

# Formulation and Optimization of Thermoplastic Polyamide Elastomer Properties by Mixture Response Surface Methodology

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**ABSTRACT:** In this study, the formulation and optimization of the properties of thermoplastic polyamide elastomers (TPAEs) were evaluated by a mixture response surface methodology. The TPAEs prepared from different chain extender blends of adipic acid, terephthalic acid (TPA), and C36 dimer acid were characterized by specific gravity measurement, water absorption measurement, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The results indicate that the specific gravity of the polymers increased and the water absorption of the polymers decreased as the content of TPA increased. The DSC data show two major endotherms corresponding to the melt of poly(tetramethylene ether) glycol (PTMEG) and nylon-6 segments. The TGA data show that the thermal degradation temperatures of the polymers increased as the C36 dimer acid content increased. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 9–16, 2002

**Key words:** copolymerization; elastomer; polyamides; polyethers; thermoplastics

## INTRODUCTION

Thermoplastic polyamide elastomers (TPAEs) are block copolymers containing soft and hard segments. TPAEs can be processed and recycled in the same way as a conventional thermoplastic material, yet possess properties and performance similar to that of vulcanized rubber at the service temperature. The influence of the chemical composition on the physical and chemical properties of TPAEs were investigated for some time.<sup>1–4</sup> In general, polyethers such as polyoxypropylene (POP) or poly(tetramethylene ether) glycol (PTMEG) are often chosen as the soft segment, and the hard segments are nylon-6, nylon-10, nylon-12, nylon-66, nylon-6,10, nylon-4,6, and some aromatic polyamides.<sup>5–13</sup> Both types of segments

are usually chemically bonded by ester linkages from a condensation of prepolymers and diacids, which serve as chain extenders. Among the TPAEs, the nylon-6-based TPAEs have high potential for industrial usage because of the low cost of caprolactam (CPL). Chung et al.<sup>14</sup> prepared a nylon-6-based block copolyetheramide by a two-step block melt condensation polymerization. The high-temperature approach is used to avoid immiscibility of starting materials during the polymerization. In the method developed by our laboratory,<sup>15–16</sup> C36 dimer acid was employed as a chain extender and interfacial agent. Because the presence of C36 dimer acid rendered the reaction mixture homogeneous, the discharged polymer melt was found to be completely transparent. After cooling, a transparent solid product was obtained. Therefore, we believe that the physical and chemical properties of block TPAEs are a result of a combination of soft segments and hard segments, as well as chain extenders.

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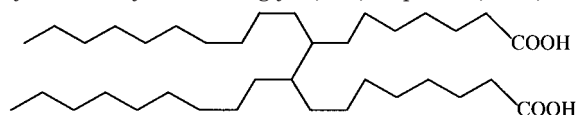
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**Table I** The Charged Molar Composition and Relative Viscosity of Seven Thermoplastic Polyamide Elastomers (TPAEs)

Formula Number <sup>a</sup>	Composition of TPAEs <sup>b</sup>					Relative Viscosity
	CPL	PTMEG	Diacid			
			AA	TPA	DA	
1	3	0.3	0.3(100) <sup>c</sup>	0(0)	0(0)	2.246
2	3	0.3	0(0)	0.3(100)	0(0)	2.285
3	3	0.3	0(0)	0(0)	0.3(100)	2.189
4	3	0.3	0.15(50)	0(0)	0.15(50)	2.270
5	3	0.3	0(0)	0.15(50)	0.15(50)	2.281
6	3	0.3	0.15(50)	0.15(50)	0(0)	2.209
7	3	0.3	0.1(33.3)	0.1(33.3)	0.1(33.3)	2.275

<sup>a</sup> Mixture design results in seven formulations.

<sup>b</sup> CPL, caprolactam; PTMEG, poly(tetramethylene ether) glycol; AA, adipic acid; TPA, terephthalic acid; DA, C36 dimer acid.



<sup>c</sup> Parentheses indicate molar percentage of composite blends of diacid.

