

Thermal Properties of Tropical Wood-Polymer Composites

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SYNOPSIS

Wood-polymer composites (WPC) of Geronggang (GE; *Cratoxylon arborescens*), a light tropical hardwood, impregnated with methyl methacrylate (MMA), styrene-co-acrylonitrile (3 : 2; STAN), methyl methacrylate-co-bis(2-chloroethyl) vinyl phosphonate (3 : 1; MVP) and methyl methacrylate-co-bis(chloropropyl)-2-propene phosphonate (3 : 1; MPP), were prepared by *in situ* polymerization using γ -radiation or catalyst-heat treatment. Thermal characterization of these WPC by limiting oxygen index measurements (LOI), thermogravimetry (TG), and differential scanning calorimetry (DSC) showed that the impregnants greatly modified the wood properties. The LOI values of the GE-MVP and GE-MPP composites were much higher than that for GE and the other composites, indicating the effectiveness of the phosphonates as flame retardants. Concomitantly, the flaming characteristics also compared favorably against that for GE and the other composites. The decomposition temperature and maximum rate of weight loss determined by TG for GE-MVP and GE-MPP were substantially reduced, whereas the char yields were greatly higher. These observations again indicate that phosphonates imparted flame-retarding properties to their composites. The thermal properties of GE-MMA and GE-STAN composites were not vastly different from that of untreated GE. Flame retardancy in the phosphonate-containing composites was effected through both the condensed- and gaseous-phase mechanisms due to the presence of phosphorus and chlorine, respectively. Indication of grafting of polymer to wood was found for GE-STAN, GE-MVP, and GE-MPP composites, but not for GE-MMA. Composites prepared by γ -radiation or by the catalyst-heat treatment had similar thermal characteristics.

INTRODUCTION

Wood-polymer composites (WPC), prepared by the impregnation of vinyl monomers followed by *in situ* polymerization by either γ -radiation or catalyst-heat treatment, generally exhibited enhanced strength properties, dimensional stability, and resistance to biodeterioration.¹⁻³ The extent of improvement in property was directly related to the polymer content, which, in turn, was dependent on the type of wood, the nature of the polymer, and the processing applied. Besides modifying the physical and mechanical properties, the incorporated polymers can also affect the thermal behavior of wood.

The impregnation of polymers, which are more flammable than wood, such as polymethyl methacrylate, polyacrylonitrile and polystyrene, raises the question of whether the thermal properties of the wood will be adversely affected. Alternatively, copolymerization of these polymers with phosphorus- and/or chlorine-containing polymers have been shown to result in WPC with flame-retarding properties.⁴⁻⁶

In this study, four types of Geronggang-polymer composites, with polymer loadings ranging between 58 and 85%, were prepared. The thermal properties were characterized by limiting the oxygen index measurements (LOI), thermogravimetry (TG), and differential scanning calorimetry (DSC). The purpose was to assess the effects of the different impregnants on the flammability and thermal decomposition behavior of the WPC. Additional information in regard to the nature and extent of wood-

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polymer interactions was also derived. This thermal characterization study complements other investigations on the behavior and properties of WPC prepared from a wide range of Malaysian tropical hardwoods and various vinyl monomers.⁷⁻¹¹

EXPERIMENTAL

Preparation of Composites

The impregnation system for WPC preparation is shown in Figure 1. For the LOI studies, oven-dried Geronggang (GE) specimens ($6.5 \times 3.0 \times 70.0$ mm) were evacuated in the impregnation chamber. The monomer or monomeric mixture was introduced at atmospheric pressure, and the wood was immersed for various periods of time. In the γ -radiation process, the samples were individually wrapped in foil and irradiated in a Co-60 source.¹² In the catalyst-heat treatment, the catalyst, azobisisobutyronitrile (AIBN) at 0.25% by weight, was included in the monomeric system. The samples were wrapped up in foil and cured in a 60°C oven for 24 h.

The GE composites prepared were GE-(methyl methacrylate) (GE-MMA), GE-styrene-*co*-acrylonitrile (3 : 2; GE-STAN), GE-(methyl methacrylate)-*co*-bis(2-chloroethyl) vinyl phosphonate (3 : 1; GE-MVP), and GE-(methyl methacrylate)-*co*-bis(chloropropyl)-2-propene phosphonate (3 : 1;

GE-MPP). The polymer loading for the composites was calculated as follows:

$$\% \text{ Polymer loading} = \frac{100 (W - W_0)}{W}$$

where W = weight of WPC and W_0 = weight of oven-dried wood.

