

# Thermal Studies: A Comparison of the Thermal Properties of Different Oligomers by Thermogravimetric Techniques

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**ABSTRACT:** Thermal properties of conventional organic oligomers and organically modified ceramic hybrid materials (Ormoresin) were characterized and compared by using thermogravimetric techniques. Thermal properties were compared in terms of initial thermal decomposition temperature ( $T_0$ , which is the temperature at which 5% weight loss occurred), the temperature at which 50% weight loss occurred ( $T_{50}$ ), and the percentage of residue remained at 600°C. Organically modified ceramic resins are found to

have improved thermal stability. It is also found that the type of inorganic material incorporated in organically modified ceramics resin (Ormoresin) has considerable influence on its thermal characteristics. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 977–985, 2004

**Key words:** inorganic materials; thermal properties; thermogravimetric analysis; resin

## INTRODUCTION

Thermal properties are relevant to the potential use of polymeric materials in many consumer-oriented applications. A detailed understanding of the thermal degradation of the material is important in the design of materials with improved properties. The threshold temperature of breakdown determines the upper limit of the temperature of fabrication. The most widely used method for studying the thermal properties is thermogravimetry (TGA). The information available consists of the number of stages of breakdown, a quantitative measure of the weight loss in any stage, and the threshold temperature.<sup>1</sup>

The organically modified ceramic hybrid materials are molecules containing a metal core bonded to reactive organic groups. The concept<sup>2</sup> is to combine properties of organic polymers (functionalization, ease of processing at low temperature and toughness) with properties of glasslike materials (hardness, chemical and thermal stability, and transparency) to generate new/synergistic properties.<sup>2</sup>

Thermal properties of two conventional organic monomers, five newly developed organically modified ceramic hybrid materials and one commercially

available epoxy resin, were studied and compared. These organically modified ceramics resins contain alkoxides or mixtures of alkoxides of silicone, aluminum, calcium, and titanium.

The processing steps are based on sol-gel-type reactions, which are already well known for the synthesis of ceramics.<sup>2</sup> In the case of organically modified ceramic hybrid materials, a second step, the formation of the additional organic network or crosslinking, follows after the buildup of the inorganic network.<sup>2</sup>

These organically modified ceramic hybrid materials are used in a wide range of applications such as wear-resistant coating, in microelectronics, microoptics, electrooptics, and photonics and as matrices for dental composites.<sup>2</sup>

For application in electronics, the hybrid materials have to withstand soldering in the temperature range of 250–350°C. These materials are stable for a few minutes at these temperatures. If thermally very stable structures such as phenyl or cyclophosphazene units are attached to the inorganic Si—O—Si network, thermal stability (determined as 5% weight loss) even above 400°C can be achieved.<sup>3</sup>

The purpose of this study was to compare the thermal stability of organically modified ceramics resins with purely organic resins. In this context, organic resins such as BisGMA and UTMA were selected to explore their potential in applications other than dental composites. Epoxy resin was selected because it is a proved material for higher thermal stability and use in electronics.

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**TABLE I**  
Refractive Indexes of the Ormocer Resins Synthesized

| Sample code               | Refractive index |
|---------------------------|------------------|
| Ormoresin R <sub>6</sub>  | 1.4726           |
| Ormoresin R <sub>15</sub> | 1.483            |
| Ormoresin R <sub>17</sub> | 1.4822           |
| Ormoresin R <sub>20</sub> | 1.4754           |
| Ormoresin R <sub>21</sub> | 1.4794           |

## EXPERIMENTAL

### Materials

The materials used in this study are bisphenol-A glycidyl methacrylate (BisGMA) and urethane tetramethacrylate (UTMA), synthesized in our laboratory, 3(trimethoxy silyl propyl methacrylate) and benzyl triethyl ammonium chloride (Aldrich Chemicals, USA), tetra isopropyl orthotitanate (Merck Schuchardt, Germany), laboratory reagent (LR) grade calcium hydroxide, LR grade aluminum hydroxide gel, AR grade hydrochloric acid, LR grade sodium hydroxide, and specially dried LR grade diethyl ether (S.D. Fine Chemicals, Mumbai, India). Epoxy resin used was Araldite GY 250 (Ciba Geigy, Mumbai, India).