Mixture response surface methodology (RSM) was developed by Claringbold<sup>17</sup> and Scheffé.<sup>18–19</sup> Cornell<sup>20</sup> provided an excellent summary on this topic in a review with an update and bibliography.<sup>21</sup> Mixture RSM was successfully applied to optimize formulations in some research by several investigators. Examples include development of sucrose polyester,<sup>22</sup> formulation of polyurethane,<sup>15</sup> and recycling of mixed plastic fractions.<sup>23</sup> However, it was not used for optimizing the physical properties of TPAE.

The objective of this study was to optimize the properties of TPAE synthesized from composite diacid blends of adipic acid, terephthalic acid, and C36 dimer acid as chain extenders by using mixture RSM. The molar ratio of the main reaction was 1 : 1 : 10 (polyether polyol, chain extender, and CPL) and followed the synthetic method developed by Chung.<sup>14</sup> Specific objectives of this investigation were as follows: (1) to determine the characteristics of TPAE prepared from composite blends of chain extenders by mixture RSM; (2) to determine the diacid levels at which TPAE has best thermal stability and least water absorption; and (3) to validate prediction models for selected attributes. A triangular contour plot and superposition technique were employed to reach the objectives.

## EXPERIMENTAL

### Experimental Design

The molar ratio of for the main reaction was 10 : 1 : 1 (CPL : polyether polyol : chain extender). A three-variable simplex centroid design<sup>24</sup> was employed in which the number of points was  $2^q - 1$ , where  $q$  is equal to the number of variables<sup>19</sup> (i.e., three in this study). This design resulted in seven diacid mixtures (Table I). The molar ratio (percentage) of composite blends of diacid was present as levels ranging from 0 to 100%. Two replications of the study were conducted.

### Materials

Synthesis of TPAEs were carried out by using commercially available chemicals. PTMEG with a molecular weight of 2000 g/mol was supplied by DuPont (Wilmington, DE). Fiber-grade CPL was obtained from China Petrochemical Development Corp. (Hsinchu, Taiwan). C36 dimer acid (DA) was received from Unichema Taiwan Ltd. (Chung-Li, Taiwan), while adipic acid (AA), terephthalic acid (TPA), and phosphoric acid were reagent grade from Merck (Taipei, Taiwan). All materials used for polymerization were used without further purification.

## Polymerization

The polymerization was carried out in a 2-L stainless steel reactor equipped with an anchor stirrer and electric heater. A typical example of the synthesis procedure of the TPAE is as follows: 338.76 g (3 mol) CPL, 600 g (0.3 mol) PTMEG, and 0.5 g phosphoric acid were reacted at 220°C. After 3 h of reaction, 43.86 g (0.3 mol) AA was added into the reactor; then, the reaction temperature was raised to 250°C and vacuum (1 mm Hg) was applied for 3 h. The product was discharged under melt conditions. In a series of these polymerizations, the reactants and procedure were identical to those described above, except chain extender blends of diacids (Table I) were used.

## Analysis and Measurements

### Viscometry

The relative viscosity of 1 g/dL solutions of the resulting copolymer in *o*-chlorophenol were measured in an Ubbelohde viscometer at 30°C.

### Specific Gravity

The specific gravity of TPAEs was measured in a pycnometer at 25°C according to ASTM D 792 Method B.

### Water Absorption

The TPAEs test specimens, measuring 0.3 mm in thickness and 8 mm in diameter, were prepared from molded disk. The specimens were dried in an oven at 80°C for 24 h and then placed in a container with boiling water for 2 h. The percentage increase in weight during immersion was calculated as follows:

Percentage water absorption

$$= \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100$$

### Melting Point

Differential scanning calorimetry (DSC) measurements were carried out with a TA Instruments DSC 2010 thermal analyzer. The sample compartment was purged with nitrogen. The usual procedure for TPAEs was as follows:

1. Equilibration for 20 min at  $-60^{\circ}\text{C}$ ;
2. First heating run at  $20^{\circ}\text{C}/\text{min}$  from  $-60^{\circ}\text{C}$  up to  $20^{\circ}\text{C}$  about  $T_m$ ;

3. Equilibration for 30 min at the latter temperature;
4. Cooling run at  $20^{\circ}\text{C}/\text{min}$  down to  $-60^{\circ}\text{C}$ ;
5. Second heating run at  $20^{\circ}\text{C}/\text{min}$ .