Limiting Oxygen Index

LOI were determined using an apparatus fabricated based on the design specified in ASTM D2863-77. The test specimen of GE or GE composite was placed vertically in the center of the apparatus. A gas mixture at a selected oxygen concentration was fed through the column at a flow rate of 4 ± 1 cm/s. After purging for about 30 s, the specimen was ignited. The criterion for a positive burn was the sustenance of 50 mm uninterrupted combustion. A single positive burn was accepted as indicating a concentration at or above the LOI, but at least three negative burns were required for identifying an oxygen concentration below the LOI. By varying the concentration of oxygen in the gas mixture, the minimum oxygen concentration that supported combustion of the sample was recorded as the LOI. The flaming time and other flaming characteristics were also noted.

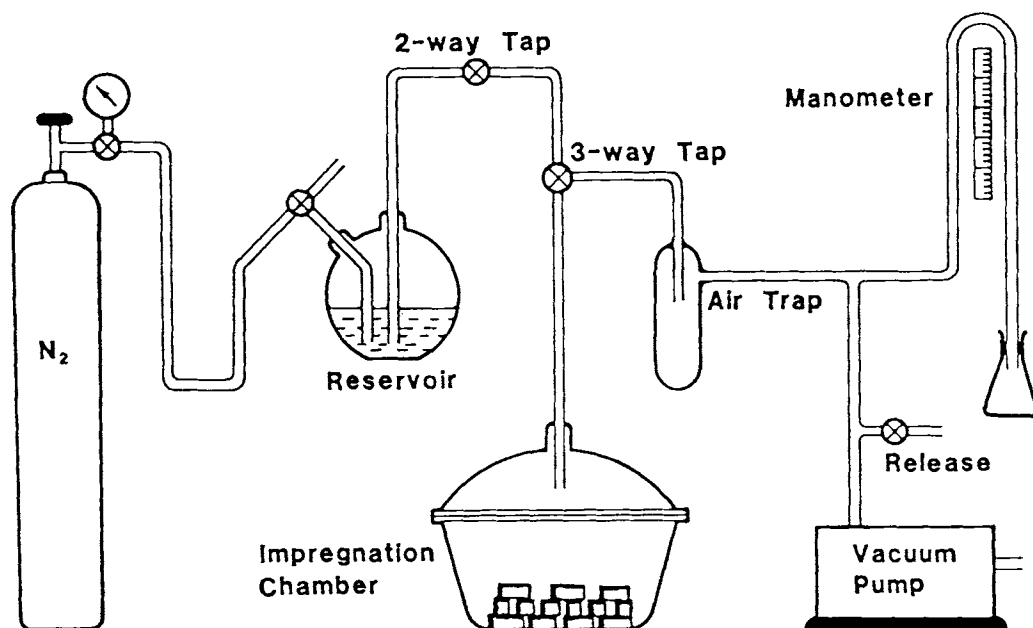


Figure 1 Setup for WPC preparation.

Thermogravimetry

A DuPont 915 thermogravimetric analyzer interfaced with a DuPont 9900 thermal analyzer/computer was used for the TG analyses. Fine shavings of GE or GE composite, weighing about 10 mg, were heated on a platinum pan from 30 to 800°C at a rate of 10°C/min. Air flow over the sample was maintained at 75 mL/min. The change in weight with temperature was processed to display a weight vs. temperature plot. The first derivative, which gave the rate of weight change with temperature, was also obtained.

Differential Scanning Calorimetry

DSC measurements were made on a DuPont differential scanning calorimeter interfaced with a DuPont 9900 thermal analyzer/computer. Samples of fine shavings of GE or GE composite, weighing about 3 mg, were placed in aluminum cups that were subsequently crimped hermetically. The sample and reference, which consisted of an empty aluminum cup similarly crimped, were heated from 30 to 500°C at a rate of 10°C/min. The air-flow rate was maintained at 75 mL/min. The DSC data were presented as heat flow vs. temperature plots.

