Curing and Pyrolysis of Cresol Novolac Epoxy Resins Containing [2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol]

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This study investigates the curing kinetics, thermal properties and decomposition kinetics of cresol novolac epoxy (CNE) with two curing agents, 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-benzenediol (ODOPN), and phenol novolac (PN). In comparison with the conventional PN system, introducing ODOPN, a phosphorus-containing bulky pendant group, into CNE increases $T_g$ by 33°C, char yield from 30% to 38%, and LOI from 22 to 31. The DSC curing study reveals that the $E_a$ of the CNE/ODOPN epoxy can be obtained by Kissinger’s method. The resulting $E_a$ values indicate that the catalytic effect of EMI is insignificant on CNE/ODOPN but is marked on CNE/PN, whose $E_a$ was reduced from 131.5 to 75.6 KJ/mole. This result may be caused by the fact that the symmetric diol attached to the 1 and 4 positions of the naphthalene ring in ODOPN sets up a steadily resonating structure and inhibits the catalytic action. Further investigating the conversion ratio with curing temperature yielded experimental data that agreed closely with Kaiser’s model. The orders of the autocatalyzed reaction, m, and the crosslinking reaction, n, are close to 0.5 and 1.0, respectively, independently of the scan rate. Finally, the TGA decomposition study by Ozawa’s method demonstrates that the mean $E_a$ declines with the phosphorus content, because the easy decomposition of the phosphorus compound in the initiation stage facilitates the formation of an insulating layer. However, results in this study further reveal an increasing tendency for $E_a$ with decomposition conversion for an ODOPN/PN mixture with the ODOPN content of over 50%, probably because of the retardation of gas diffusion by the insulating layer of phosphorus compound.

INTRODUCTION

Epoxy, one of the most important polymeric materials in the electric, electronic, or aerospace industries, has excellent physical properties such as moisture resistance, good thermal stability, excellent mechanical strength, and high electric resistance. Therefore, epoxy is the most commonly used high-performance polymer in the world. However, the flammability of epoxy resin is a major limitation in applications that depend on high flame resistance. Epoxy compounds, including some halogen atoms to retard flames have thus been frequently used over the last three decades. Unfortunately, halogen-containing materials

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release corrosive and toxic hydrogenated or aromatic halogens on combustion (1, 2). This concern has motivated the search for environmentally friendly, non-halogenic flame retardants—so-called “green products.” Organophosphorus compounds, which exhibit high flame resistance but generate little toxicity during combustion, have recently attracted much attention and are becoming increasingly popular (3–30).

Modifying the epoxy by incorporating an O=P–O group into the epoxy backbone has been extensively studied (3–12). Banks et al. (13) examined how covalently bound phosphorus influenced the flame retardancy of polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN) and polyacrylamide (PAM). Kannan et al. (14) developed flame retardant phosphorus-containing polyester amide. Even when the required flame retardancy was achieved, the polymers were found to degrade rapidly on heating, due to the cleavage of the O=P–O group in the main chain. Several scholars have thus searched for epoxy systems with pendant phosphorus groups to increase the temperature of degradation while maintaining flame retardancy (15–30).

Since a cyclic organic phosphorus compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), was synthesized in the 1970s, a series of compounds derived from aryl phosphinate have been developed and used as flame retardant curing agents or additives. Among them, a unique compound, ODOPB [2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-benzenediyl], derived from DOPO, was synthesized and characterized by Wang et al. (16). ODOPB has excellent flame retardancy and curing activity. Wang demonstrated that ODOPB was a good flame retardant curing agent that could be applied to an epoxy system, such as the diglycidyl ether of bisphenol A (DGEBA), o-cresol novolac epoxy (CNE), as well as to some polyester systems. The rigid structure of ODOPB and the pendant P group is such that the resulting phosphorus-containing epoxy resin has better flame retardancy, a higher glass transition temperature, and greater thermal stability than the regular halogen-containing epoxy resin. Notably, Wang reported that only 2% of the phosphorus content in the CNE sufficed to increase markedly the flame retardancy.