The melting point,  $T_m$ , was given as the maxima of the thermal transitions.

### Thermal Degradations

A thermal gravimetric analyzer (TGA 2950, TA Instruments) was used as a heat source to conduct the thermal degradations under nitrogen. Samples were conditioned at  $80^{\circ}\text{C}$  for 24 h. The heating was at a rate of  $20^{\circ}\text{C}/\text{min}$  from room temperature to  $800^{\circ}\text{C}$ . The decomposition temperature at 5% weight loss was given from the TGA thermograms.

### Statistical Analysis

The data were analyzed with the statistical analysis system.<sup>25</sup> Multiple regression analysis was used to fit a quadratic canonical polynomial mode, described by Scheffé<sup>18</sup> as follows:  $Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_1 \beta_2 X_1 X_2 + \beta_1 \beta_3 X_1 X_3 + \beta_2 \beta_3 X_2 X_3$ , where  $Y$  is a dependent variable (each property of TPAE),  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ,  $\beta_1 \beta_2$ ,  $\beta_1 \beta_3$ , and  $\beta_2 \beta_3$  are the corresponding parameter estimates for each linear and cross-product term produced for the prediction model,  $X_1$  is the chain extender prepared from adipic acid,  $X_2$  is the chain extender prepared from terephthalic acid, and  $X_3$  is the chain extender prepared from C36 dimer acid. The intercept and quadratic terms were removed from the models in accordance with procedures described by Cornell.<sup>24</sup> The intercept is not included in the analysis because the mixture components should be equal to 100% of the mixture. The stepwise option was employed to eliminate insignificant variables in a model.

### Optimization

The predicted models were used to generate triangular contour plots. In this study, ranges of acceptability used in formulation optimization were determined for the specific gravity, water absorption, melting point, and decomposition temperature at 5% weight loss by means of the following criteria: (1) specific gravity  $< 1.03$ ; (2) water absorption  $< 13.8\%$ ; (3) melting temperature  $> 204.7^{\circ}\text{C}$ ; and (4) decomposition temperature at 5% weight loss  $> 348.8^{\circ}\text{C}$ . The optimum area obtained by superposition are acceptable areas represented the combi-

**Table II** Observed Experimental Values and Predicted Values for Some Properties of TPAEs from Composite Blends of Chain Extender of Adipic Acid, Terephthalic Acid, and Dimer Acid

Formula Number	Specific Gravity	Water Absorption (wt %)	Melting Point (°C)	Decomposition Temperature (°C) at 5% Weight Loss
TPAE1	1.0451	23.57	196.4	346.4
	<u>1.0454</u> <sup>a</sup>	<u>23.60</u>	<u>196.3</u>	<u>346.7</u>
TPAE2	1.0502	1.97	198.9	349.8
	<u>1.0505</u>	<u>2.00</u>	<u>198.8</u>	<u>350.1</u>
TPAE3	1.0236	12.41	209.5	349.7
	<u>1.0239</u>	<u>12.44</u>	<u>209.4</u>	<u>350.0</u>
TPAE4	1.0322	15.48	197.6	349.9
	<u>1.0308</u>	<u>15.35</u>	<u>198.1</u>	<u>348.9</u>
TPAE5	1.0373	13.91	201.6	347.9
	<u>1.0359</u>	<u>13.78</u>	<u>202.1</u>	<u>346.9</u>
TPAE6	1.0500	34.48	201.7	349.8
	<u>1.0486</u>	<u>34.35</u>	<u>202.2</u>	<u>348.8</u>
TPAE7	1.0347	23.68	201.5	345.4
	<u>1.0378</u>	<u>23.98</u>	<u>200.5</u>	<u>347.9</u>
Chi-square test	1.000	1.000	1.00	1.000

<sup>a</sup> Underline indicates predicted value from the model listing in Table III.

nation of mixtures that would meet preset criteria for an acceptable formulation.

