

FLAME RETARDANT PROPERTIES OF PHENOLIC THERMOSET AMENDED
WITH SILOXANE AND MONTMORILLONITE CLAY

THESIS

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ABSTRACT

Significant growth of phenolic resin systems has occurred within the last decade due to their importance in aircraft interiors and some segments of mass transportation. While phenolic matrix composites are inherently fire retardant, better properties are required in some applications (such as submarines), where safety tolerances can be very demanding. The direction of this research was to determine if pendant dimethylsiloxanes or montmorillonite clay (nano-layered aluminosilicates) would enhance the fire retardant properties of a phenolic system crosslinked with 1,3-bisoxazoline. Additionally, we sought to determine whether their effect on the modulus and other mechanical properties was complementary.

The first investigation dealt with the covalent addition of an epoxy-siloxane pendant to a novolak phenolic backbone, followed by crosslinking. Some recent patents have suggested that siloxanes are effective fire retardants for phenolic systems, although whether these commercial siloxanes are covalently attached, or part of a blend, is unclear. We attempted to produce only covalently attached siloxanes, with IR and NMR evidence for the reaction, and a stoichiometric excess of phenolic -OH to assure relatively complete reaction. Varying siloxane composition in these plaques did not improve the peak heat release rate (PHRR) within the $\pm 10\%$ standard deviation observed, nor was the mass loss affected. Values were found to be about 180 kW/m^2 and 66%, respectively (at 75 kW/m^2 heat flux test conditions.) The flexural properties generally decreased; for

instance, the flexural modulus dropped from 734 Kpsi for the neat phenolic to 500 Kpsi for the 8% siloxane-modified phenolic. Lower modulus was to be expected given the flexibility of the incorporated siloxane bonds.

The second investigation dealt with incorporation of nano-sized clay platelets into the phenolic using two approaches, solvent and extrusion, each followed by crosslinking with 1,3-bisoxazoline. Only one formulation of quaternary ammonium ion-exchanged clay produced an homogenous blend. This was co-precipitated with the phenolic in a toluene-ethanol solvent, evaporated and subsequently crosslinked. The solvent-processed blends showed a 5% increase in the PHRR, while the glass transition temperature (T_g) dropped from 264°C to 154°C. Both results are explained by occluded solvent in the crosslinked plaques, despite extended processing times designed to remove the solvent before crosslinking.

Extruded blends showed some reproducible improvement in the PHRR, but not significant within the limitations of a standard deviation of $\pm 10\%$. The flexural properties were not improved for the clay-modified phenolics. However, X-ray diffraction and transmission electron microscopy images showed evidence of intercalation of the polymer into clay galleries, which is an important beginning in understanding eventually how to exfoliate the clay into these systems.

The production of materials with both clay and siloxane was also attempted. The siloxane modification seemed to change the rate at which crosslinking can occur in the presence of clay, and plaques could not be poured before the material set up, preventing either mechanical or mass loss calorimetry testing.

1.0 INTRODUCTION

1.1 Resin System

Phenolic resins comprise a large family of polymers and oligomers composed of a wide variety of structures based on the reaction products of phenols or substituted phenols with formaldehyde. The first work with phenolic resin was initiated by Baekeland in 1900¹ using phenol and formaldehyde as the starting materials. He established not only the difference between the acid- and base-catalyzed products, but also the importance of the excess of the phenol or formaldehyde in producing the intermediate. Baekeland also developed the technology to convert the reactive resin, which had a tendency to foam and cure to a brittle product, into a useful molded material by adding wood or mineral fibers and molding it under heat and pressure. The final molded parts were tough and thermally stable.²

Early phenolic resins consisted of either self-curing, resoles, which are made with an excess of formaldehyde, or novolaks, which are thermoplastic in nature and required a hardener. The incorporation of alkyl phenols into the resins (Table I) reduces reactivity, hardness, crosslink density and color formation, but increases solubility in non-polar solvents and flexibility.³

Table I. Substituted Phenols Used for Phenolic Resin.

Substituted Phenol	Resin Application
Cresol	coatings, epoxy hardeners
<i>p-t</i> -Butylphenol	coatings, adhesives
<i>p</i> -Octylphenol	carbonless paper, coatings
<i>p</i> -Nonylphenol	carbonless paper, coatings
<i>p</i> -Phenylphenol	carbonless paper
Bisphenol A	low color molding compounds, coatings
Resorcinol	adhesives
Cashew nutshell liquid	friction particles

1.1.1 Polymerization.

The reaction of formaldehyde with phenol leads to either a heat-reactive resole or a stable novolak depending on the ratio of phenol to formaldehyde and the catalyst used, such as strong acid or alkaline bases as shown in Figure 1.⁴

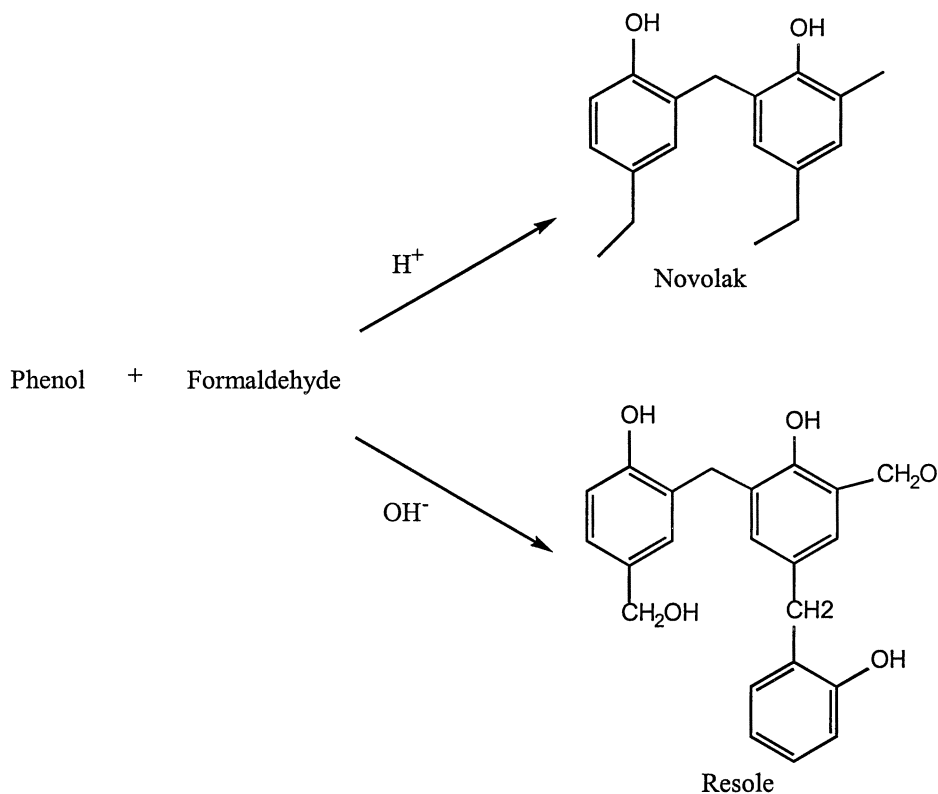


Figure 1. Formation of Novolak and Resole.

1.1.2 Resole

Resoles are produced with a molar ratio of formaldehyde to phenol of 1.2:1 to 3.0:1. Common alkaline catalysts used are NaOH, Ca(OH)₂, and Ba(OH)₂. Resoles cover a wide range of structures and properties: solid or liquid, water soluble or insoluble, alkaline or neutral, slow-curing or highly reactive. Under basic conditions, the reaction of phenol and formaldehyde involves the addition of formaldehyde to the phenolate species leading to *ortho*- and *para*-hydroxymethyl phenols (Figure 2).

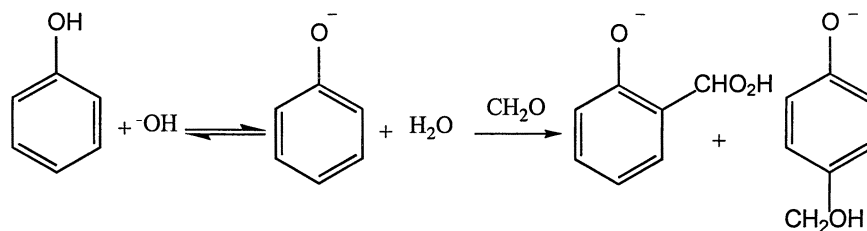


Figure 2. Phenolate Formation.