### Synthesis and characterization of BisGMA

BisGMA was synthesized in the laboratory by using a reported procedure.<sup>4</sup> The synthesized BisGMA was characterized by using various techniques and details were reported elsewhere.<sup>5</sup>

### Synthesis and characterization of UTMA

Details of synthesis and characterization of UTMA were reported previously.<sup>6</sup>

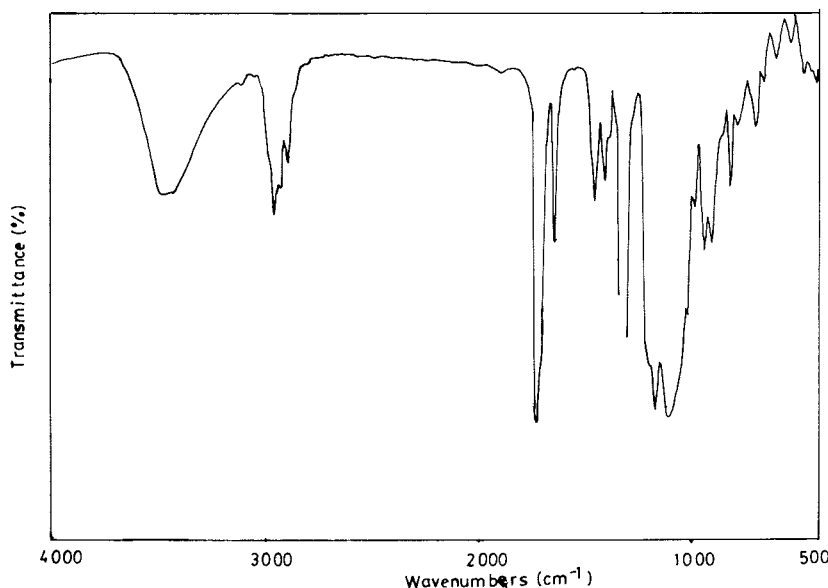
### Synthesis and characterization of organically modified ceramic hybrid materials (Ormoresin)

#### Ormoresin R<sub>6</sub>

Ormoresin R<sub>6</sub> was prepared by hydrolyzing 1 mol 3-trimethoxy silyl propyl methacrylate with 3 mol distilled water in the presence of 6*N* HCl under stirring for 6 h. The hydrolyzed silane was kept at room temperature overnight for postcondensation. This was then extracted with ether, washed with distilled H<sub>2</sub>O until acid free, and dried after evaporating ether. HPLC analysis was carried out by using ethanol solution. For the resin C<sub>18</sub> column of HPLC equipment (Waters Associates, model 440) was used (flow rate, 1 mL/min; 486 tunable UV detector, 210 nm). Methanol was used as the mobile phase.

#### Ormoresin R<sub>15</sub>

Preferential hydrolysis and postcondensation of 3-trimethoxy silyl propyl methacrylate was carried out as in the case of Ormoresin R<sub>6</sub>. The hydrolyzed silane was extracted with ethanol and mixed with 1% aluminum hydroxide in the presence of 1*N* NaOH solution, under stirring for 2 h. Ethanol was separated and the resin was dried at 37°C for 48 h.



**Figure 1** FTIR spectrum of Ormoresin R<sub>6</sub>.

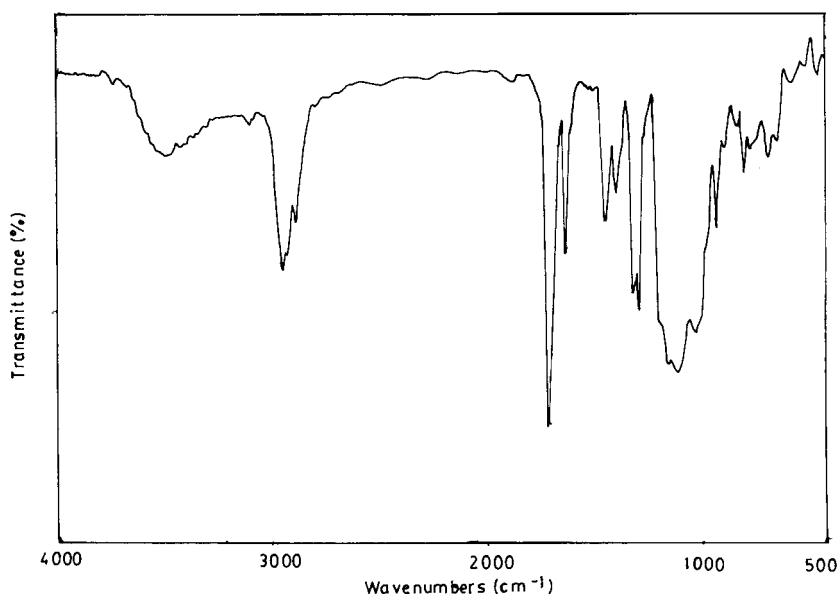


Figure 2 FTIR spectrum of Ormoresin R<sub>15</sub>.

#### Ormoresin R<sub>17</sub>

The silane was hydrolyzed at lower pH as mentioned above. The hydrolyzed silane was neutralized with 1N NaOH solution and dissolved in diethyl ether to get 40% solution of the polycondensed silane in diethyl ether. The ether solution was mixed with 1% calcium hydroxide and 0.5% pyrogenic silica, stirred well at room temperature, and dried at 37°C.