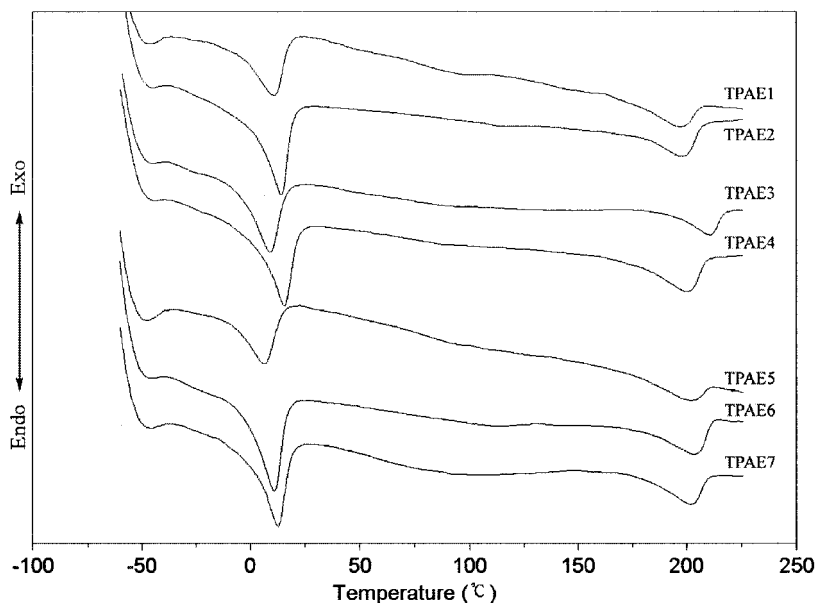
### Model Verification

The predicted values for each dependent variable were calculated from the corresponding reduced models. The chi-square test described by Ott<sup>26</sup>

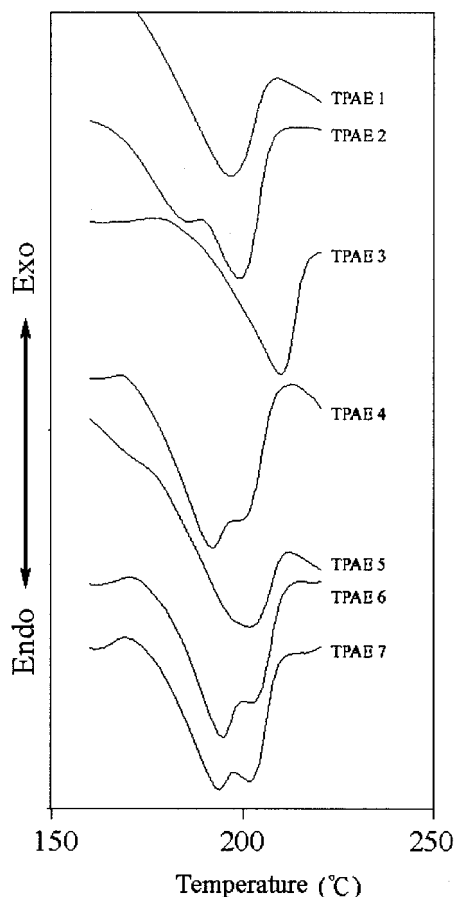
was performed to determine whether the observed values were significantly the same as the predicted values from the predicted model.