In this work, following Wang’s study, a new compound similar to ODOPB, namely ODOPN [2-(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphorin-6-yl)-1,4-naphthalenediyl], was synthesized and characterized. The o-cresol formaldehyde novolac epoxy (CNE), a resin frequently employed to encapsulate microelectronic devices, was used as the main epoxy ingredient. A series of CNE epoxies, with various phosphorus contents, were derived from ODOPN. The effect of ODOPN’s functionality on the flame retardancy and the glass transition temperature was examined. The characteristics of all the cured resins were evaluated by differential scanning colorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), and determining the limiting oxygen index (LOI). All the data were then compared to those for the neat CNE system; that was, CNE cured with phenol novolac (PN).

**EXPERIMENTAL**

**Synthesis of ODOPN**

DOPO (from TCI), 1,4-naphthaquinone (from TCI), 3-nitrobenzoyl chloride, 4-nitrobenzoyl chloride (from Fluka), and 10% Pd/C (from Lancaster) were used without further purification. Following a modified method of Endo et al. (31), Wang and Lin (19), the ODOPN was synthesized by adding DOPO with 1,4-naphthaquinone ([Scheme 1](#)). Liou has reported details of the synthesis and characterization of ODOPN (32).

**Curing Reagent**

The epoxy used was CNE with EEW 195 g/eq, which was kindly provided by Chang Chun Petrochemical (Taiwan). ODOPN was synthesized and applied as a flame retardant curing agent. Another curing agent, phenol novolac (PN) with the polymerization degree of six, was also supplied by Chang Chun Petrochemical.
A curing accelerator of 2-ethyl-4-methyl imidazole (2-E-4-MI; or EMI) was purchased from Acros and used as a catalyst. All reagents (Scheme 2) were reagent grade and used without further purification.

Curing Procedure

The weight ratio of CNE to the diol curing agent was 1.72 g/1 g in PN, and 1.09 g/1 g in ODOPN respectively to maintain a molecular equivalent ratio of 1:1. Imidazole, 2% by weight, was added as a catalyst for most of the curing work. Additionally, various amounts of ODOPN were mixed with PN, in the ratios of 0/100, 25/75, 50/50, 75/25, 100/0, to act as new agents for curing CNE resin to determine the effect of phosphorus on flame retardancy. In this paper, following the procedure of Barton et al. (33) and Su (34), a “dynamic curing process” was performed using a DSC instrument (Perkin-Elmer 7e). Samples were thermally cured and scanned under nitrogen (30 cm³/min) in the calorimeter, at a heating rate of 20, 10, 5, or 2.5°C/min from 30°C to 300°C. As well as dynamic curing, isothermal curing was also performed in an oven at 160°C for 120 min, followed by postcuring at 250°C for 6 hours. The \( T_g \) values of the samples were then measured by DMA.

Characterization

The LOI (Limiting Oxygen Index) is often used to evaluate the flame retardancy of a material. It is defined as the fraction of oxygen in an oxygen-nitrogen mixture that is just sufficient to support the combustion of a specimen after ignition. In this work, the LOI was measured using a flame meter modified from that of Nair et al. (35). Powdered samples (500 mg) were placed in a ceramic cup (Dia.: 40 mm, Hi.: 4 mm) in the middle of an Atlas cylindrical chamber (Dia.: 80 mm, Hi: 200 mm) and a flame was applied from the top of the chamber for 10 s. A flow rate of 12 L/min of various ratios of \( \text{N}_2/\text{O}_2 \) was maintained. The percentage of oxygen in the mixture that just sufficed to sustain the flame for 30 s was taken as the LOI. The benefit of this method for measuring LOI is that up to 9/10 of the testing material that would be consumed by regular ASTM measurement, can be saved. The deviation of LOI was around 5%.

TGA measurements were taken using a TA Instrument TGA 2950 in a nitrogen or air atmosphere. Dynamic mechanical analyses (DMA) were performed using a Perkin-Elmer DMA 7e. The tan\( \delta \) was determined as a function of scanning temperature at a heating rate of 3°C/min from ambient to 220°C, at a frequency of 1 Hz and an oscillating amplitude of 4 \( \mu \)m. A 12-mm-long, 10-mm-wide, and 2-mm-thick sample was used. The test was performed in the three point bending mode, at a tension ratio of 110%.