#### Ormoresin R<sub>20</sub>

Ormoresin R<sub>20</sub> was prepared by dissolving Ormoresin R<sub>6</sub> in diethyl ether to get a solution of 40%. To the

solution tetra isopropyl orthotitanate (1% with respect to Ormoresin R<sub>6</sub>) is added after making the solution alkaline by adding 1N NaOH solution. The solution is stirred vigorously for 3 h and dried at 37°C after evaporating ether.

#### Ormoresin R<sub>21</sub>

Ormoresin R<sub>21</sub> was prepared by dissolving Ormoresin R<sub>6</sub> in diethyl ether to get 40% solution. To the ether solution, 2% pyrogenic silica was added in the presence of 0.5% benzyl triethyl ammonium chloride. The mixture was stirred for 4 h and ether was evaporated.

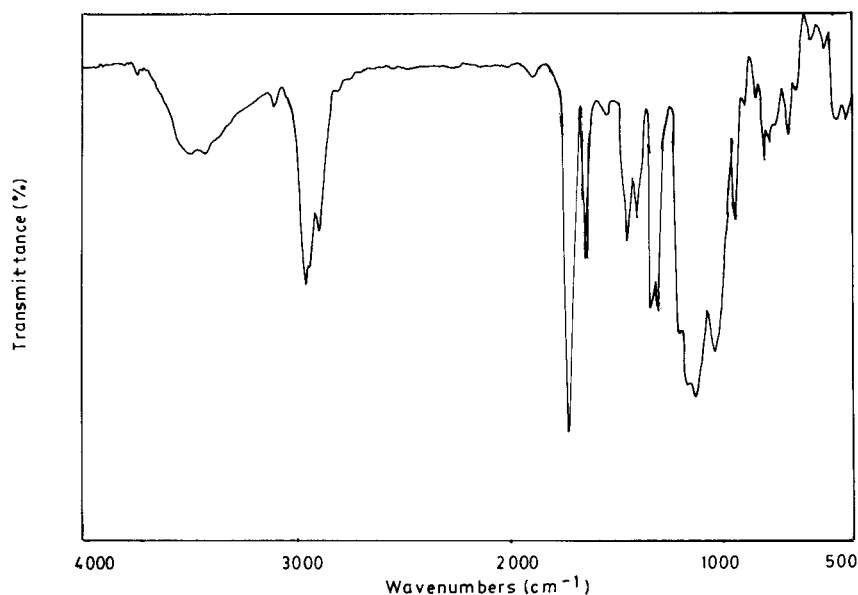


Figure 3 FTIR spectrum of Ormoresin R<sub>17</sub>.

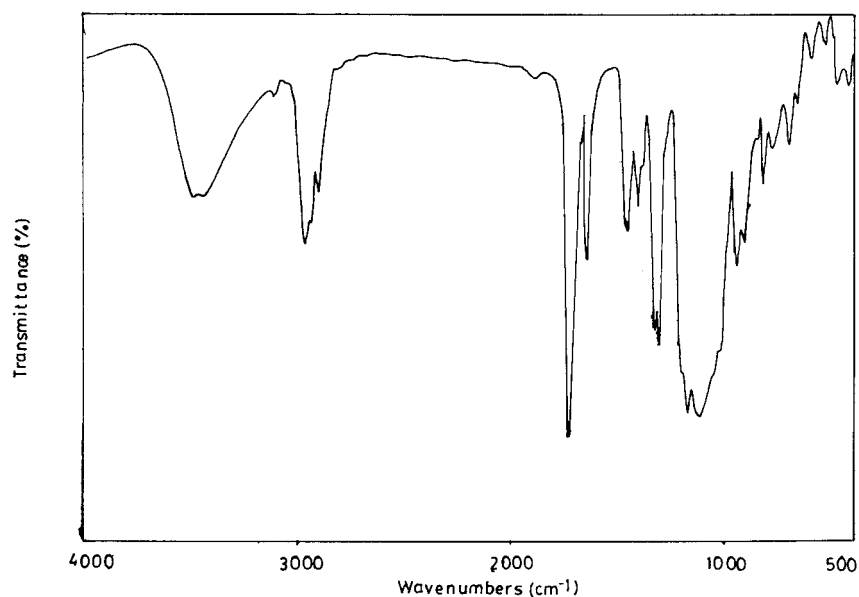


Figure 4 FTIR spectrum of Ormoresin R<sub>20</sub>.

#### Characterization of Ormoresins

Refractive indexes of all the resins were measured by using an Abbey Refractometer (model 3 T; Atago, Japan). The infrared spectra were recorded by using a Fourier transform infrared spectrophotometer (model FTIR Nicolet Impact 4000, USA).