### RESULTS AND DISCUSSION

To compare the properties of TPAEs with similar molecular weight, it is important to adjust exactly



**Figure 1** DSC thermograms of TPAEs from the first heating scans.



**Figure 2** DSC thermograms of TPAEs from the second heating scans at melting temperature region.

the stoichiometric balance of the diacid and diol to obtain high molecular weight polymers. The solution viscosity is frequently used for estimating the molecular weights of polymer. In Table I, the relative viscosities of seven TPAEs were all in the range of 2.189–2.285. Hence, it appears that the polymerization of TPAEs was successfully con-

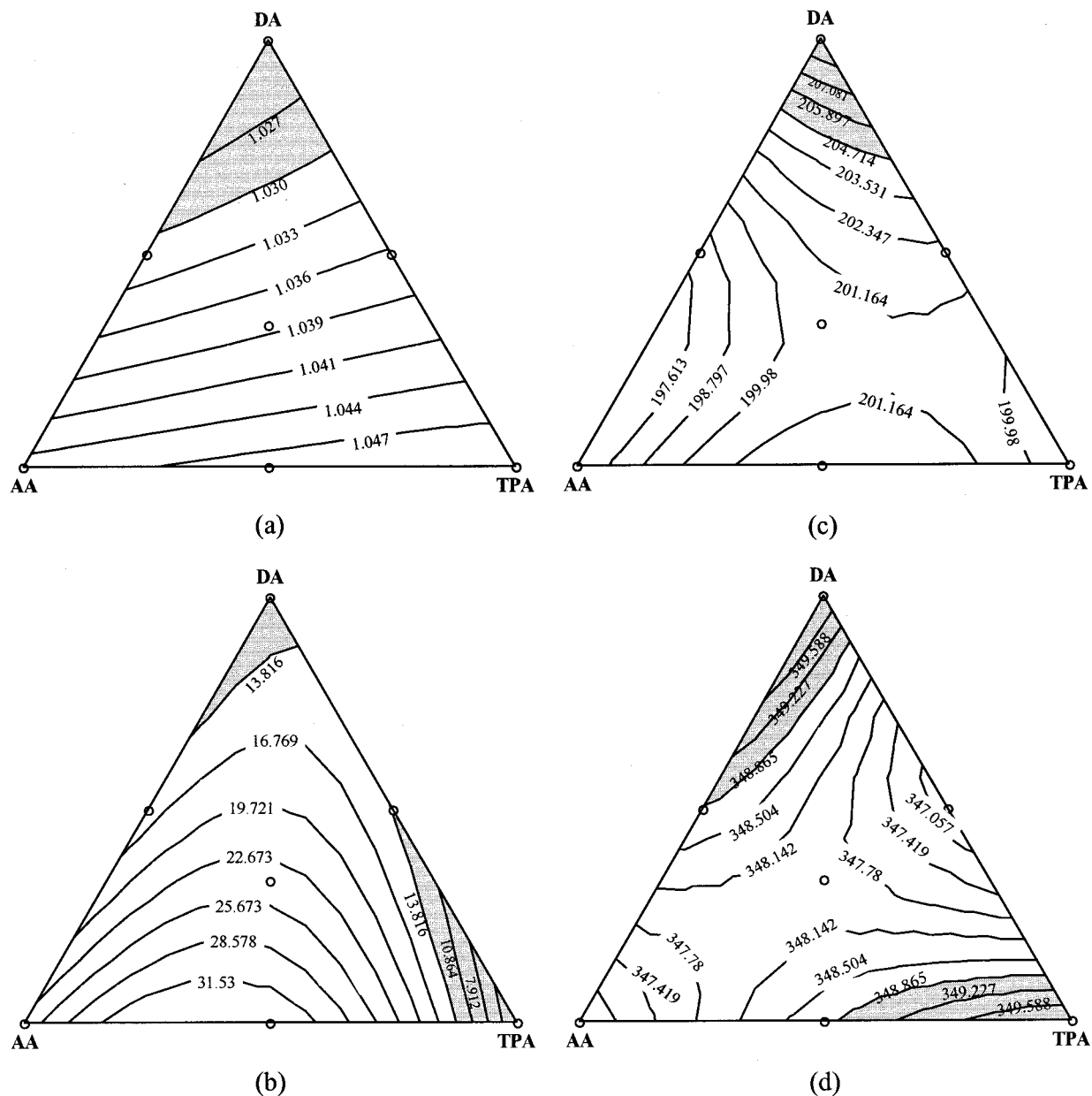
trolled to obtain similar molecular weight of each sample.