The ratio of the two isomers depends on the nature of the cation and pH. *Para*-substitution is favored by potassium and sodium cations and higher pH, whereas *ortho* orientation is favored at lower pH and by divalent cations, such as calcium, barium, and magnesium cations.⁵ Investigation showed that the base-catalyzed reaction of phenol and formaldehyde increases the amount of *p*-hydroxymethyl phenol compared to the acid catalyzed reaction. The reaction leads to a 2:1 ratio of *para/ortho* isomers; but, the separation of the two isomers is hard to achieve.⁴

Some resoles are obtained using amine catalysts, which affect chemical and physical properties because the amine is incorporated into the backbone of the resin. Ammonia and hexamethylenetetraamine are frequently used in practice to produce solid, grindable, water-insoluble resoles for molding compounds. Compared to the resin obtained from catalysis water NaOH, this resin has higher molecular weight, less free phenol, and a higher Tg, the last being due to the hydrogen bonding interactions between backbone amine units and the phenolic hydroxyl groups.⁶

1.1.3 Novolak

Phenolic-novolaks are thermoset resins, the molecular weight of which varies some 500 to 5000 g/mol. In a conventional novolak process, molten phenol is placed into a reactor, followed by a precise amount of acid catalyst. For safety reasons, formaldehyde is then added slowly in a stepwise fashion, since the reaction enthalpy is above 80 kJ/mol.⁷⁻⁸ The molar ratio of formaldehyde to phenol is 0.75:1 to 0.85:1. A small amount of solvent is used, such as toluene and xylene, in the process to remove the heat of the reaction, and the reaction is completed after 6-8 hours at 94°C. Methylene glycol is converted to a hydrated carbonium ion which adds to the *ortho* and *para* position of the phenol with the elimination of water. The next step is for the hydrated benzylic carbonium ions to react at the free *ortho* and *para* positions on another phenol molecule to form methylene-linked bisphenols. The nonreacted phenol and water are then removed under high vacuum, since traces of phenol and water affect the cure and final resin properties. Bisphenol F can be considered the simplest novolak and is mixture of isomers; the *o,p'* isomer predominates, followed by the *p,p'* and *o,o'* (Figure 3).

Phenolic resins with a 500-1000 g/mol molecular weights are essentially linear because of the much lower reactivity of the doubly-reacted phenolic units. In higher molecular weight polymers, the low concentration of end groups and unreacted phenol causes branching.⁹ End groups are more reactive than the backbone group; in fact, phenolics with higher end group content will cure faster because of this higher resin reactivity.

The amount and type of acid used affect the properties and structures of the resin. The most used catalysts for novolak are sulfuric acid, sulfonic acid, oxalic acid, and

hydrochloric acid. However, the use of hydrochloric acid has been abandoned because of the formation of the toxic chloromethyl by-product.

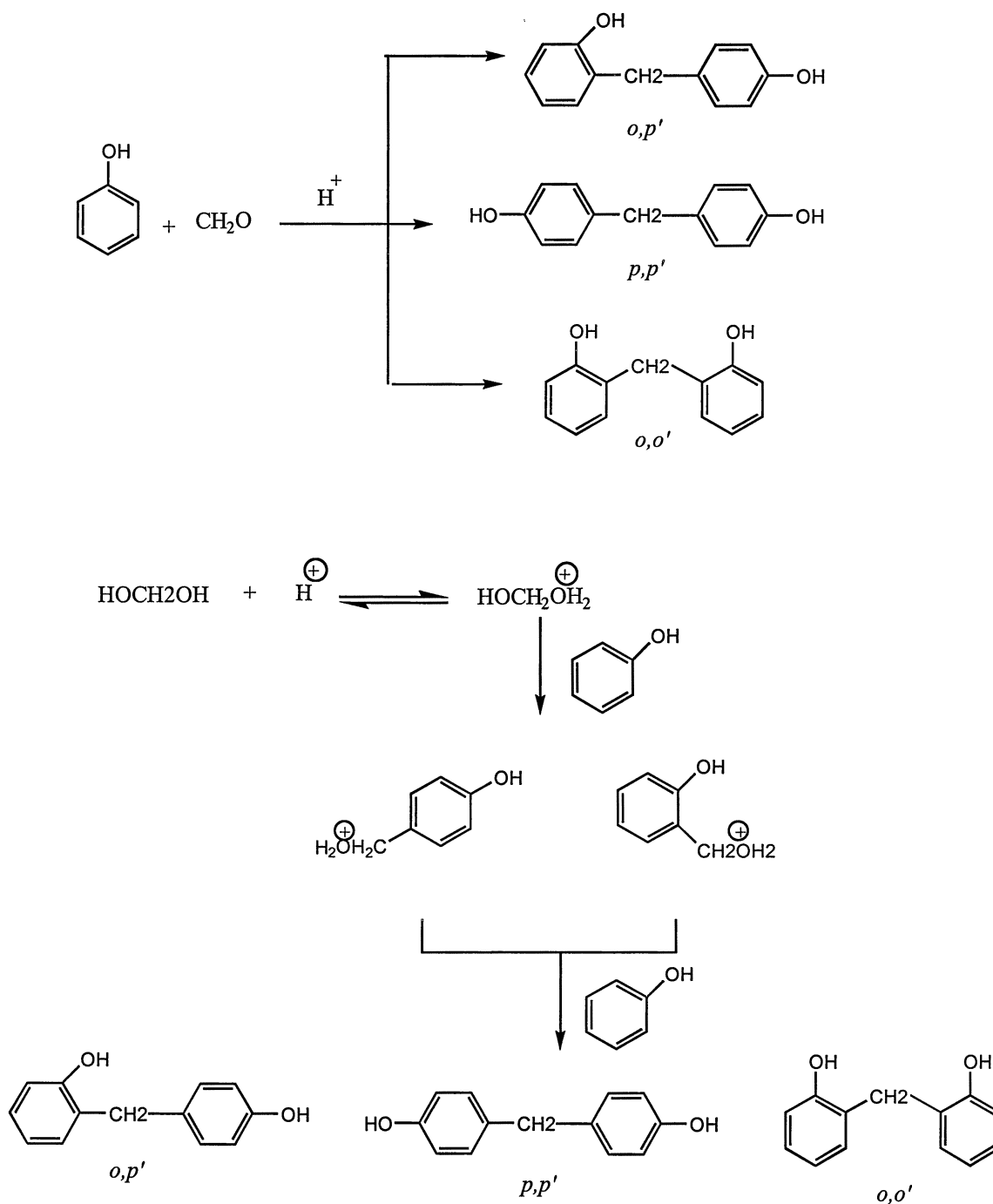


Figure 3. Bisphenol F-Resin Formation.

1.1.3.1 Cross-linked Phenolic Novolak

Novolak resins are generally cured with hexamethylenediamine (HEXA) as the crosslinking agent. Recent studies⁴ showed that the cure begins with the formation of benzoxazine, progresses through a benzylamine intermediate, and finally forms the cured phenolic novolak (Figure 4). Still, a complete understanding of the mechanism of HEXA-cured novolak has been lacking due to the crosslinking and the intractability of the product.⁴ Non-HEXA curing consists of using hydroxymethyl derivatives of phenol, bisoxazolines, bisbenzoxanes and solid resole. Another study⁴, which compared HEXA to bisbenzoxazines, showed that the use of bisbenzoxazine in the novolak does not emit ammonia at low curing temperatures.

Culbertson, at Ashland Chemical Company^{10,11}, reported that 1,3-bisoxazoline, known as 1,3-BOX reacts with novolak as a crosslinking agent in the presence of a triphenylphosphine catalyst. Devinney and Kampa¹² have developed a novel, reinforced thermoset resin system based on a 40/60 ratio of 1,3-BOX to phenolic, which was named PEAR, for Poly Ether Amide Resin, by Ashland. Recently, the technology was sold to Pear Development Company of Oakville, Toronto, Canada. The PEAR system provides significantly reduced flammability, greater strength, (modulus higher than 700 Kpsi, is among the highest for neat thermoset resins) and excellent toughness.