RESULTS AND DISCUSSION

Curing Kinetics

Figures 1a to d present DSC thermograms of CNE cured by ODOPN or PN, in the presence or absence of EMI, obtained at various heating rates. The data are analyzed according to Kissinger’s (36, 37) method. The governing equation is as follows.

\[
E_a = (-)R \times \frac{d[\ln(T_P^2)]}{d[T_P]} \quad (1)
\]

where \( E_a \) is the activation energy; \( \beta \) is the heating rate; \( R \) is the ideal gas constant, and \( T_P \) is the peak temperature of the DSC thermogram. Accordingly, a plot of \( \frac{-\ln(\ln(T_P^2))}{T_P^{-1}} \) should be a straight line with a slope of \( E_a/R \). Figure 2 presents a typical plot for the treatment pertaining to Fig. 1a, that is of the CNE/ODOPN/EMI system, and the activation energy can thus be calculated. Figures 1b to d are treated similarly and the results are tabulated in Table 1. Table 1 shows that the catalyst EMI is quite active in the CNE/PN system. Adding 2% EMI to CNE/PN reduced

![Scheme 2.](image)
Fig. 1. DSC thermograms of epoxy curing at various heating rates for (a) CNE/ODOPN with EMI, (b) CNE/ODOPN without EMI, (c) CNE/PN with EMI and (d) CNE/PN without EMI.
Fig. 1. Continued.
the curing $E_a$ from 131.5 J/mol to 75.6 J/mole. However, Table 1 also indicates that the catalytic effect of EMI on the ODOPN system is negligible. The symmetric diol attached to the 1,4 position of a naphthalene ring in ODOPN is thought to establish a steady resonance-structure and inhibit any catalytic action (Scheme 1). In contrast, the sequence of benzene rings attached with irregular hydroxyl groups in PN (Scheme 2) would cause a strong steric effect to hinder the curing reaction without the help of EMI. However, since the PN does not establish any resonance-structure such that the ring opening reaction of CNE with the hydroxyl groups can easily be catalyzed by the EMI. The activation energy calculated above was also denoted as $E_a$, and used in further analysis as follows.

Notably, even when $T_{\text{max}}$ in Fig. 1d was observed clearly to determine $E_a$, the system suffered rapid degradation because the reaction temperature was too high to be sustained without the help of an EMI catalyst. Figure 1d is thus not considered any further. Figures 1a to c can be further translated into Figs. 3a to c by integrating the DSC thermopeak to yield the reaction conversion as a ratio of partial area up to a particular temperature to the total area. Kaiser (38), assuming that the reaction was autocatalyzed (39), suggested the following relationship to simulate the conversion trace.

$$\ln \left( \frac{d\alpha}{dt} \right) = \ln (Z) - \frac{E_a}{(R \ast T)} + n \ast \ln (1 - \alpha) + m \ast \ln (\alpha)$$

where $E_a$ is the apparent activation energy of curing calculated from Eq 1 and treated as a constant; $n$ is the order of reaction, and $\alpha$ is the conversion ratio at a given temperature (Figs. 3a to c). According to Eq 2, at the initial stage in which the conversion ratio is around zero, $\ln (1 - \alpha)$ was insignificant and the term $n \ast \ln (1 - \alpha)$ was therefore negligible. The order of autocatalyzed reaction, $m$, was found by plotting $\ln (d\alpha/dt) - \ln (Z) + E_a/(R \ast T)$ as a function of $\ln (\alpha)$. However, in the final stage in which the conversion ratio is almost one, the $\ln (\alpha)$ was negligible and the term $m \ast \ln (\alpha)$ also became negligible. The order of the crosslinking reaction, $n$, was determined by plotting $\ln (d\alpha/dt) - \ln (Z) + E_a/(R \ast T)$ as a function of $\ln (1 - \alpha)$. Table 2 summarizes these results, demonstrating

![Graph](image_url)