The properties of the prepared TPAEs are illustrated in Table II. The TPAEs have specific gravities that are similar to commercial product polyether block amide (PEBAX) and are among the lowest of the thermoplastic elastomers. The range of water absorption is wide, from 1.97 to 34.48%, varying with the different diacid compositions. DSC thermograms of these seven block TPAEs from the first heating scans (Fig. 1) show two major endotherms corresponding to the low melting point of the PTMEG segment and a much higher one from the nylon-6 segment. The second heating scan of some TPAEs (Fig. 2) show a split higher in melting temperature. These phenomena may be from the crystalline chain extender. The nylon-6 melting temperatures of TPAEs are affected by the composition of chain extender. Formula 3 (prepared from 100% C36 dimer acid chain extender) shows an extremely high melting point in comparison with other samples. The highest melting points of each formulation are further studied by mixture response surface methodology. The range of decomposition temperatures at 5% weight loss is narrow, from 345.43 to 349.81°C. The decomposition temperatures vary insignificantly. Some reports<sup>27,28</sup> indicate that the thermal decomposition of polyether-based TPAEs start at the C—O bond and subsequent unzip the polyether chains. This may be why the obtained TPAEs showed nearly unchanged decomposition temperature despite different recipes. The thermal decomposition of TPAEs should start at the PTMEG segments.

Results of the regression analyses are presented in Table III, which lists parameter estimates for the prediction models for the properties of TPAEs. The stepwise regression was specified

**Table III** Parameter Estimate for Variables Used in Prediction Models for the Properties of TPAEs from Composite Blends of Chain Extender of Adipic Acid, Terephthalic Acid, and Dimer Acid

Chain Extender	Specific Gravity	Water Absorption (wt %)	Melting Point (°C)	Decomposition Temperature (°C) at 5% Weight Loss
AA ( $\beta_1$ )	1.045	23.605	196.318	346.696
TPA ( $\beta_2$ )	1.051	2.007	198.848	350.035
DA ( $\beta_3$ )	1.024	12.442	209.448	350.086
AA $\times$ DA ( $\beta_1\beta_3$ )	-0.016	26.200	-19.053	1.648
TPA $\times$ DA ( $\beta_2\beta_3$ )	-0.005	-10.689	-8.393	1.828
AA $\times$ TPA ( $\beta_1\beta_2$ )	0.002	86.177	18.547	-12.732



**Figure 3** Triangular contour plots for theoretical properties for blends containing composite chain extender from AA, TPA, AND DA. (a) Specific gravity; (b) water absorption; (c) melting point; (d) decomposition temperature at 5% weight loss. The shaded regions represent the accepted area. See Table I for abbreviations.

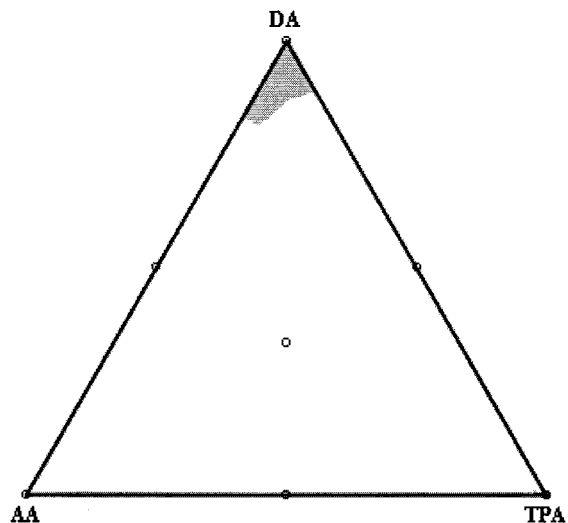
to eliminate the insignificant variables (all variables in the model were significant at the 0.15 level). Triangular contour plots, produced from the parameter estimates from each of the attributes, were generated. The triangular contour plots of the properties of TPAEs are shown in