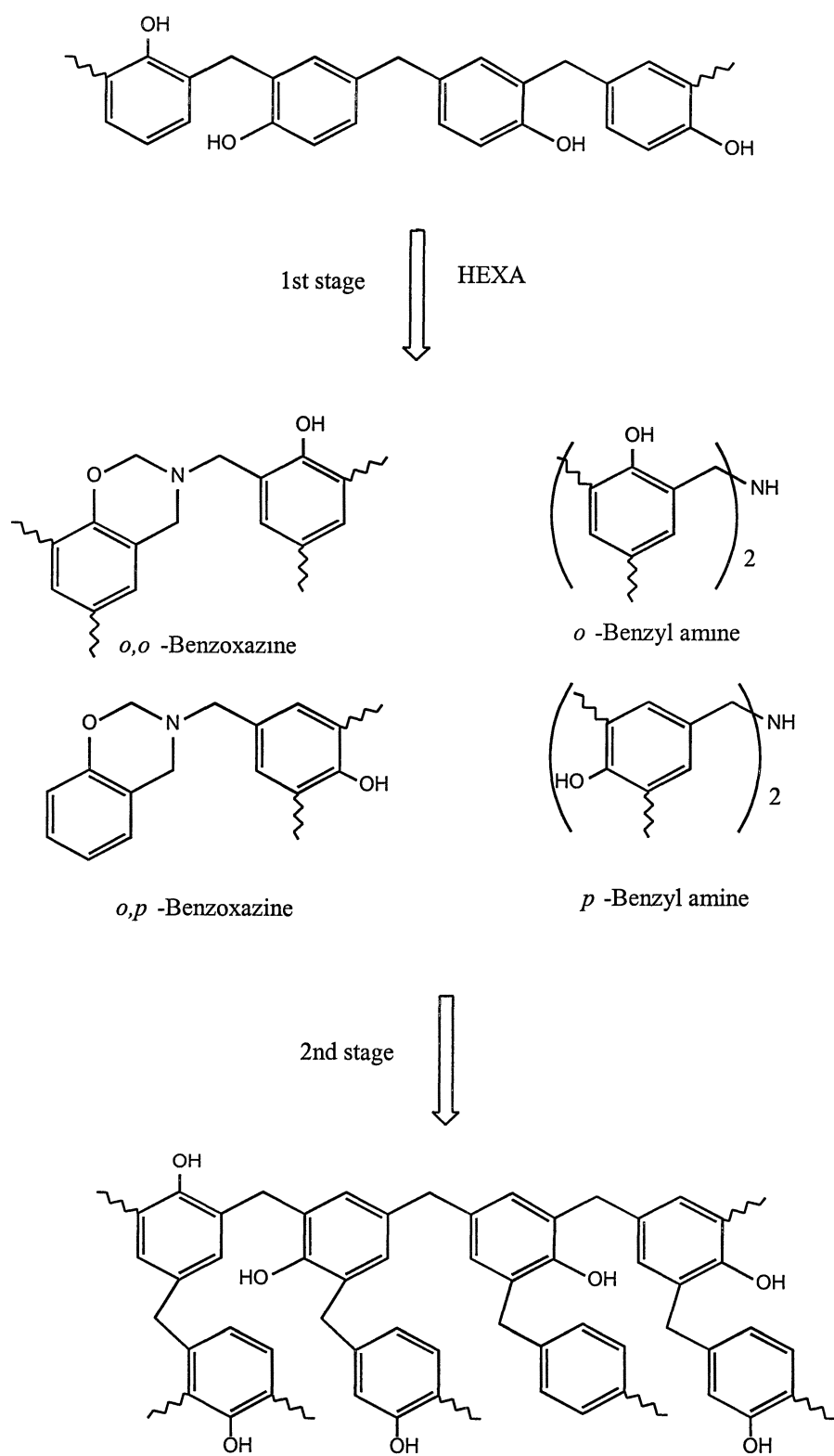


Figure 4. Proposed Cure of Novolak by HEXA

1.2 Montmorillonite Clay and Its Applications

Clays occupy a prominent position among industrial minerals. They have a dramatic impact on life itself, from the soils in which we grow food, to buildings, decorations, industrial products, and high-technology ceramic components for space travel. Clays are utilized in many forms for a wide variety of applications.

Our research is focused on the layered montmorillonite clay that is originally extracted *via* an expensive process from a rock named bentonite, which consists of smectite clay and impurities as shown in Figure 5.

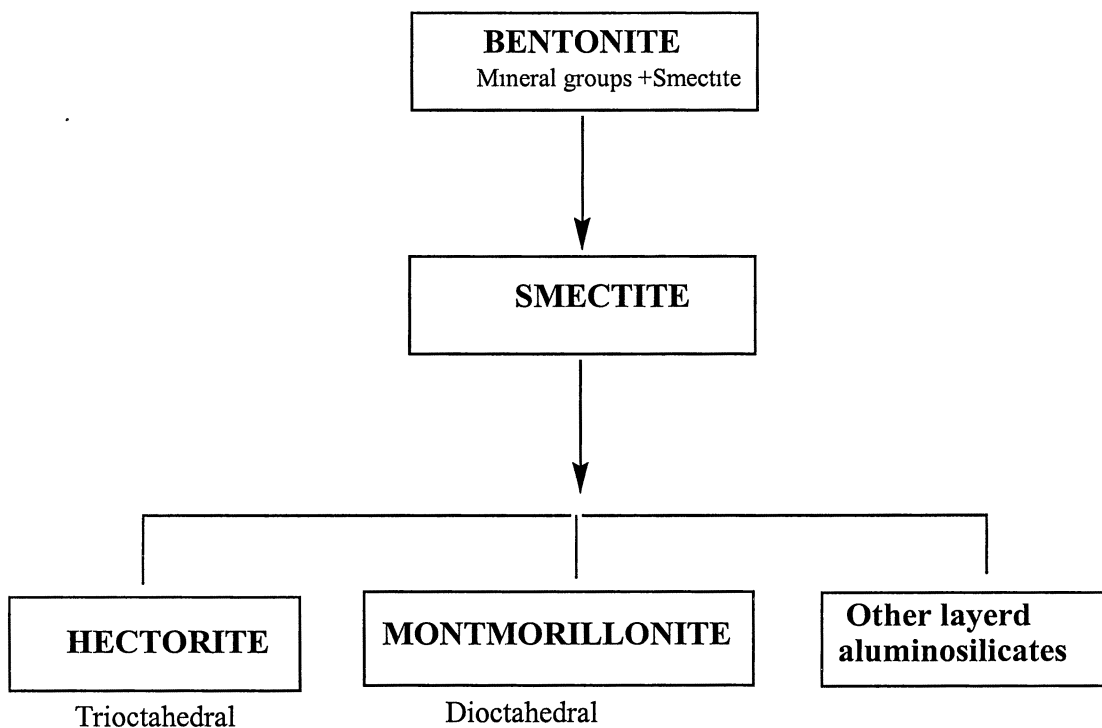


Figure 5. Origin of Montmorillonite Clay.

The unique characteristic of smectite which sets it apart from other minerals is its ability to swell in water. There are many types of smectite; however, the two of greatest commercial importance and value are montmorillonite and hectorite. Commercial availability of hectorite is very limited; whereas, montmorillonite deposits are vast. Montmorillonite is classified as magnesium aluminum silicate and hectorite is classified as magnesium silicate. Their differences in chemical compositions lead to a difference in their crystal shape.

Montmorillonite clays have layered lattice structures in which the clay platelets consist of stacked, two-dimensional oxyanions separated by layers of hydrated cations (Figure 6). The oxygen atoms define layers approximately 10 Å thick which contain two sheets of tetrahedral Si sites which subsequently sandwich a central sheet of octahedral sites. The central octahedral sheet is usually occupied by aluminum or magnesium, sandwiched between two sheets of tetrahedral silicon.

The negative charge on the layers is balanced by interlayer or gallery cations, and in nature these are usually Ca^{+2} and Na^{+} .¹³ The platelets are then stacked into crystallites, called tactoids, with the continuous occupying galleries with the cations between them. The gallery cations in natural smectite can be exchanged with almost any desired cation, including alkylammonium, alkylphosphonium and other organic cations. Normally the polymer matrix is drawn into the gallery and begins the process of increasing the spacing between the platelets (d-spacing). Only when the platelets are separated from their crystallites and surrounded by polymer is the blend considered to be a nanocomposite.

Polymer-clay nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated the polymerization of vinyl monomers intercalated into

montmorillonite clay. The most recent methods to prepare polymer-clay nanocomposites have been developed by several groups. In principal these methods achieve nanoscale level distribution of the layered montmorillonite, and consist of the three main processing approaches:^{14,15}

- *In situ* intercalation of the monomer followed by polymerization;
- solvent swelling of the polymer montmorillonite, followed by drying; and
- melt blending, such as extrusion.

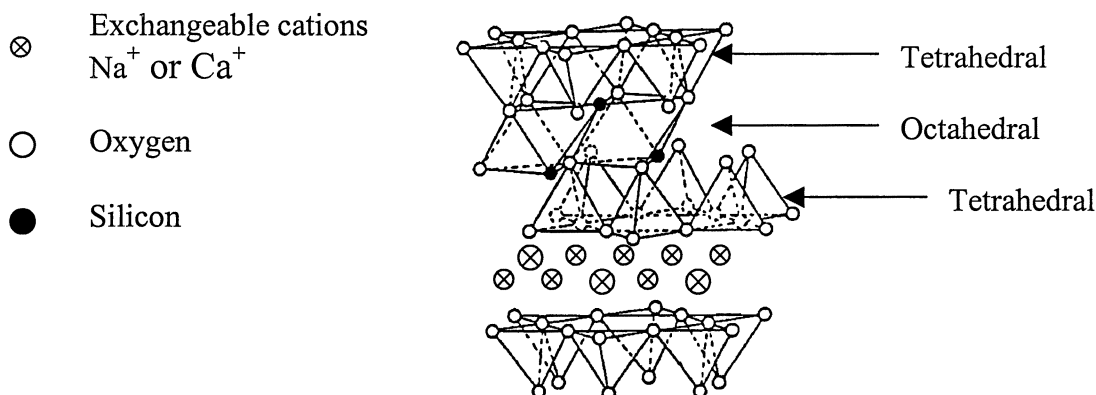


Figure 6. Structure of 2:1 Layered Silicates.

Gilman introduced several terms to describe the state of dispersion of these clays in polymers.^{16,17} The three terms typically used are delaminated (or exfoliated), intercalated and immiscible. Figure 7 shows a schematic illustration of the three different levels of composite dispersion.

Delaminated (exfoliated) structures exist when individual silicate layers are no longer close enough to interact with another layer's cation¹⁷ and the layers are spaced too far apart to see reflection by wide angle X-ray diffraction (XRD). Recent studies suggest

that the observation of random orientation of the platelets by transmission electronic microscopy (TEM) is a more rigorous technique than XRD for determining delamination.