Elemental Analyses

Fine shavings of unburnt GE composites, incompletely burnt and with char remaining after the LOI experiments, were analyzed for phosphorus and chlorine. The analyses were carried out by the Microanalytical Laboratory, Department of Chemistry, National University of Singapore.

GERONGGANG/POLYMER BLENDS

Mixtures of the bulk polymer and GE were prepared, which were equivalent to the polymer loadings of the corresponding GE composites. These physical polymer blends were then analyzed by TG and DSC as described previously for the GE composites.

RESULTS AND DISCUSSION

LOI and Flaming Characteristics

The LOI values and flaming characteristics of GE and GE composites are summarized in Table I, together with literature values of LOI for poly(methyl methacrylate) (PMMA), polystyrene-*co*-acryloni-

trile (PSTAN), and cellulose for comparison.¹³ GE, with an LOI value of 22–23%, can be considered to be less flammable than the polymers PMMA and PSTAN, which were reported to have LOI values of 17.7 and 19.0%, respectively. However, it is interesting to note that GE-MMA and GE-STAN composites, with polymer loadings averaging from 58 to 79%, had LOI values very similar to that of GE, between 22 and 25%. Chan et al.¹⁴ observed the same phenomenon in their work with rubberwood and rubberwood composites. It appears that the impregnation of a more flammable polymer did not make GE more flammable. A possible explanation is that because the polymer was embedded inside the wood its influence on combustion processes, which proceeded from the outside, was limited.

The LOI values of GE-MVP and GE-MPP were about 28–29%, which were significantly higher than that of GE, indicating the effectiveness of the phosphonates as flame retardants. This observation is consistent with the findings of other researchers.^{5,14} The much lower cost of MPP suggests that it would be the preferred alternative for practical applications.

Besides the LOI values, the flaming characteristics are very important in assessing the effects of the different polymers on flammability properties of the composites. GE-MMA and GE-STAN burned with a greater generation of smoke and soot than did GE, and the dripping of polymer melt, observed particularly during the combustion of GE-MMA, presents a serious fire hazard. The use of PMMA and PSTAN as impregnants must therefore take these factors into consideration. On the other hand, GE-MVP and GE-MPP burned with a candlelike and localized flame, with very little smoke generated and minimal dripping of polymer melt during the combustion. The char was in the form of a rigid rod at the end of the burning period. These flaming characteristics are indicative of the flame-retarding action of the phosphonates.¹⁵

The LOI values and flaming characteristics of GE-MMA and GE-STAN prepared by γ -radiation or by catalyst-heat treatment were almost identical.

TG and DSC Characterization of GE

The thermal behavior of GE characterized by TG and DSC is shown in Figure 2(i), and important data derived from these thermograms are summarized in Table II. The TG curve for GE is typically that of wood, in which pyrolysis of wood components took place below 250°C. From the literature, pyrolysis of hemicelluloses, lignin, and cellulose occurred

Table I Limiting Oxygen Indices and Flaming Characteristics

| | Polymer Loading (%) | LOI (%) | Flaming Time (min) | Description of | | |
|----------------------|---------------------|--------------------|--------------------|-------------------------------------|----------------------|-----------------------------------|
| | | | | Flame | Smoke | Char |
| GE | – | 22–23 | 1.25 | Strong flame engulfing whole length | Some black smoke | Rigid rod breaks under own weight |
| GE-MMA | 68 | 22–23 | 2.5 | Strong flame | Black smoke | Rigid rod breaks under own weight |
| Ge-MMA ^a | 68 | 24–25 | 1.5 | Strong flame | Black smoke | Rigid rod breaks under own weight |
| GE-STAN | 58 | 22–23 | 2.0 | Strong flame engulfing whole length | Black sooty smoke | Full length of char |
| GE-STAN ^a | 79 | 23–24 | 2.5 | Strong flame engulfing whole length | Black sooty smoke | Full length of char |
| GE-MVP | 83 | 28–29 | 1.9 | Candlelike, localized | Little smoke | Rigid rod of char |
| GE-MPP | 82 | 28–29 | 2.1 | Candlelike, localized | Tall stream of smoke | Full length of char |
| PMMA | | 17.7 ^b | | | | |
| PSTAN | | 19.0 ^b | | | | |
| Cellulose | | 18–21 ^b | | | | |

^a Catalyst-heat treatment.^b Ref. 13.

at 200, 220, and 250°C, respectively.^{16,17} Volatilization began at 250°C, and a maximum rate of weight loss of 28.0%/min was recorded at 320°C. The residue remaining at 350°C of 28.5% was subsequently oxidatively combusted and approached 0% around 500°C.