#### Determination of thermal stability

Thermal stability was evaluated by using thermogravimetry (simultaneous DTA-TGA, TA Instruments

Inc.) based on ASTM E-1131-98 by using SDT-2960. The heating rate used was 10°C/min, in nitrogen atmosphere. Thermogravimetric analysis of BisGMA, UTMA, Ormoresin R<sub>6</sub>, Ormoresin R<sub>15</sub>, Ormoresin R<sub>17</sub>, Ormoresin R<sub>20</sub>, Ormoresin R<sub>21</sub>, and epoxy resin (Araldite GY 250) was carried out.

### RESULTS AND DISCUSSION

Refractive indexes of all the ormo resins used in this study are given in Table I. All the ormo resins are translucent and viscous in nature.

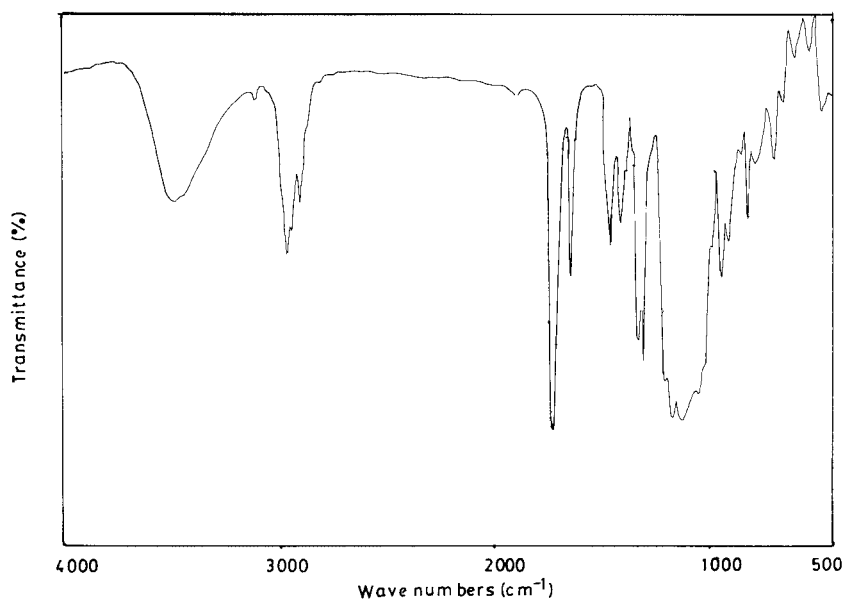


Figure 5 FTIR spectrum of Ormoresin R<sub>21</sub>.

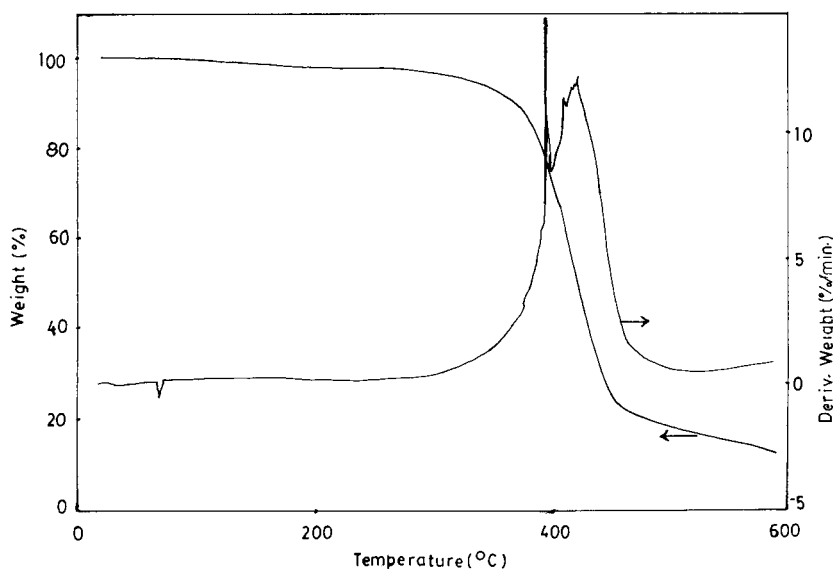


Figure 6 TGA and DTG curves of BisGMA.

FTIR spectrum of Ormoresin  $R_6$  (Fig. 1) is typical for polymerized silica as indicated by the sharp peaks of the strong O—Si—O asymmetric stretch at  $1000\text{--}1200\text{ cm}^{-1}$ , symmetric Si—O—Si stretch at  $700\text{--}800\text{ cm}^{-1}$ , and Si—O—Si asymmetric stretch at  $1298\text{ cm}^{-1}$ . The other peaks obtained are  $1718\text{ cm}^{-1}$  (C=O group), bending vibrations of the C=CH<sub>2</sub> at  $939\text{ cm}^{-1}$ , stretching vibrations of the C=CH<sub>2</sub> at  $1635\text{ cm}^{-1}$ , and C—H stretching at  $2800\text{--}3000\text{ cm}^{-1}$ . The broad band at  $3494\text{ cm}^{-1}$  is associated with Si—OH stretching vibrations and hydrogen-bonded water.