**Table 1.** $E_a$ of CNE Curing, Calculated from Figs. 1a to d by Kissinger’s Method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Activation Energy of Curing (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNE/ODOPN with 2-E-4-MI</td>
<td>91.3</td>
</tr>
<tr>
<td>CNE/ODOPN without 2-E-4-MI</td>
<td>96.2</td>
</tr>
<tr>
<td>CNE/PN with 2-E-4-MI</td>
<td>75.6</td>
</tr>
<tr>
<td>CNE/PN without 2-E-4-MI</td>
<td>131.5</td>
</tr>
</tbody>
</table>
Fig. 3. Conversion curves from Figs. 1a to c at different heating rates: □: 2.5°C/min, ◇: 5°C/min, △: 10°C/min, ×: 15°C/min, ○: 20°C/min. Corresponding solid curves are predicting from Kaiser's equation (Eq 2).
that the order of the crosslinking reaction \((n)\) approximately equals one, independently of the scan rate. Moreover, the order of the autocatalyzed reaction is close to 0.5. Interestingly, Table 2 shows that the \(m\) and \(n\) values increased as the catalytic EMI was added. The catalytic EMI might have participated in the reaction by increasing the frequency of reaction collisions. Additionally, Table 2 shows that the PN system had low \(m\) and \(n\) values, indicating that the PN curing is less sensitive to the concentration of the reactants than is ODOPN curing.

Integrating Eq 2 yields the conversion ratio at a given temperature (using \(m\) and \(n\) as in Table 2). Figures 3a to c summarize the results for convenient comparison with the experimental data obtained here. Figures 3a, b show excellent agreement with the Kaiser’s prediction. Furthermore, Fig. 3c shows that discrepancies are more apparent at a higher heating rate. The rapid increase of viscosity at a high heating rate during curing might slow the crosslinking reaction. This retardation is more pronounced for the curing agent with that has large molecular size such as PN (Mw: 800 g/mole) than one with relatively small molecular size such as ODOPN (Mw: 380 g/mole).

### Thermal Stability Analyses and Flame Retardancy Measurements

Figure 4 plots the \(\tan \delta\) against temperature, obtained by DMA for the CNE system included 2% EMI and cured with a mixed curing agent, ODOPN/PN, in the ratios of 100/0, 75/25, 50/50, 25/75, and 0/100. \(\tan \delta\) curves show a major relaxation that corresponds to \(T_g\) for most cured epoxies. \(T_g\) was found to increase with ODOPN content. Unlike ODOPN (380 g/mole), PN (800 g/mole) is too bulky to form a dense amorphous region that leads to a lower \(T_g\). Furthermore, incorporating a naphthalene ring into ODOPN may increase the network’s rigidity, suppress the mobility of the polymer chains, and thus increase \(T_g\). Table 3 presents details that relate to \(T_g\).

Thermogravimetric analysis (TGA) is the conventional way to evaluate the thermal stability of epoxy resins. Figure 5 shows a typical TGA thermograms at various heating rates in nitrogen for CNE epoxies cured with ODOPN. The rate of degradation at a specific temperature can be determined as the tangential slope of a TGA trace. In general, the temperature at the maximum rate of degradation, \(T_{\text{dmax}}\), and the residual weight fraction, denoted as the char yield, are of primary importance. Table 4 summarizes the TGA results for CNE cured with ODOPN/PN mixtures in ratios of 100/0, 75/25, 50/50, 25/75, and 0/100, respectively, in which the \(T_{\text{dmax}}\) and char yield at the rate of heating 10°C/min were tabulated. The table shows that the ODOPN system has the lowest \(T_{\text{dmax}}\) but the highest char yield. Moreover, it shows that \(T_{\text{dmax}}\) declines as phosphorus content increases. Char yield, however, increases with phosphorus content. Both results are attributable to the initial decomposition of the phosphorus compound. In the early decomposition, the dehydration of the phosphorus-containing polymer is initiated, producing a layer composed of phosphate groups on the polymer’s surface that therefore insulates the underlying polymer from heat and oxygen. Moreover, the vapor released in dehydration may dilute the flammable gases and quench the flame. Therefore, the decomposition temperature declined as the phosphorus content increased. Notably, \(T_{\text{dmax}}\) of ODOPN, although lower than that of PN, far exceeds that of other linear or cyclic phosphorus systems (40–42). Sato et al. (43–47) reported that polymers with a high aromatic content are fire-retardant and thermally stable. Accordingly, the high \(T_{\text{dmax}}\) of the ODOPN system is attributable to the four benzene rings attached to the unit structure of the ODOPN molecule.