From the DSC studies, two exotherms related to the two phases of volatilization/decomposition at around 290°C and oxidative combustion at 360°C were observed. The corresponding heats of decomposition and combustion were calculated to be 55 J/g and 140 J/g, respectively. An endothermic peak

around 150°C was attributed to glass transitions and phase changes of *in situ* hemicelluloses and lignin.¹⁸

TG and DSC Characterization of GE Composites

The TG and DSC thermograms for GE composites are presented in Figure 2(ii)–(v). The thermal behavior of GE composites was compared with that of GE, based on the initial decomposition temperature (T_d), char yields at 350 and 500°C, and maximum rate of weight loss from the TG curves and the de-

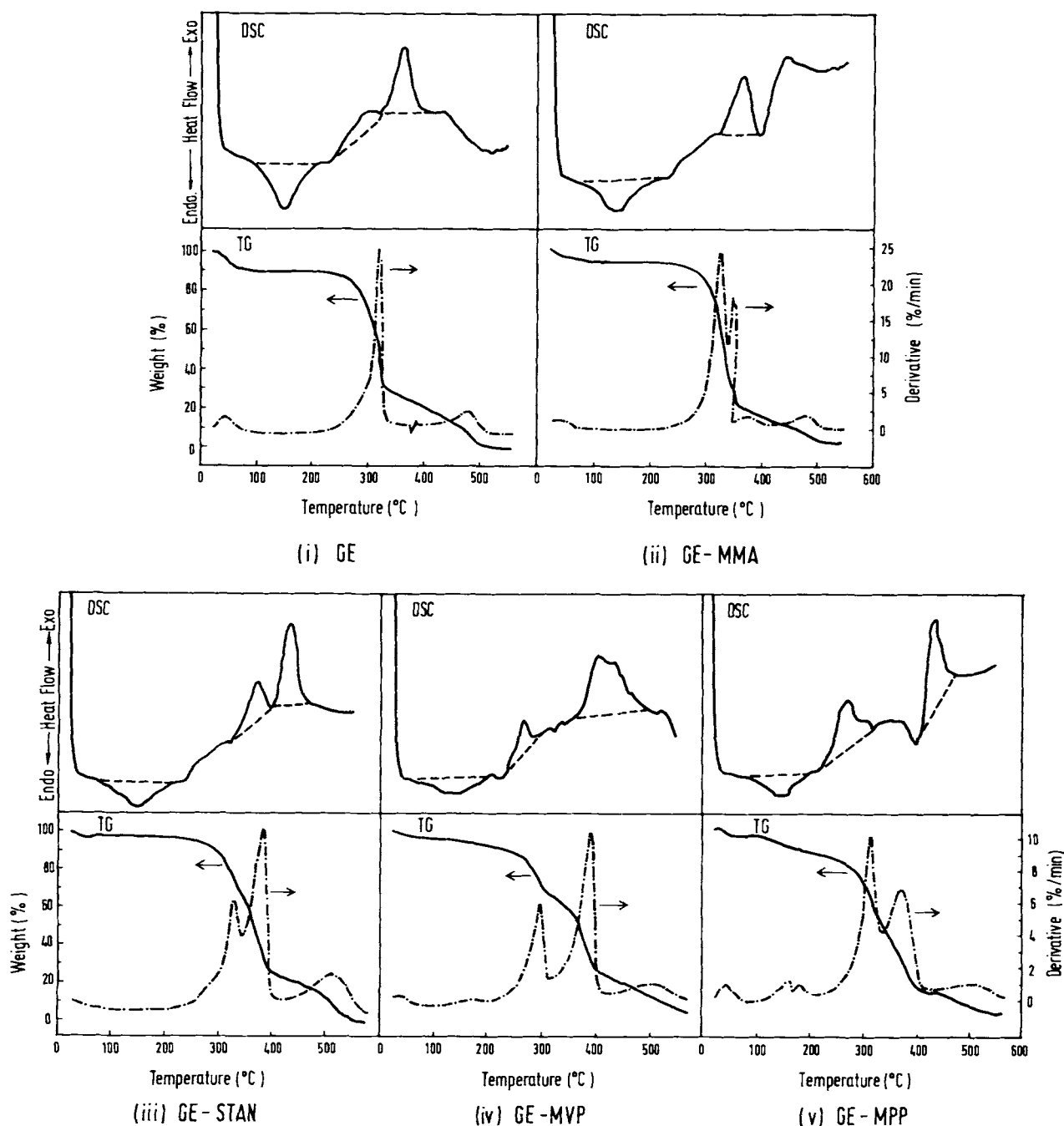


Figure 2 TG and DSC thermograms of GE and GE-composites: (i) GE; (ii) GE-MMA; (iii) GE-STAN; (iv) GE-MVP; (v) GE-MPP.

composition/combustion exotherms from the DSC curves. The data are tabulated in Table II.

The initial decomposition temperatures (T_d) of GE-MVP and GE-MPP at 194 and 162°C, respectively, were significantly lower than that for GE, GE-MMA, and GE-STAN, which were between 240 and 270°C. The lower T_d of the phosphonate-containing composites is related to the low T_d of 180

and 150°C found for poly(methyl methacrylate)-*co*-bis(2-chloroethyl)vinyl phosphonate (PMVP) and poly(methyl methacrylate)-*co*-bis(chloropropyl)2-propene phosphonate (PMPP), respectively, compared to the higher T_d of PMMA and PSTAN of 260 and 340°C.¹⁴

Jain et al.¹⁸ proposed that a lower T_d results in a lower percentage of volatiles produced and, there-

Table II Summary of TG and DSC Data

| | Polymer Loading (%) | Decomposition Temp (T_d) (°C) | Char Yield (%) | | Max Rate of Wt Loss %/min (Temp) | Decomposition Exotherm | | Combustion Exotherm | |