FTIR spectra of Ormoresin  $R_{15}$ , Ormoresin  $R_{17}$ , Ormoresin  $R_{20}$ , and Ormoresin  $R_{21}$  (Figs. 2-5) are similar to that of Ormoresin  $R_6$ . All the spectra are typical of polymerized silica.

Thermogravimetric traces of BisGMA are given Figure 6. We can see that the onset of decomposition temperature is at about  $400^\circ\text{C}$ . A single step of degradation is discernible in the degradation process as illustrated in the DTG graph. Presence of thermally stable phenyl groups in the BisGMA mol-

ecule is attributed to its thermal stability. Twelve percent of residue as a carbonaceous char remained at  $591^\circ\text{C}$ . The initial thermal decomposition ( $T_0$ ) is at  $336^\circ\text{C}$  and 50% weight loss occurred ( $T_{50}$ ) at  $422^\circ\text{C}$  (Table II).

The results of the thermogravimetric studies of UTMA resin is shown in Figure 7. The onset of decomposition temperature is below  $200^\circ\text{C}$ . Fifty percent weight loss occurs at  $321^\circ\text{C}$  because of decomposition of the precursor. From Table II, we can see that  $T_0$  is  $150^\circ\text{C}$  and  $T_{50}$  is  $321^\circ\text{C}$ .

Thermogravimetric trace of Ormoresin  $R_6$  is given in Figure 8. The major decomposition occurred above  $369^\circ\text{C}$ . Residue (48.5%) remained as a carbonaceous char at  $600^\circ\text{C}$ . Two steps are discernible in the degradation process as illustrated in the DTG graph in Figure 4. The first step at  $124^\circ\text{C}$  is due to the liberation of volatile substances, resulting in a weight loss of about 2%. The weight loss of the hydrolyzed and polycondensed silane precursor (Ormoresin  $R_6$ ) at  $430^\circ\text{C}$  is attributed to the decom-

TABLE II  
Comparison of  $T_0$  and  $T_{50}$  Values of Different Oligomers Studied

| Resin used         | Inorganic content             | $T_0$ ( $^\circ\text{C}$ ) | $T_{50}$ ( $^\circ\text{C}$ ) | % residue |
|--------------------|-------------------------------|----------------------------|-------------------------------|-----------|
| Bis GMA            | Nil                           | 336                        | 422                           | 12        |
| UTMA               | Nil                           | 150                        | 321                           | 2.85      |
| Ormoresin $R_6$    | (precursor)                   | 369                        | 550                           | 48.5      |
| Ormoresin $R_{15}$ | Al(OH) <sub>3</sub>           | 353                        | 520                           | 47        |
| Ormoresin $R_{17}$ | Ca(OH) <sub>2</sub> + silica  | 392                        | 435                           | 33        |
| Ormoresin $R_{20}$ | Tetra isopropyl orthotitanate | 313.8                      | 589                           | 49.7      |
| Ormoresin $R_{21}$ | Silica                        | 378                        | 551                           | 48.39     |
| Epoxy resin        | Nil                           | 286.7                      | 340                           | 1.97      |

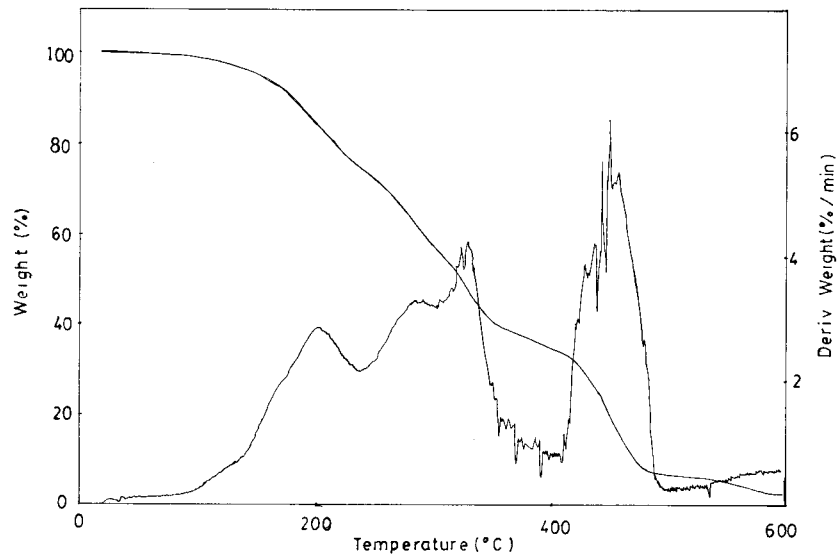


Figure 7 TGA and DTG curves of UTMA.

position of the precursor because of its organic component, which was completely removed at about 600°C, leaving a residue of about 48.5% because of the presence of inorganic component. From Table II, it can be seen that the  $T_0$  and  $T_{50}$  values of Ormoresin R<sub>6</sub> are higher than organic resins (BisGMA and UTMA).

