for encouragement.

**References**