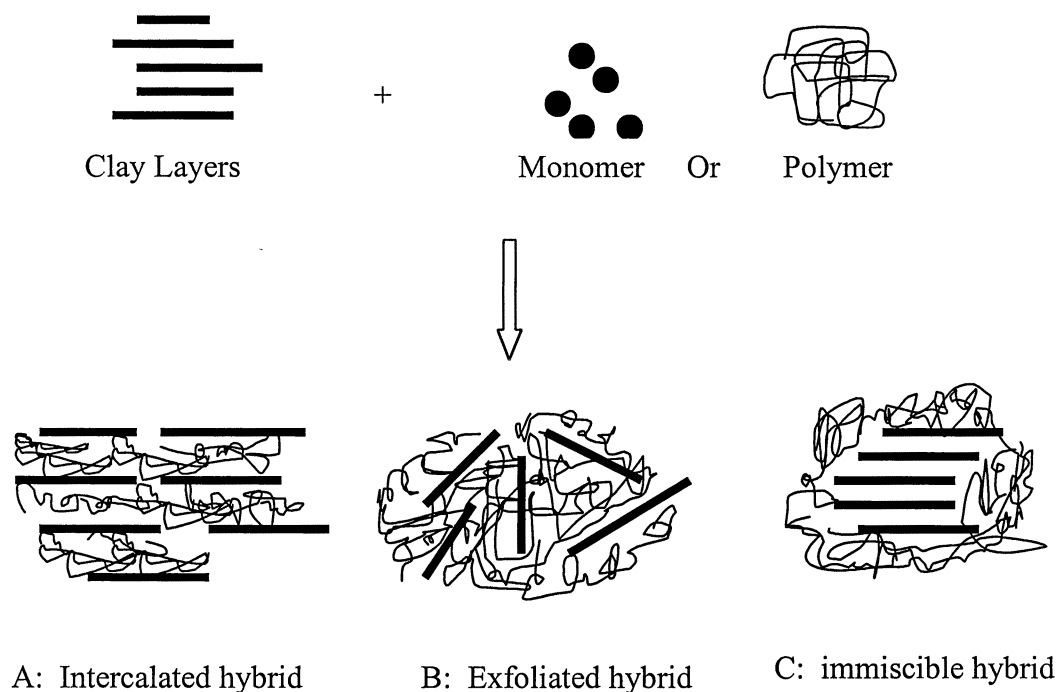


Figure 7. Illustration of The Three Types of Polymer-Clay Nanocomposites.

Intercalated systems exist when the polymer chains have entered between the clay layers, but have not pushed the layers sufficiently far apart to give an exfoliated structure. In an intercalated system the well-ordered multi-clay layered structures will give an XRD pattern with a d-spacing larger than the d-spacing of the original clay.

An immiscible system exists when the clay layers never separate when mixed with the polymer. These tactoids give a XRD pattern that show no spacing change when compared to the original d-spacing of the clay. Basically, immiscible montmorillonite polymer blends are not nanocomposites, but rather, constitute a filled polymer blend.

Polymer-clay nanocomposites have unique properties when compared to conventional filled polymers. For example, the mechanical properties of nylon-6/layered-silicate nanocomposites, with a silicate mass fraction of only 5% show excellent improvement of properties over those for the pure nylon-6. The nanocomposite exhibits a 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength, and 126% increased flexural modulus. The heat distortion temperature is increased from 65°C to 152°C, and the impact strengths are lowered by only 10%.¹⁸ Decreased gas permeability and increased solvent resistance also accompanies the improved mechanical properties as well as improved flammability performance.

The first mention of the potential flame retardant properties of these materials appeared in 1976 as a Japanese patent application on the nylon-6 clay nanocomposites.¹⁹ However, not until more recent studies of improved thermal stability were reported, in both a polydimethylsiloxane (PDMS)/clay nanocomposite²⁰ and in a polyimide clay nanocomposites,²¹ did the serious evaluation of the flammability properties of these materials begin.

In Burnside's studies on PDMS/clay nanocomposites¹⁹ an improvement in thermal stability similar to that reported by Blumstein was observed; however, in this case the PDMS nanocomposites were not prepared by *in situ* polymerization, but by sonication of silanol-terminated PDMS with montmorillonite, which had been ion-exchanged from sodium cation to partially hydrated dimethyl ditallow ammonium cation. In contrast to Blumstein's materials, this nanocomposite contained primarily polymer (PDMS, mass fraction 90%) and only a 10% mass fraction of montmorillonite. Furthermore, the nanocomposites had a featureless X-ray pattern indicating a disordered

delaminated nanostructure. In this case, the nanostructure showed a 140°C higher decomposition temperature than the pure PDMS. The increased thermal stability was attributed to hindered diffusion of volatile decomposition products from the nanocomposite.

Giannelis' studies of aliphatic polyimide-clay nanocomposites demonstrated four important issues associated with polymer-clay composites.²⁰ First, he found that melt processing could be used to prepare both intercalated and delaminated composites.²¹ Second, the study found that an immiscible polyimide-clay mixture, which contained the same amount of silicate (mass fraction 10%) as the intercalated and delaminated nanocomposites, showed no enhancement in the thermal stability. This suggests that the nanostructure is critical to improve thermal stability. Third, the TGA data showed that the intercalated polyimide nanocomposite was more thermally stable than the delaminated nanocomposite. Fourth, Giannelis described self-extinguishing flammability behavior for the polyimide-clay mixture.

Many polymer nanocomposites have also been investigated. For example exfoliated, layered silicate-epoxy-nanocomposites were prepared by Pinnavia *et al.*^{22,23} Ogata and Ogiwara²⁴⁻²⁵ investigated organophilic clay-polyethylene oxide nanocomposites intercalated and prepared by solvent casting with chloroform. Recently, the Toyota group^{14,16} used polymer melt mixing to prepare polypropylene-clay nanocomposite.

2.0 EXPERIMENTAL

2.1 Background

2.1.1 Materials

All materials were used as shipped from the supplier. Table II describes the materials used in this study.

Novolak phenolic resin (HRJ-2190) is a clear, orange brittle material, and is processed at 90°C. Torque measurement was recorded at 90°C and 60 rpm in a Haake torque rheometer with 50ml head and standard rotors.

1,3-Bisoxazoline was obtained as a white powder, with a melting point of 160°C. Due to the high melting point all our reactions were performed in the 150-160°C temperature range.

Montmorillonite clays were provided by Southern Clay Products, in a white powder form, and were used as received; no cation exchange was performed. The different clays with different exchange cations used for this research were:

- Clay with Na^+ cation in the gallery, designated “Na”
- Clay with $(\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_2\text{tallow})$ quaternary ammonium cation surface treatment, designated (MMBT)
- Clay with $((\text{C}_2\text{H}_3\text{OH})_2 \text{N}^+\text{tallow})$ quaternary ammonium cation surface treatment, designated (TEEM)

Tallow is a mixture of fatty acids ($\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}^+$);²⁶ obtained from cattle fat. Figure 8 represent a schematic of the gallery of MMBT-clay.

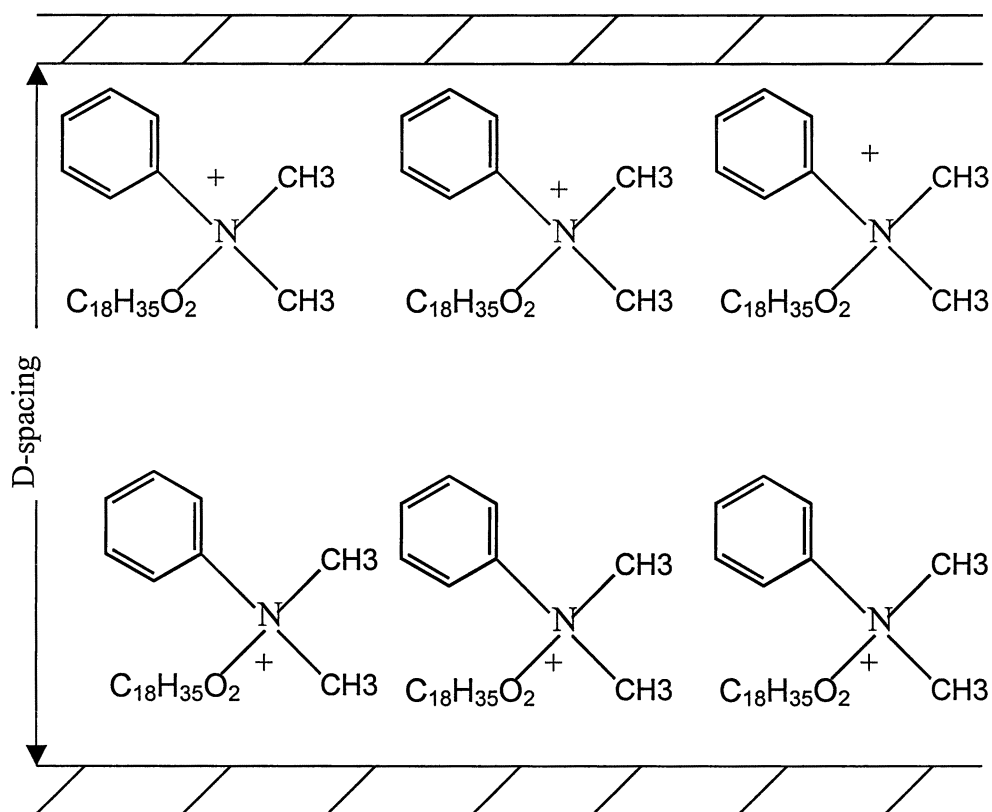
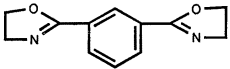
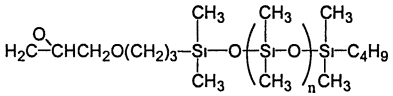


Figure 8. Schematic of Montmorillonite-Clay Gallery with Quaternary Ammonium Ions.