Van Krevelen (48) had thoroughly studied the relationship between char yields and flame retardancy and established that the char residue following pyrolysis was linearly proportional to the oxygen index (LOI). Increasing char yield can reduce the generation of combustion gases, limit the heat emitted by the pyrolysis reaction, decrease the solid’s conductivity of heat, and thus reduce the flammability of materials. In this study, the cured epoxies were further examined by measuring their LOI. Column four in Table 4 shows the result, which demonstrates that the LOI of CNE/ODOPN is 31, considerably exceeding that of the neat system, CNE/PN, of 22 (49). Table 4 also reveals that, as predicted from the char yields, LOI increases with phosphorus content. Researchers generally agree that such a material, with a LOI that exceeds 26, can

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**Table 2. Values of m, n, and Ln(Z) Obtained From the Treatment of Figs. 1a to c by Kaiser’s Method.**

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>m</th>
<th>n</th>
<th>Ln(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNE/ODOPN with 2-E-4-MI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.42</td>
<td>1.41</td>
<td>24.50</td>
</tr>
<tr>
<td>5</td>
<td>0.47</td>
<td>1.47</td>
<td>24.79</td>
</tr>
<tr>
<td>10</td>
<td>0.48</td>
<td>1.50</td>
<td>25.13</td>
</tr>
<tr>
<td>15</td>
<td>0.49</td>
<td>1.42</td>
<td>25.03</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td>1.39</td>
<td>24.96</td>
</tr>
<tr>
<td>CNE/ODOPN without 2-E-4-MI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.56</td>
<td>1.14</td>
<td>22.55</td>
</tr>
<tr>
<td>5</td>
<td>0.55</td>
<td>1.17</td>
<td>22.63</td>
</tr>
<tr>
<td>10</td>
<td>0.53</td>
<td>1.24</td>
<td>22.83</td>
</tr>
<tr>
<td>15</td>
<td>0.51</td>
<td>1.28</td>
<td>23.00</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td>1.3</td>
<td>23.10</td>
</tr>
<tr>
<td>CNE/PN with 2-E-4-MI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.42</td>
<td>0.89</td>
<td>21.60</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
<td>0.89</td>
<td>21.81</td>
</tr>
<tr>
<td>10</td>
<td>0.45</td>
<td>0.90</td>
<td>22.22</td>
</tr>
<tr>
<td>15</td>
<td>0.50</td>
<td>0.91</td>
<td>22.42</td>
</tr>
<tr>
<td>20</td>
<td>0.51</td>
<td>0.92</td>
<td>22.53</td>
</tr>
</tbody>
</table>
be considered to exhibit good flame retardancy. From the results obtained in this research, adding ODOPN up to a phosphorus content of 2.9% enables this threshold to be met, which conclusion is consistent with Wang’s previous work on CNE cured with ODOPB (16).

Degradation Kinetics

The activation energy of degradation for a given TGA weight fraction (wt%) can be determined by Ozawa’s method Eq 3. The definition of each parameter in Eq 3 is similar to Eq 1 in that the peak temperature is here obtained from the TGA scan of degradation, instead of from the DCS scan of curing. This practical approach to investigating decomposition has been often applied to various aromatic polymers (50) including polyimides, poly(ether sulfone), poly(p-xylylene) and epoxy-containing ODOPB (19). Notably, Cabbalera et al. (51) have proposed a modified equation from Eq 3 for a polymer-blend system in which the thermal decomposition was taken place heterogeneously. However, in this work, even the curing agent ODOPN/PN is a mixture, the epoxy after curing can be treated as a homogeneous system owing to the covalent crosslinking bonds initiated by either ODOPN or PN. As shown in Fig. 6, log β is linearly related to the reciprocal peak temperature for the CNE/ODOPN system. This result implies that a single activation energy governs the thermal decomposition of the CNE/ODOPN system. The mean activation energy can be calculated by averaging out $E_a$ from Eq 1 for each conversion ratio. Following the same approach, the mean $E_a$ values for the degradation of CNE epoxies cured with ODOPN/PN mixtures were similarly calculated, plotted in Fig. 7 and tabulated in the final column of Table 4. Figure 7 and Table 4 reveal that the CNE epoxy-containing ODOPN has the lowest degradation $E_a$; in contrast, the CNE/PN has the highest degradation $E_a$. Additionally, experimental results also reveal that the mean $E_a$ declines with the phosphorus content, because the ease of decomposition of the phosphorus compound during the initiation stage to form an insulating layer. A similar explanation was given in the previous discussion of $T_{dmax}$. Notably, Fig. 7 shows that even initiating the formation of an insulating layer makes those phosphorus containing epoxies