Figure 3. The contour behavior of the specific gravity [Fig. 3(a)] shows that the specific gravity of the TPAEs increased as the content of TPA increased and specific gravity of the TPAEs decreased as the content of dimer acid increased. This suggests that the straight rigid terephtha-

late structure in the polymer chain increases the polymer packing as well as specific gravity. Oppositely, the C36 dimer acid molecule has two side chains that significantly affected the polymer packing and reduced the polymer specific density. The contour behavior of water absorption [Fig. 3(b)] reveals the hydrophobic behavior of TPA and dimer acid in the TPAEs. It is apparent that the water absorption was decreased significantly as the content of TPA and C36 dimer acid increased.

The contour behavior of the melting temperature [Fig. 3(c)] shows that a higher melting point is obtained as the content of C36 dimer acid increased. One possible mechanism to explain such higher melting points may start with the flexibility of C36 dimer acid, which induced the nylon-6 crystallization, and the effect of crystallinity on melting points. As shown in Figure 3(c), the higher melting temperature of the TPAEs increased as the content of C36 dimer acid increased, whereas TPA provided less benefit when it was used in these TPAEs. The contour behavior of the decomposition temperature at 5% weight loss [Fig. 3(d)] shows no significant increased decomposition temperature ( $<2^{\circ}\text{C}$ ) when C36 dimer acid and TPA are used as heat stability modifying agents for TPAEs. This suggests that the thermal decomposition begins at the PTMEG segments and more specifically at the ether linkage of PTMEG.<sup>28</sup> This reveals that the chain extenders have less effect on the heat resistance of polymers.

The properties (specific gravity, water absorption, melting point, and decomposition temperature at 5% weight loss) of TPAEs were optimized to obtain the optimum ratio of starting diacid for TPAE synthesis. The bases for chosen acceptable properties were low specific gravity, low water absorption, high melting point, and high decomposition temperature. The criteria described in the experimental method were employed to demonstrate the technique of mixture RSM. Researchers who are interested in the varied application of TPAEs should choose their own criteria. Optimum areas for these four properties are outlined on the surface contour plots as shaded regions in Figure 3. Acceptable regions for formulations producing values within the optimum criteria ranges are shown in Figure 4, obtained by superposition technique [Fig. 3(a–d)]. The shaded area in Figure 4 represents the region in which low specific gravity, low water absorption, high melting point, and good thermal stability of TPAEs could be synthesized with the desired properties.



**Figure 4** Optimum regions obtained by superimposing contour plots of major physical properties (specific gravity, water absorption, melting point, and decomposition temperature) for blends containing composite chain extender prepared from AA, TPA, and DA. See Table I for abbreviations.

Observed and predicted values from the prediction models for the properties are presented in Table II. The chi-square tests indicate that the observed values are significantly the same ( $P$  0.95, degrees of freedom = 6) as the predicted values for all models. This indicates that parameter estimates presented in Table III can be used to predict the actual properties of TPAEs.

Mixture RSM can be used to determine the effects of variation in levels of TPAE prepared from adipic acid, terephthalic acid, and C36 dimer acid regarding the properties of the seven TPAE formulations investigated. Optimization based on four attributes (specific gravity, water absorption, melting temperature, and decomposition temperature at 5% weight loss) indicated that a mixture of diacid (mainly dimer acid) reacted with CPL and PTMEG can be used to synthesize a TPAE with the specified optimized properties. These findings and this experimental methodology could be useful in the synthesis of TPAEs from composite of polyols, CPL, and diacids as well as in the characterization of TPAEs for various applications.

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