|----------------------|---------------------|-----------------------------------|----------------|-------|----------------------------------|------------------------|--------------------|---------------------|--------------------|
| | | | 350°C | 500°C | | Peak Temp. (°C) | ΔH_d (J/g) | Peak Temp. (°C) | ΔH_d (J/g) |
| | | | | | | | | | |
| GE | – | 250 | 28.5 | 0 | 28.0 (320°C) | 290 | 55 | 350 | 140 |
| GE-MMA | 70 | 270 | 27.4 | 3.2 | 25.0 (320°C) | nd | nd | 360 | 128 |
| GE-MMA ^a | 70 | 240 | 21.6 | 0 | – | nd | nd | 359 | 95 |
| GE-STAN | 70 | 270 | 64.0 | 11.6 | 13.0 (375°C) | nd | nd | 366 | 105 |
| GE-STAN ^a | 70 | 270 | 57.6 | 10.0 | – | nd | nd | 364 | 75 |
| GE-MVP | 85 | 194 | 59.0 | 13.6 | 11.7 (375°C) | 260 | 70 | 400 | 300 |
| GE-MPP | 80 | 162 | 42.0 | 6.4 | 10.3 (320°C) | 272 | 90 | 367 | 52 |

nd = not detectable.

^a Heat-catalyst treatment.

fore, a high char yield. This was substantiated by the high char yields obtained for GE-MVP and GE-MPP at 350°C of 59 and 42%, respectively. The char yield for GE-STAN was also notably high, ranging between 58 and 64%, and can be attributed to the cyclization of the polyacrylonitrile fraction that forms a graphitelike resin, resulting in high char formation.¹⁹ The char remaining after oxidative combustion determined at 500°C was similarly higher for GE-MVP, GE-MPP, and GE-STAN. The char yields for GE-MMA were 22–27% at 350°C and 0–3% at 500°C. The observed low char yields can be attributed to the rapid unzipping of PMMA chains to highly flammable volatile MMA.¹⁹ Studies using rubberwood to form various composites showed very similar results.¹⁴

The maximum rate of weight loss for the phosphonate-containing composites and GE-STAN were correspondingly much lower than that for GE and GE-MMA, around 10–13%/min as compared to 25–28%/min.