Table II: Physical Properties of Raw Materials.

Material	Company	Comment
Novolak phenolic (HRJ-2190)	Schenectady	Mw=2865 g/mol
	International	Tm=120 (°C)
1,3-Bisoxazoline	Mikumi Seiyaky	Tm=160 (°C)
	(Japan)	
Mono (2,3-epoxypropyl) propyl-ether terminated dimethylsiloxane	Gelest	Mw=1000
		
Na, MMBT, MEET	Southern Clay Products	19-21Å layer spacing
Bis(2-ethylhexyl) phosphite	Aldrich	Mw=302g/mol
$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}]_2\text{P}(\text{O})\text{H}$		

2.1.2 Processing Methods

2.1.2.1 Siloxane-Modified Phenolic Resin

First, 40 g of phenolic resin and 8 g of dimethylsiloxane were placed in a dry, 500 ml, round-bottom flask. The reactants were heated to 150°C and stirred mechanically for 20 hours. The 1,3-bisoxazoline was then added and heated to 150°C, this temperature being

necessary due to the high melting point of the 1,3-BOX. After being mixed to complete homogeneity of the melt, the mixture was then placed in a vacuum oven at the same temperature for at least 50 minutes to remove all air bubbles. The 2 g of bis-(2-ethylhexyl) phosphite catalyst were added to the melt just after degassing, and degassing was continued for 10 additional minutes. After application of a teflon-based mold release, the melt was poured slowly between two preheated plates separated by a silicone gasket, and finally cured for 4 hours at 200°C and 2 hours at 220°C. Other blend compositions were processed similarly.

2.1.2.2 Montmorillonite-Phenolic Blend

2.1.2.2.1 Solvent Approach

MMBT was incorporated into the novolak phenolic-1,3-BOX matrix with the aid of solvents. First, the phenolic was dissolved in ethanol (40/50 mass ratio) to obtain the saturation of the solvent. Saturation was necessary to reduce interaction of the clay with ethanol, because MMBT forms a precipitate, whereas with toluene, gel formation is obtained (formation of gel means the clay has swollen). After the phenolic was completely dissolved, 25g of toluene were added to the solution. The 5g of clay were added slowly to the flask, with mechanical stirring. The stirring must be at a high speed to facilitate the intercalation of the clay. The stirring was maintained for 24 hours to allow swelling and intercalation. Then the solvent was removed, initially by rotary evaporation under vacuum and reheated in a vacuum oven at 150°C to complete solvent removal. The catalyst was added and the blend was molded and cured as described in section 2.1.

2.1.2.2.2 Extrusion Approach

The phenolic resin was mechanically crushed and mixed with clay (100/11 mass ratio) to give a blend ratio which will later be diluted by the addition of 1,3-BOX. The blends were prepared by melt-mixing in a CTW100-conical twin-screw extruder at 100 rpm with a length-to-diameter ratio of 25 and cylinder diameters of 31.8/20 mm for the feed and die ends, respectively. Configuration of the mixing elements is shown below (Figure 9).



Figure 9. Twin Screw Extruder.

The blended phenolic/MMT resin (45g) was mechanically crushed with 60g of bisoxazoline powder and placed in an oven at 150°C. After a complete melt was obtained, the catalyst was mixed in and a vacuum was applied to remove air bubbles. The blend was then molded, and cured as described in section 2.1.

3.0 RESULTS AND DISCUSSION

The potential fire hazard of any material is influenced by the dynamics of the many products created during the combustion including heat release, mass loss, smoke evolution, and evolution of toxic gases (e.g., CO). In reporting fire hazards, the objective is to measure those products and the rate of the evolution as interpreted by national standards to be relevant to the safe escape of human being. The amount of heat produced per volume of sample is one of those standards, in those materials which burn very hot and quickly contribute to catching everything else in the room on fire.

We have concentrated on measuring the dynamics of the heat produced while burning modified phenolics. We also report mass loss, in that the rate of mass loss and the rate of heat release should be related by the thermodynamics of decomposition, vaporization, and combustion of gases. The mass remaining is also important to fire safety in that structural materials which retain their mass longer during a fire may prevent the collapse of objects while humans are escaping, and continue to serve as insulators to slow the spread of the fire. The data collected from the mass loss calorimeter available in our laboratory are:

- Peak heat release rate (PHRR) and time to sustained ignition
- Total heat release (THR)
- Mass loss in percentage
- Average HRR at 180 seconds

In addition, flexural and thermal properties were determined. Incorporation of organic fillers to improve fire retardancy often involves a trade off in mechanical properties for instance, we would expect lower modulus on incorporation of siloxane or lower ductility on incorporation of clays.

These results are discussed in the context of fire performance *versus* mechanical properties for the siloxane, clay, and multi-additives blend.

3.1 Analysis Methods

3.1.1 Flammability Analysis

The heat of combustion is defined as the quantity of heat released when a unit of fuel is fully oxidized. This is determined using an oxygen bomb calorimeter and well reported in handbooks. If all fires involved complex oxidation, then the heat released could be determined simply by weighing the sample as it burns and multiplying the mass loss by the heat of combustion. In reality, combustion does not usually proceed to complete oxidation, but the effective heat of combustion is constant for a given material when burned at a given heat flux under constant ventilation conditions. The effective heat of combustion is determined by an instrument such as a cone calorimeter. Heat release is then determined as the product of the effective heat of combustion and the mass loss rate. Once the effective heats of combustion are known for a material over a range of conditions the heat release can be calculated from mass loss data. Since heat of combustion data were not readily available for our blends, our data were taken from differences in voltages of the thermopiles aligned at the entrance and exit of the mass loss calorimeter (Figure 10). These voltages are converted to heat using a calibration from

methane flow performed daily just prior to the experiment. Correlation of these heat release rate data are under investigation by Koo *et al.*²⁷

While the values may be somewhat lower than those obtained from a cone calorimeter, all data can be compared as a material-screening tool.

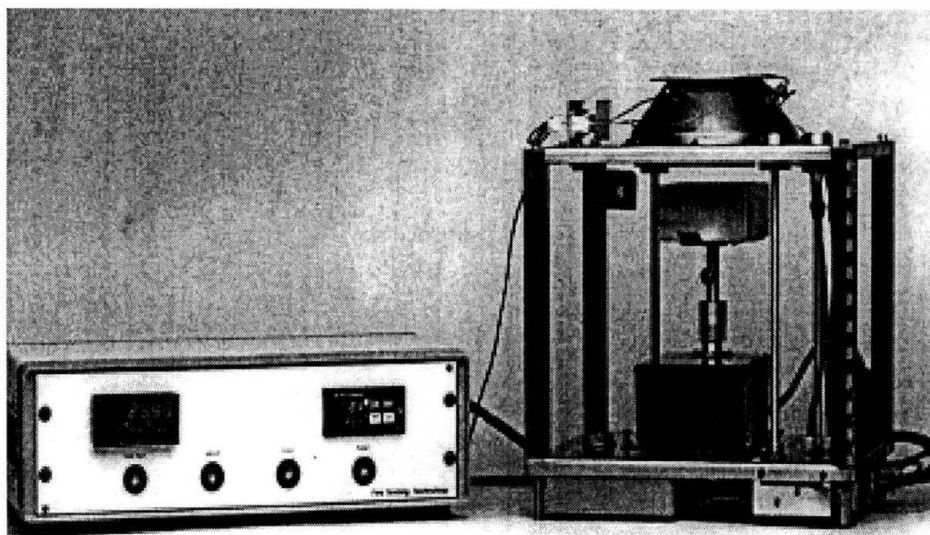


Figure 10 Mass Loss Calorimeter Used for Flammability Test.

The mass loss calorimeter (MLC) apparatus was used for evaluating the flammability of the materials. The heat flux of the MLC was set at 75 kW/m^2 and tests were generally conducted for ten minutes (600s). All the specimens were square (10 cm $\times$ 10 cm); and were wrapped in aluminum foil with an edge frame on top of the sample. Under exposure to the radiant heat flux, ignition of the off-gas from each specimen was accomplished with a high-voltage spark igniter. The primary output of the test is the heat release rate (HRR), which was plotted as a function of time. The parameters that are of

interest are the peak heat release rate (PHRR), the average heat release rate at 180 sec, and total heat release over the 10 min. In addition, continuous mass loss measurements were taken.