Thermogravimetric trace of Ormoresin R<sub>15</sub> is given in Figure 9. From the figure, it can be seen that incorporation of 1% aluminum hydroxide into Ormoresin R<sub>6</sub> increased the onset of decomposition temperature from 124 to 316°C. Three steps of de-

composition are visible in the TGA and DTG curves: two sharp decomposition steps at 350 and 520°C and a major decomposition step at 404°C. The two steps at 350 and 520°C are characteristic steps of incorporated aluminum hydroxide, which is revealed from the thermograms of other Ormoresins, where these two steps are absent. Other Ormoresins contain inorganic materials other than aluminum hydroxide. The major weight loss at 404°C is attributed to the decomposition of the Ormoresin because of its organic component, which was completely removed at about 600°C. A residue of about 47% is

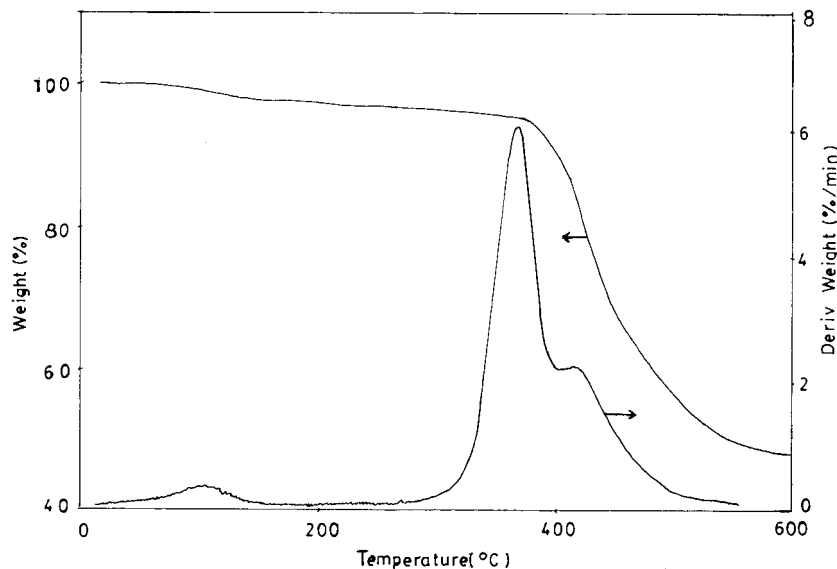


Figure 8 TGA and DTG curves of Ormoresin R<sub>6</sub>.

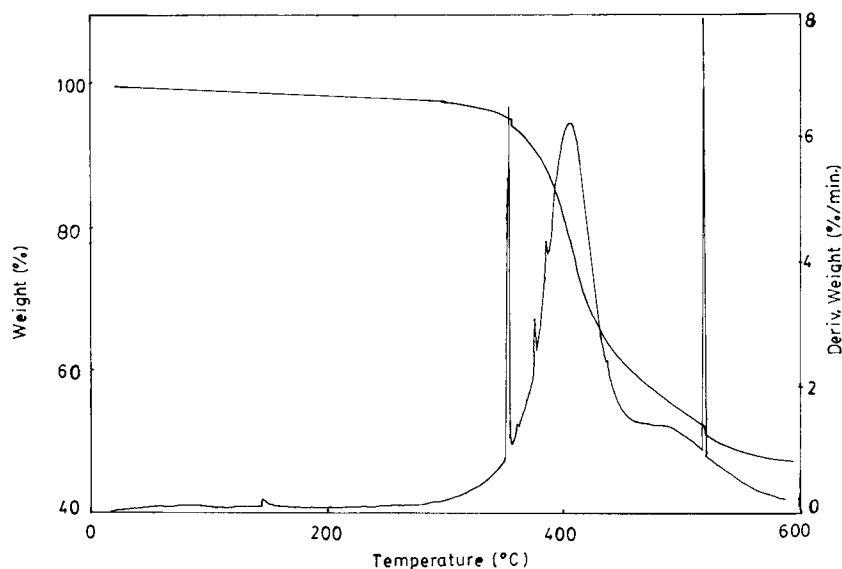


Figure 9 TGA and DTG curves of Ormoresin R<sub>15</sub>.

remained as carbonaceous char due to the presence of inorganic component. From Table II, it can be seen that the  $T_0$  is 353°C and  $T_{50}$  is 520°C.