It was more difficult to compare data from the DSC thermograms, as endothermic or exothermic peaks tended to be broad and sometimes not very distinct. The decomposition and combustion exotherms of GE-MVP and GE-MPP occurred at around 260–272°C and 400–367°C, respectively. The higher temperature at which combustion of pyrolytic products took place for these composites is again indicative of the flame-retarding action of the phosphonates.²⁰

The low heat of combustion recorded for GE-MPP of 52 J/g is further evidence of MPP acting as a flame retardant, as a lower heat of combustion means less heat being generated and radiated back to support combustion. The relationship between

flammability and low heat of combustion was established by Ohe and Matsura.²¹ However, a very high heat of combustion of 300 J/g was recorded for GE-MVP, although MVP has been shown to exhibit flame-retarding properties. It is suggested that at the high combustion temperature of 400°C for GE-MVP many different reactions were occurring at the same time, contributing to the high heat of combustion observed.

An endothermic peak in the region of 150°C, similar to that observed for GE, was also present for the different GE composites and can be similarly attributed to phase changes of wood components.

Mechanism of Flame-Retarding Action

Since phosphorus (P) and chlorine (Cl) are known to be associated with the flame-retarding behavior of the phosphonates, elemental analyses of the unburnt composite, incompletely burnt composite, and char for phosphorus and chlorine were determined and are listed in Table III.

Taking into account the % polymer loading and the % of P or Cl determined from elemental analyses of the unburnt composites, the ratios of MMA to the corresponding phosphonate for GE-MVP and GE-MPP were estimated to be 13 : 1 and 12 : 1, respectively. These ratios are much higher than the 3 : 1 MMA:phosphonate mixture used for preparing the composites. It appears that there was preferential uptake of MMA. Nevertheless, in spite of the relatively small quantity of phosphonate incorporated in both GE-MVP and GE-MPP, it was effective in imparting flame retardancy to the composites.

Combustion of wood, like other polymeric material, is known to proceed as a two-stage process.

Table III Elemental Analyses of P and Cl in GE-MVP and GE-MPP

| | Phosphorus Content (%) | | Chlorine Content (%) | |
|-------------------------|------------------------|--------|----------------------|--------|
| | GE-MVP | GE-MPP | GE-MVP | GE-MPP |
| Unburnt composite | 1.70 | 1.66 | 3.51 | 3.06 |
| Incompletely burnt char | 1.62 | 1.91 | 2.62 | 1.50 |
| Char | 1.53 | 1.13 | 0 | 1.05 |

It begins with the thermal degradation to form low molecular fragments, which is an endothermic process, requiring the transfer of energy to the wood from an external source. When the rate of pyrolysis becomes high enough to provide a steady concentration of gaseous fuel in the air layer above the wood surface, in excess of the lower explosion limit of the fuel-oxidant mixture, ignition can occur. Ignition can take place either by an outside source or, if the temperature is sufficiently high, by spontaneous auto-ignition.²² Based on this model of wood combustion, flame-retarding action can be effected either through the gaseous-phase or the condensed-phase mechanism. A flame-retardant that acts by the gaseous-phase mechanism essentially inhibits the exothermic oxidative reactions in the flame, thus reducing energy feedback to the wood surface, which, in turn, renders the material less flammable. Halogen-based flame retardants are known to operate in this mode. Flame-retardants that act in the condensed phase alter the mode of pyrolysis to favor the formation of nonvolatile residue rather than flammable gases. Organophosphorous compounds operate in this manner.²³

Flame retardants that function in the condensed phase are characterized by enhanced char formation and their retention in the char or incompletely burnt residue. Flame retardation by a vapor-phase mechanism is characterized by the loss of the flame retardant from the burning element.^{24,25} From the results of the elemental analyses, in both GE-MVP and GE-MPP, the P content of the incompletely burnt char and char were close to that of the unburnt composite, within $\pm 10\%$ and $\pm 30\%$, respectively. The retention of P and the high char yields observed in the TG experiments suggest that the mode of operation of P in flame retardancy was through the condensed-phase mechanism. This observation is consistent with those of other researchers studying the effects of P compounds on flame retardation of cellulosic materials.²⁶ In addition, flame retardants functioning in the condensed phase have been shown to be more effective in cellulosic materials.²⁵

On the other hand, Cl was seen to be lost from the incompletely burnt composite and from the char for both GE-MVP and GE-MPP. In the case of GE-MVP, 25% was lost from the incompletely burnt composite, with none left in the char. For GE-MPP, 51% was lost from the incompletely burnt composite and 66% from the char. It is evident from these results that Cl imparted flame retardancy through a gaseous-phase mechanism.