Table 3. $T_g$ Values of CNE Epoxy Cured With Different Curing Agents.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$ by DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODOPN</td>
<td>189.1</td>
</tr>
<tr>
<td>ODOPN75/PN25</td>
<td>186.9</td>
</tr>
<tr>
<td>ODOPN50/PN50</td>
<td>184.9</td>
</tr>
<tr>
<td>ODOPN25/PN75</td>
<td>183.0</td>
</tr>
<tr>
<td>PN</td>
<td>156.6</td>
</tr>
</tbody>
</table>

Fig. 4. The determination of $T_g$ by DMA for cured CNE epoxy with an ODOPN/PN mixture in different weight ratios. □□: 0/100, ◆◆: 25/75, ΔΔ: 50/50, ××: 75/25, --: 100/0.
exhibit a low \( E_a \), the \( E_a \) increases with decomposition conversion. A higher decomposition conversion is believed to correspond to the formation of a thicker insulating layer. Therefore, \( E_a \) may be increased since a thick layer retards the diffusion of the gas. The assertion is further verified by the declining tendency of \( E_a \) against decomposition conversion for CNE/PN system, in which no insulating layer was formed.

**CONCLUSIONS**

CNE epoxies cured using two different curing agents, ODOPN, and PN, were prepared. In comparison with the conventional PN system, introducing ODOPN, a phosphorus-containing bulky pendant group, into CNE can increase \( T_g \) by 33°C, char yield from 30% to 38%, and LOI from 22 to 31. The DSC curing study indicates that \( E_a \) of the CNE/ODOPN epoxy can be obtained by Kissinger's method. The resulting \( E_a \) values demonstrate that the catalytic effect of EMI is insignificant on CNE/ODOPN but is quite considerable on CNE/PN, for which \( E_a \) was reduced from 131.5 to 75.6 KJ/mole. This result may be attributed to the fact that the symmetric diol attached to the 1 and 4 positions of a naphthalene ring of ODOPN establishes a steadily resonating structure and inhibits catalytic action. Further investigating the relationship between reaction conversion ratio and curing temperature reveals that experimental curves can be well simulated by Kaiser's model. The orders of the autocatalyzed reaction, \( m \), and the crosslinking reaction, \( n \), are close to 0.5 and 1.0 respectively, independently of the scan rate. Finally, the TGA decomposition study, along with Ozawa’s method, demonstrates that the mean \( E_a \) declines with phosphorus content, because of the ease with which the phosphorus compound decomposes during the initiation stage to form an insulating layer. Results in this study further demonstrate that \( E_a \) tends to increase with decomposition conversion for an ODOPN/PN mixture with the ODOPN content of over 50%, probably because of the retardation of gas diffusion by the insulating layer of the phosphorus compound.

**ACKNOWLEDGMENTS**

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**REFERENCES**

Fig. 6. Treatment of Fig. 5 by Ozawa’s method to obtain the activation energy of degradation at various conversion ratios ($E_a$ of degradation for 70%, 60%, 50%, 40%, 30%, 20%, is 173.5, 165.0, 160.2, 155.4, 151.6, and 147.7 KJ/mol respectively).

Fig. 7. $E_a$ of degradation against conversion ratio (%) for CNE cured with an ODOPN/PN mixture in five different ratios (◆: 0/100, ■: 25/75, ▲: 50/50, ×: 75/25, -: 100/0).
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