3.1.2 Thermal Analysis

3.1.2.1 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) of the virgin material was carried out with a heating rate of 20°C/min under a flow of dry air and argon (17mL/min) using a Rheometric Scientific (TG 1000 M3).

3.1.2.2 Dynamic Mechanical Thermal Analysis

Glass transitions were determined by DMTA (dynamic mechanical thermal analysis) on a Rheometric Scientific (DMTA IV) in the single cantilever bending mode. The Tg's were evaluated as the peak in the *tan delta* with a temperature ramp of 5°C/min at 1 Hz.

3.1.3 Transmission Electron Microscopy

Thick sections of the sample were microtomed at room temperature using a 4° diamond knife, and mounted on 200 mesh copper grids. The specimens were viewed on a JEOL 200 CX transmission electron microscope with a filament operating at 200kV. Individual photomicrographs were taken under a condition to develop the image and provide contrast without melting the sample.

3.1.4 Flexural Testing

The flexural properties were measured with a Sintech 1/D in a 3-point bending mode, a method which is generally applicable to rigid and semi-rigid materials. The test is accomplished by applying a certain load with a speed of 0.0533in/min on a rectangular-shaped specimen which has been cut according to test method in ASTM D5947, (1/2 in wide, 3 in long, and 1/8 in thickness), and which rests on two supports and is loaded by means of a loading nose midway between the support as shown in Figure 11 (ASTM-D790). Our primary interests were the following two properties:

1.Flexural strength: The flexural strength occurs at the midspan. It can be calculated for any point on the curve according to the following equation:

$$S=3PL/2bd^2$$

where S (psi) is the stress in the outer fiber at midspan, P (lbf) is the load at a given point on the load-deflection curve, L (mm) is the support span, b (in) and d (in) are width and depth, respectively of the specimen.

2.Modulus of elasticity: The tangent modulus of elasticity is the ratio, within the elasticity limit, of the stress to corresponding strain. It is measured by the slope of the curve strain *versus* stress using the equation below:

$$E_H=L^3m/4bd^3$$

where E_H is the modulus of the elasticity in bending (psi), L is the support span (in), b and d are the width and depth of the specimen (in), respectively, and m is the slope of the tangent to the initial straight-line portion of the load-deflection curve (lbf/in). All the results were obtained directly from the instrument at room temperature and 60% relative humidity.

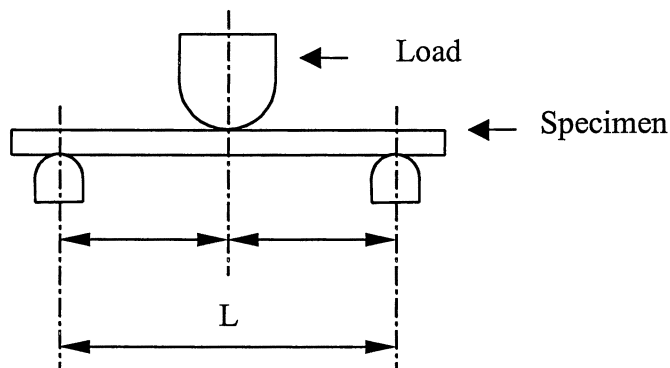


Figure 11. Three-Point Bending Set-up.

3.2 Covalent Pendant Addition of Epoxy-Terminated Dimethylsiloxane

3.2.1 Reaction

Reaction of dimethylsiloxane with the phenolic backbone (Figure 12) was carried out as described previously in the experimental section. The purpose of this reaction was to create a covalent bond between the siloxane and the phenolic functional groups so that a siloxane would be pendant to the backbone of the phenolic chain.

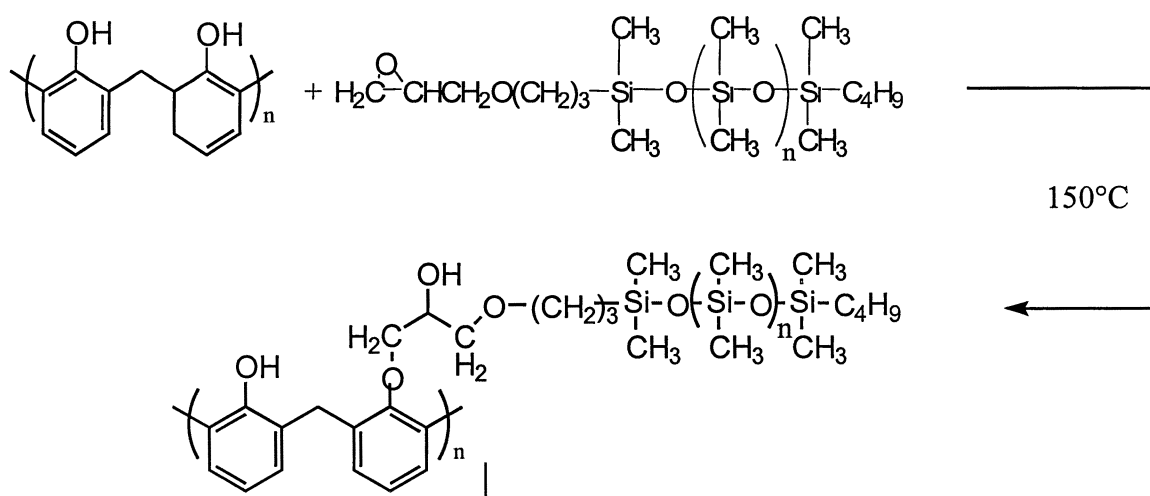


Figure 12. Reaction of Dimethylsiloxane and Phenolic Resin.

NMR and IR spectra were then obtained on the neat phenolic resin to characterize the reaction.

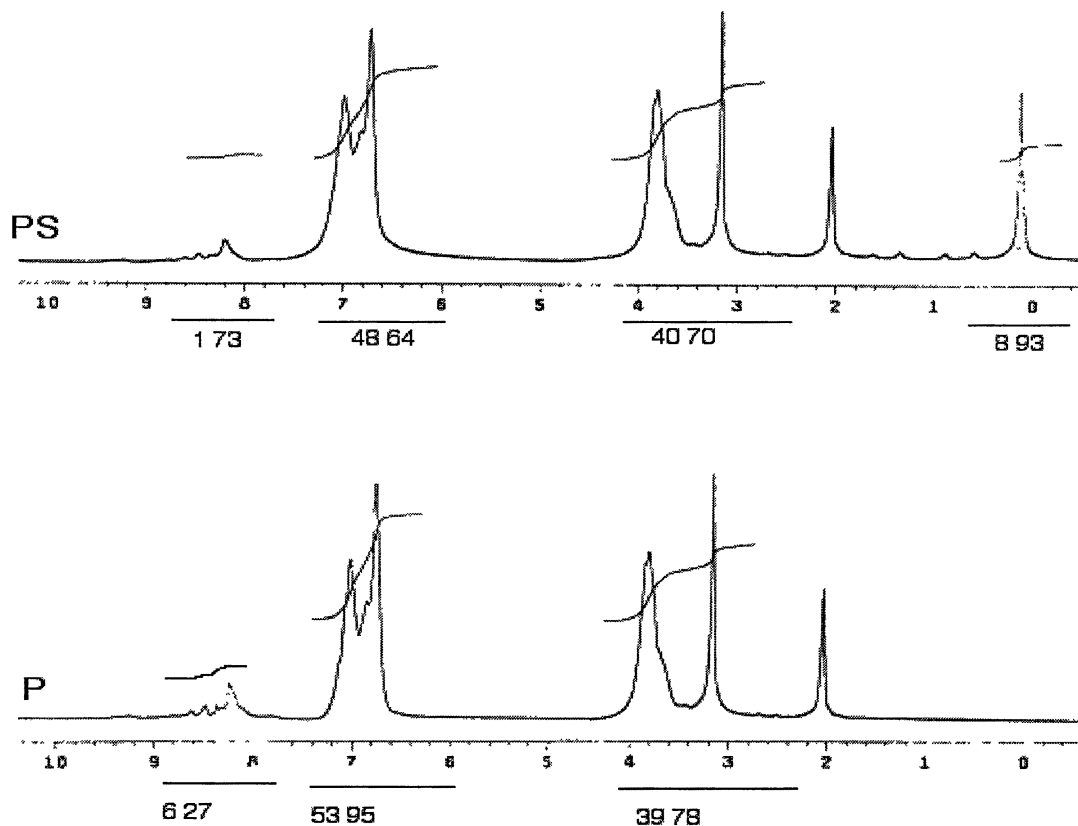


Figure 13. Proton NMR of the Neat Phenolic Resin (P) and the Reacted Phenolic with Dimethylsiloxane (PS).