Grafting of Wood Components and Polymer

To obtain information regarding the nature and extent of interaction between wood components and the respective polymer, the TG and DSC thermograms of GE composites were compared with that of the corresponding physical blend. In addition, so-called theoretical TG curves were constructed from the TG curves of GE and the bulk polymer, based on their proportion in the composites, and were compared as well. The premise is that if chemical interactions existed between wood components and the polymer, the TG and DSC thermograms for the GE composite would be different from that of either the physical blend or the theoretical curves.

The TG and DSC thermograms of the different composites are shown in Figure 3(i)-(iv). Comparison of the GE composite thermograms with that of the physical blend and the constructed theoretical curves showed that the GE-MMA composite curves were fairly similar to that of the physical blend and theoretical curves. On the other hand, the thermograms for GE-STAN, GE-MVP, and GE-MPP were quite different from the blend and theoretical curves. This seems to indicate that grafting of STAN, MVP, and MPP to wood components has taken place. The evidence of grafting from this study alone is, however, not conclusive. Further evidence of grafting in the GE-STAN composite is shown more clearly from our FTIR studies.²⁷ Work is currently being undertaken to confirm grafting for the GE-MVP and GE-MPP composites using electron

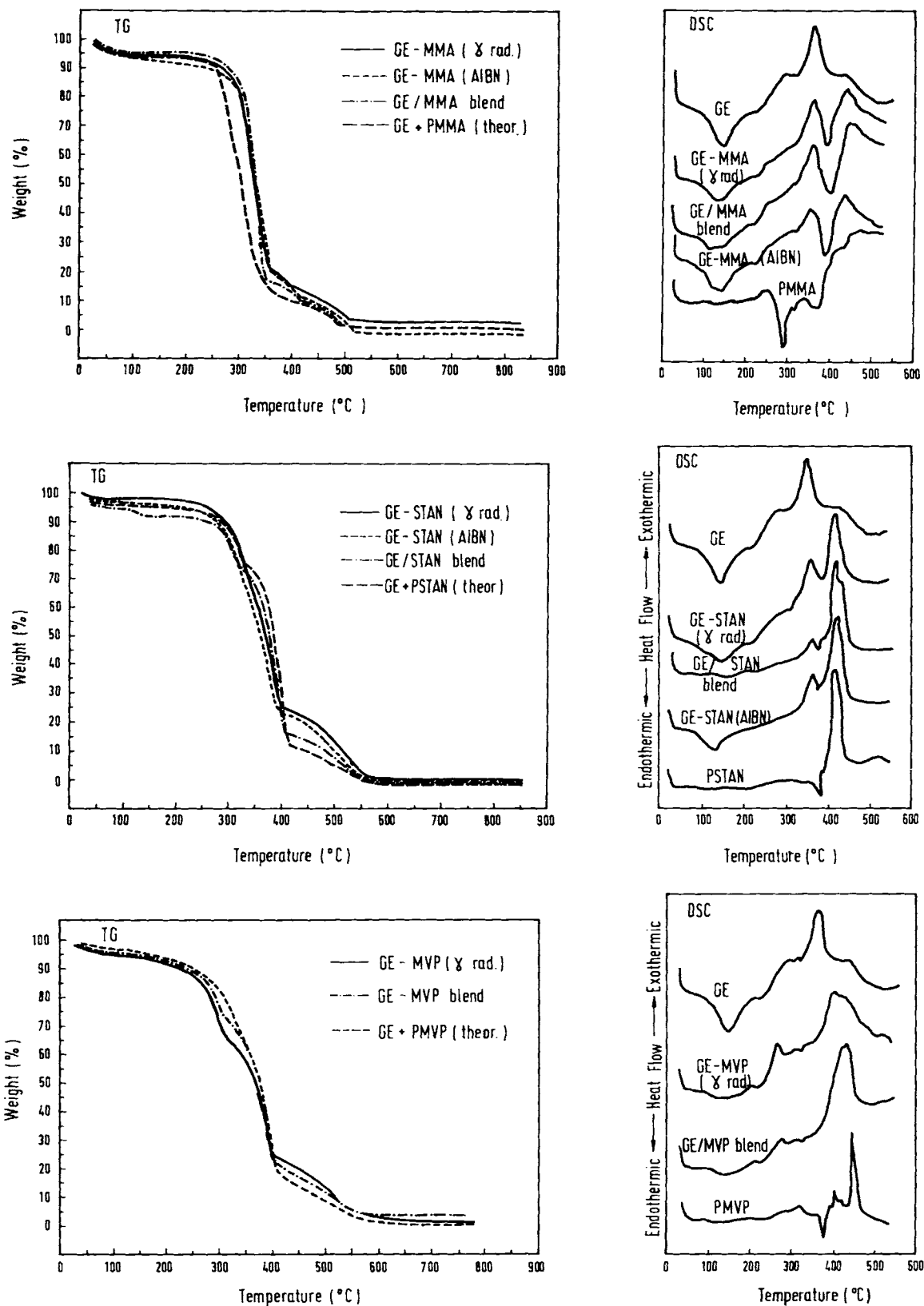


Figure 3 (i) TG and DSC of γ -radiation, AIBN, blend, and theoretical GE-MMA. (ii) TG and DSC of γ -radiation, AIBN, blend, and theoretical GE-STAN. (iii) TG and DSC of γ -radiation, AIBN, blend, and theoretical GE-MVP. (iv) TG and DSC of γ -radiation, AIBN, blend, and theoretical GE-MPP.

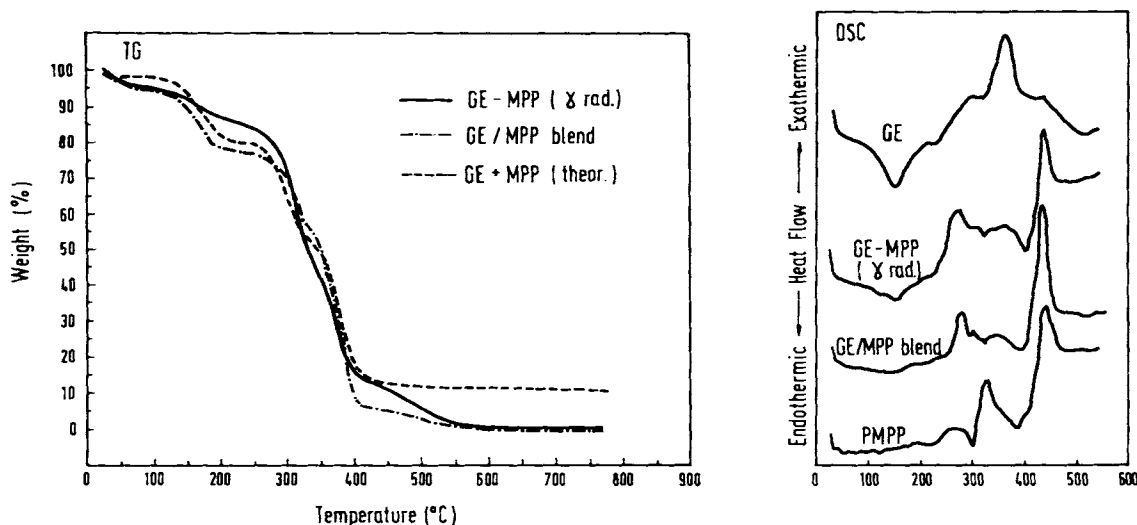


Figure 3 (Continued from the previous page)

spectroscopy for chemical analysis (ESCA) and solid-state NMR.

TG and DSC curves of the different composites, prepared either by γ -radiation or catalyst-heat treatment, shown in Figure 3(i)–(ii), were identical, indicating similar thermal properties. FTIR studies have shown that they are very similar chemically and they also have very similar bulk properties.^{27,28}

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