Thermogravimetric trace of Ormoresin R<sub>17</sub> is given in Figure 10. From the figure, we can see that the degradation pattern of Ormoresin R<sub>17</sub> is different from Ormoresin R<sub>6</sub> and Ormoresin R<sub>15</sub>. It can be seen that incorporation of 1% calcium hydroxide into Ormoresin R<sub>6</sub> increased the onset of decomposition temperature from 124 to 357°C with a weight loss of 2%. The single step of decomposition at 398°C as visible in the DTG graph is due to the

decomposition of Ormoresin because of the organic content.  $T_0$  value of Ormoresin R<sub>17</sub> (Table II) is 392°C, which is the highest value among the various oligomers evaluated.  $T_{50}$  is 435°C. The percentage of carbonaceous char at 590°C is 33. It can be seen that incorporation of calcium hydroxide improves the initial thermal stability as evident from the higher  $T_0$  value. However, at higher temperature, the degradation rate is higher compared to Ormoresins that contain other inorganic materials.

From the TG and DTG thermograms of Ormoresin R<sub>20</sub> (Fig. 11), we can see that there is a mild degradation step

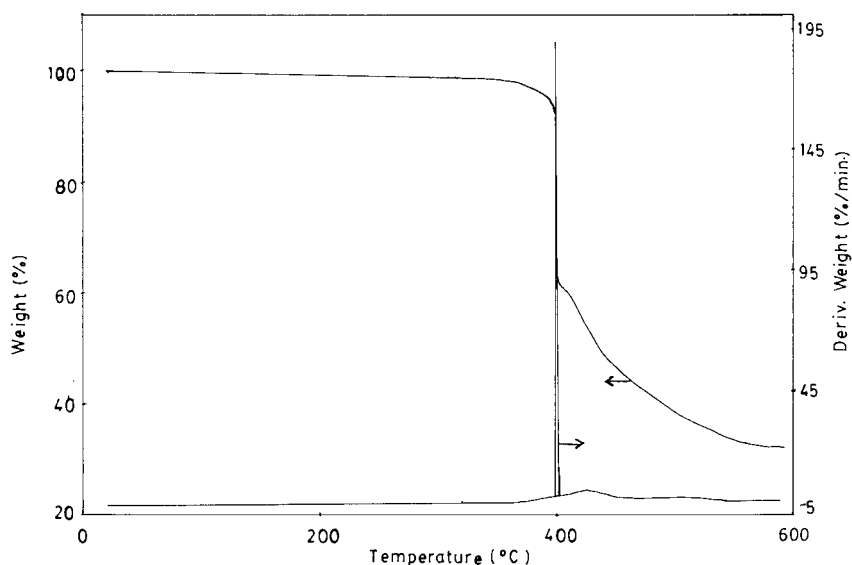


Figure 10 TGA and DTG curves of Ormoresin R<sub>17</sub>.

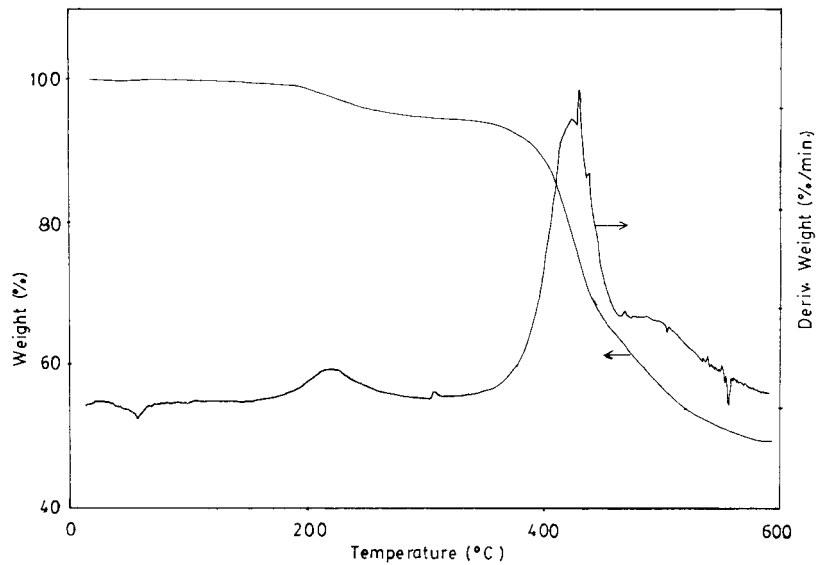


Figure 11 TGA and DTG curves of Ormoresin R<sub>20</sub>.

at about 224°C with a weight loss of less than 2%. This may be due to the liberation of volatiles. Two steps of degradation are visible in the TGA and DTG thermograms. The major degradation at 421°C is due to the decomposition of the organic content. From Table II, we can see that Ormoresin R<sub>20</sub> has the lowest  $T_0$  values and highest  $T_{50}$  values compared to other Ormoresin.