Proton NMR spectra of the phenolic and reaction product are shown superimposed in Figure 13. The neat phenolic resin (P) in acetone at ambient temperature showed a ratio of hydroxyl hydrogen to benzylic hydrogens of 0.11. After the reaction, the ratio decreased to 0.03, meaning that the number of hydroxyl protons of the neat phenolic decreased during the reaction. The phenolic hydrogens do not disappear completely

because the reaction is not completed, and cannot expected to be completed, in view of the complexity

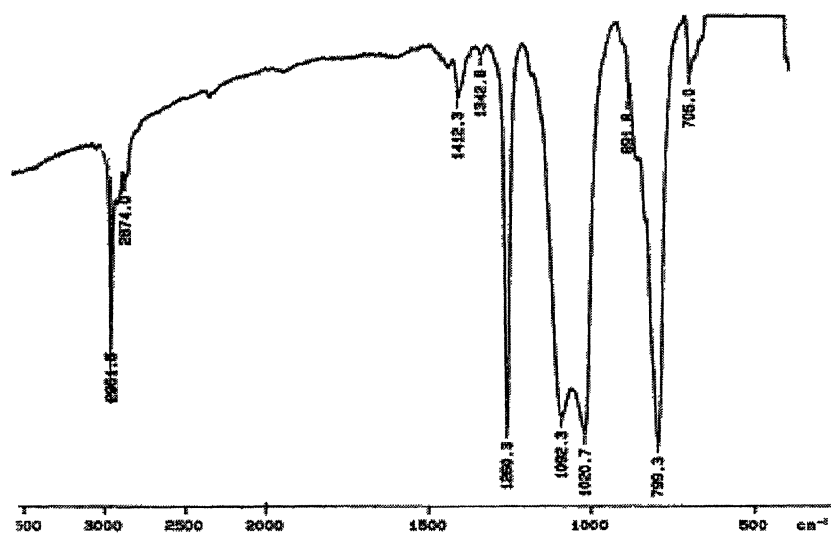


Figure 14. IR Spectra of the Neat Epoxy-Terminated Dimethylsiloxane

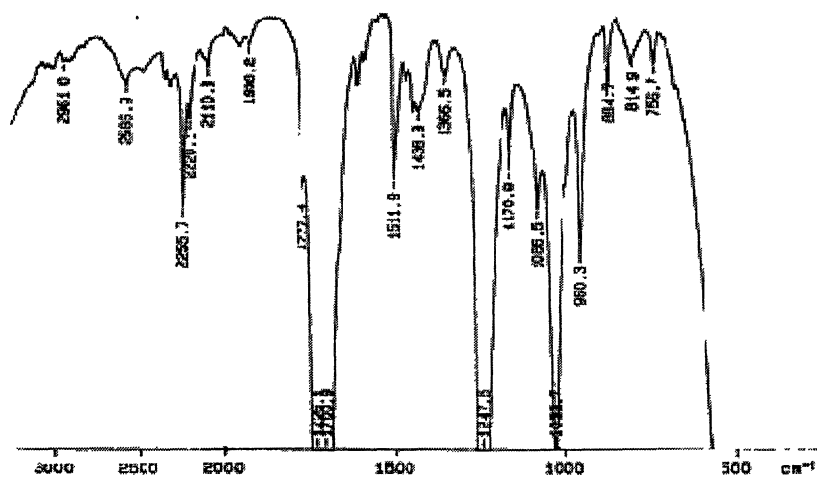


Figure 15. IR Spectra of the Siloxane-Modified Phenolic

of backbone-type reactions. However, the 8:40 weight ratio of siloxane to phenolic was targeted only at siloxane per mole of phenolic, the remaining phenolic OH available for crosslinking later.

To corroborate NMR evidence of reaction, IR spectra were taken and showed a disappearance of the intensity of the peak at 799cm^{-1} (Figure 15), which is assigned to the epoxy bond (C-O) stretch.²⁸

3.2.2 Fire Retardant Properties

Siloxane-modified phenolic was cured with 1,3-BOX and the cured plaques were tested under a heat flux of 75kW/m^2 in the mass loss calorimeter. Table III shows a summary of average values for PHRR, total heat release (THR), and heat release rate at 180 seconds. Calculations were based on burn time of 600 seconds. The percent of the siloxane modifier was varied from 0 to 8% by weight.

Table III: Summary of Heat Release Rate Data at 75kW/m^2 .

Material	PHRR (kW/m^2)	Avg.HRR at 180s (kW/m^2)	THR (kJ)	Mass Loss (%)
PB	185 ± 15	$119\pm$	54 ± 4	24
PBS-5%	203 ± 10	124 ± 12	57 ± 7	34
PBS-8%	179 ± 17	116 ± 22	50 ± 4	38

PB is crosslinked phenolic with BOX, **PBS-5%** is phenolic modified with 5% siloxane and crosslinked with BOX, **PBS-8%** is phenolic modified with 8% siloxane and crosslinked with BOX.

The PHRR of the PBS-5% seems to be the highest at 203kW/m^2 compared with the control at (185kW/m^2). However, these values are indistinguishable when the standard deviation is taken into account. The total heat release (THR) is defined as the area under the curve for heat release rate *versus* time. Average heat release rates at different times as well as THR likewise did not appear to be affected by the percent of siloxane within the limits of the standard deviation. Examples of the heat release rate and mass loss can be seen below in Figure 16.

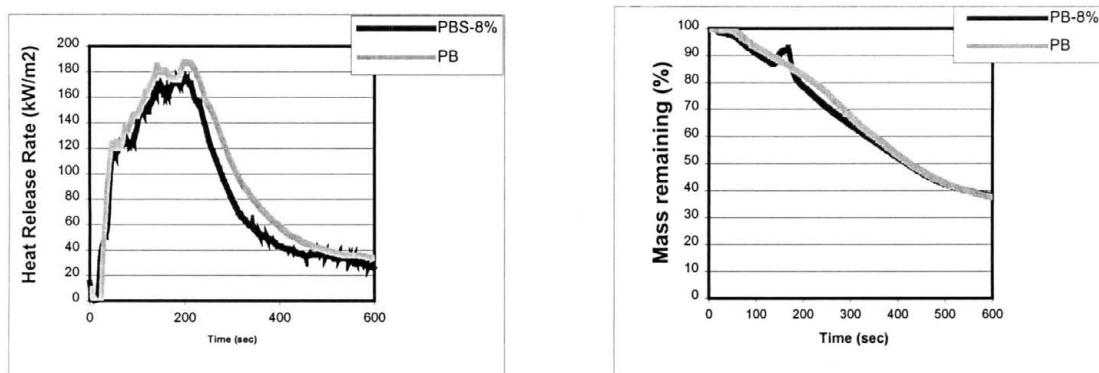


Figure 16. Comparison of Heat Release Rate and Mass Loss of Neat Resin to Siloxane-Modified Phenolics.

3.2.3 Thermal properties

To evaluate the thermal stability of the samples, we measured the 10% mass loss and the char yield using thermal gravimetric analysis in oxidizing and inert atmospheres

(Table IV). Figures 17 and 18 show some representative TGA curves and their derivatives for the PB and PBS-8% in air, respectively.

The addition of the siloxane, even in different concentrations, does not alter the 10% weight loss in either inert or air environments. Also, Table IV data show no differences in the char yields in argon or air with changes in amount of siloxane. These results were not expected, knowing that the siloxane added is thermally stable; however, the concentration of the siloxane in the phenolic/1,3-BOX matrix is not very high. Increasing the concentration of the siloxane in the reaction in order to increase the thermal stability was not possible because two immiscible phases formed.

Table IV: Summary of Thermal Properties of the Siloxane-modified Phenolics.

Material	Tg (°C)	Temp (°C) 10% mass loss Air	Temp (°C) 10% mass loss Argon	% Char (Air) at 900 °C	% Char (Argon) at 900 °C
PB	265±3	405±5	402±5	4	37
PBS-5%	-63/226±3	400±5	398±5	3	37
PBS-8%	-67/250±3	404±5	401±5	4	36

The glass transition temperatures were determined as the peak of the *tan delta*. The *tan delta* as analyzed by DMTA is the ratio of the loss modulus (E') to storage modulus (E).

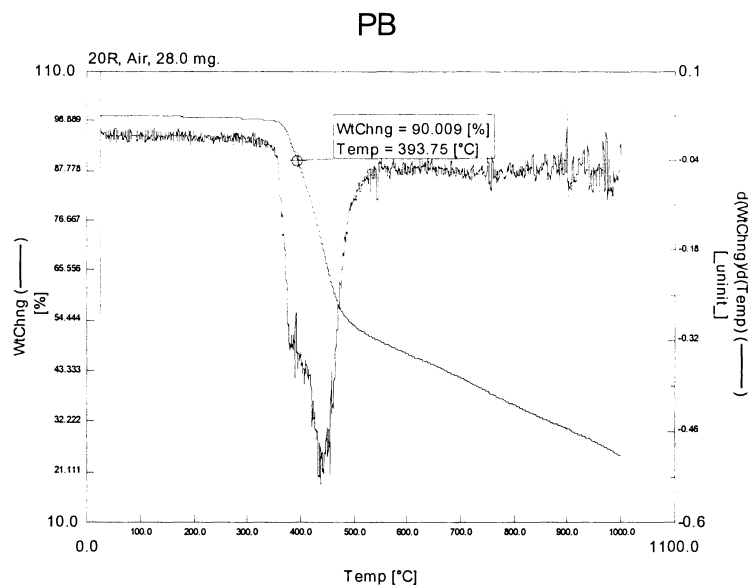


Figure 17. Mass Loss vs. Temperature and the TGA at 20°C/min of the Neat Phenolic.