TGA and DTG thermograms of Ormoresin R<sub>21</sub> are given in Figure 12. A weight loss of 2% occurred at 200°C. The major decomposition occurred at 430°C. On comparison of the thermograms of different oligomers, we can see that the degradation patterns of the precursor

(Ormoresin R<sub>6</sub>) and Ormoresin R<sub>21</sub> are identical. The only change is a slight increase in  $T_0$  value of Ormoresin R<sub>21</sub>. It can be concluded that the incorporation of silica alone to the Ormoresin precursor matrix has no considerable effect on the decomposition pattern.

TGA and DTG thermograms of epoxy resin are given in Figure 13. We can see that degradation starts at 237°C and the major decomposition is at about 353°C. From Table II, it can be seen that  $T_0$  is 287°C and  $T_{50}$  is 340°C. On comparison (Table II), it can be seen that all the ormoresins have better thermal stability than epoxy resin.

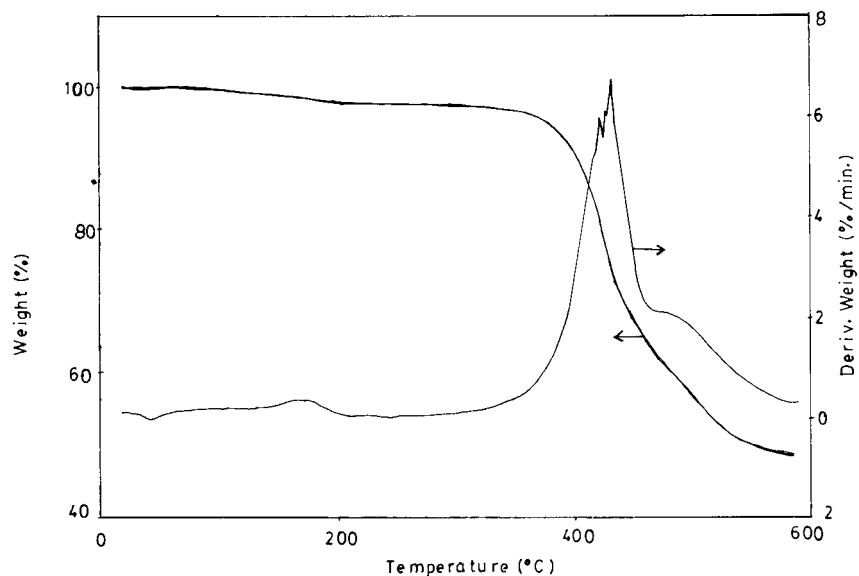


Figure 12 TGA and DTG curves of Ormoresin R<sub>21</sub>.



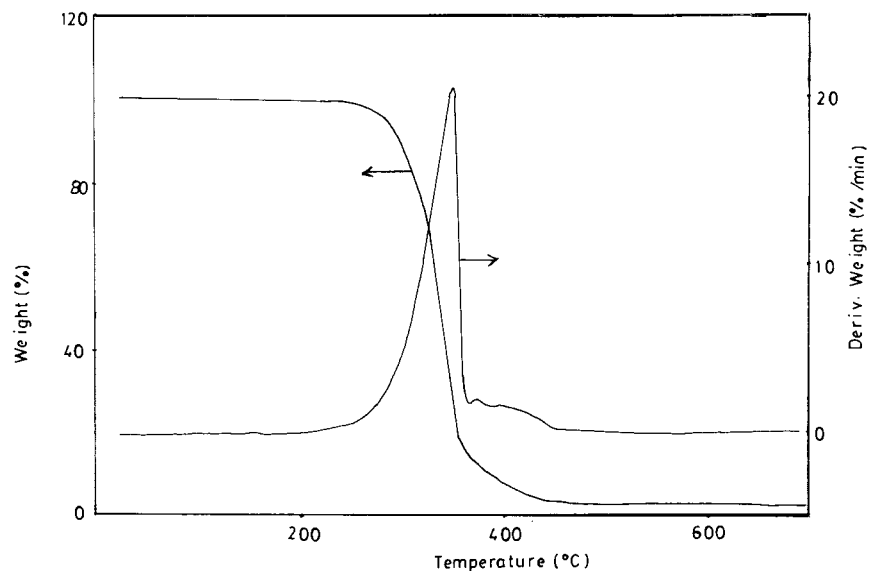


Figure 13 TGA and DTG curves of epoxy resin.

### CONCLUSION

Comparison of the thermal properties of the various oligomers by thermogravimetric analysis showed that Ormo-resins have improved thermal stability. The increase in the overall thermal stability of Ormo-resins is attributed to the presence of incorporated inorganic content.

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