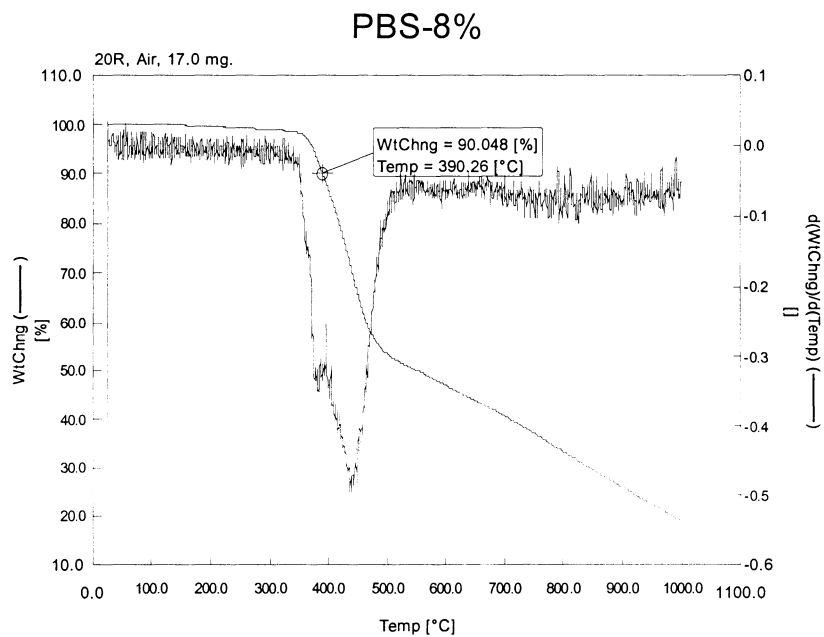


Figure 18. Mass Loss vs Temperature and the TGA at 20°C/min of the PBS-8%.

As shown in Figure 20 an additional peak appeared at -67°C for the 8% siloxane-modified phenolic. The intensity of this peak is very small compared to the main *tan delta* peak.

This second glass transition temperature is called a beta transition due to the oligomeric nature of the pendant siloxane in the backbone of the phenolic. Generally, siloxane polymers have very low glass transition temperatures due to the flexibility of the silicon-oxygen bond.²⁹ Miscibility of the phenolic and the siloxane would be indicated if these peaks moved together as % siloxane composition change. However, the phenolic peak moved lower, at 5% concentration, to 225°C (Appendix II), and up again at 8% to 249°C and the *beta* peak did not appear to move with change of the percent siloxane compositions.

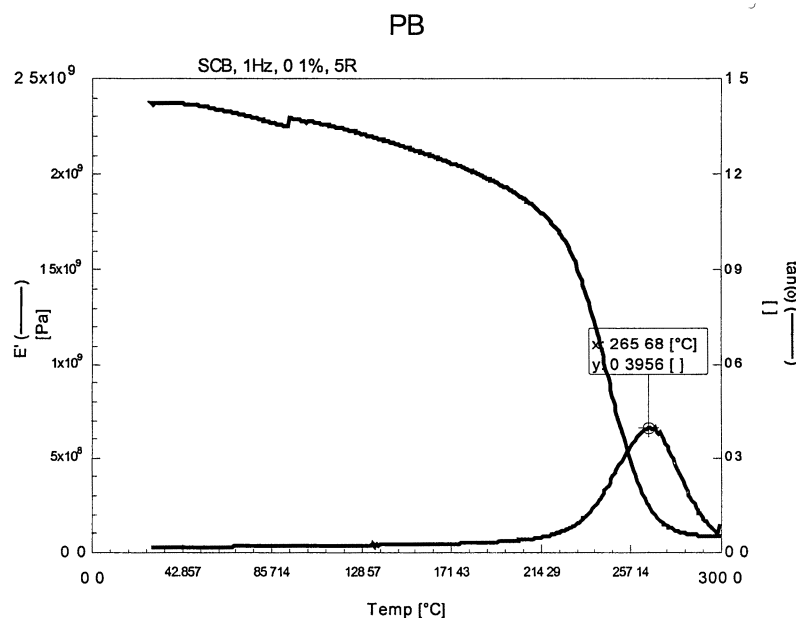


Figure 19. Loss Modulus (E'') and Tan delta of the Neat Phenolic.

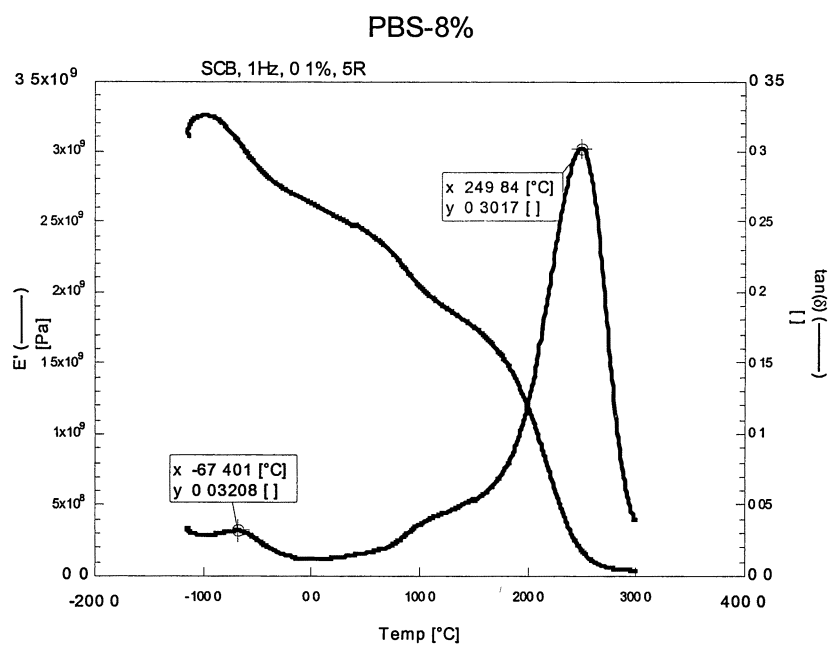


Figure 20. Loss Modulus (E') and Tan delta of the PBS-8%.

3.2.4 Flexural Properties

A comparison of the flexural properties for these different materials is given in Table V. As previously mentioned, the low T_g siloxane was expected to reduce the modulus of this material, and was verified by testing.

Table V: Summary of Flexural Properties of Siloxane-modified Phenolics.

Material	Flexural Modulus (Kpsi)	Flexural Strength (Kpsi)
PB	734±16	21±1
PBS-5%	511±4	12±2
PBS-8%	500±4	13±2

The modulus of crosslinked phenolic dropped from 734 Kpsi to 500 Kpsi following the addition of 8% dimethylsiloxane and 5% siloxane showed a drop to 511Kpsi, essentially the same effect. In general when mixing two polymers the modulus can be modeled as a nearly linear function³⁰ that depends on the composition of the additive in the matrix. We know that the polydimethylsiloxanes have very low modulus, again because of the flexibility of oxygen-silicon bond. This is the rubbery aspect of the dimethylsiloxanes, which means that upon incorporation the phenolic, material will lose its stiffness.

3.3 Solvent Blending of Nanocomposite Clay and Phenolic *versus* Extrusion

Blending

3.3.1 Processing

3.3.1.1 Solvent Processing Blend

The initial approach to process these materials was to determine the solubilities or swellabilities of phenolic and different clay/surface treatment materials in various solvents in search of a common solvent. This solvent technique has been widely used for water-soluble polymers intercalated with nanocomposites.³¹⁻³² However, the novolak phenolic used in this study was not soluble in water, but soluble in ethanol. We did a complete study on the montmorillonite clay products available to us. When the solvent was added to clay we found two phenomena: precipitation of the clay or formation of a gel, noted by a qualitative visual observation. The increase of the viscosity during stirring is a sign of a swelling of the clay (gel formation).

Throughout this study, we didn't find any clay which was soluble in ethanol. In fact, we changed our approach by using a mixture of solvents as described in the experimental

section. The only clay found to be soluble using this co-solvent approach was MMBT (methyl, methyl, benzyl, tallow side chains on the quaternary ammonium ion surface treatment) in an ethanol and toluene mixture. This approach worked only if the ethanol was saturated with phenolic. Toluene was mixed with the phenolic saturated ethanol, then clay was added as gentle mixing was applied; when the viscosity of the mixture appeared to increase (swelling of clay) the 1,3-BOX was added and the solution was mixed for a 24 hours. The solvent mixture was removed using rotary evaporation under a high vacuum, and then cured in the presence of the catalyst.

X-ray diffraction (XRD) data for phenolic-MMBT, shown in Figure 21, verify intercalation of the clay as evidenced by the shift of the peak from 19 Å (clay peak before intercalation) to 40 Å. Increase in the d-spacing is caused by polymer intruding into the clay galleries. This is further proven by TEM analysis in Figure 22 showing intercalation or opening of the galleries in the clay tactoid, and some exfoliated material (Figure 23).

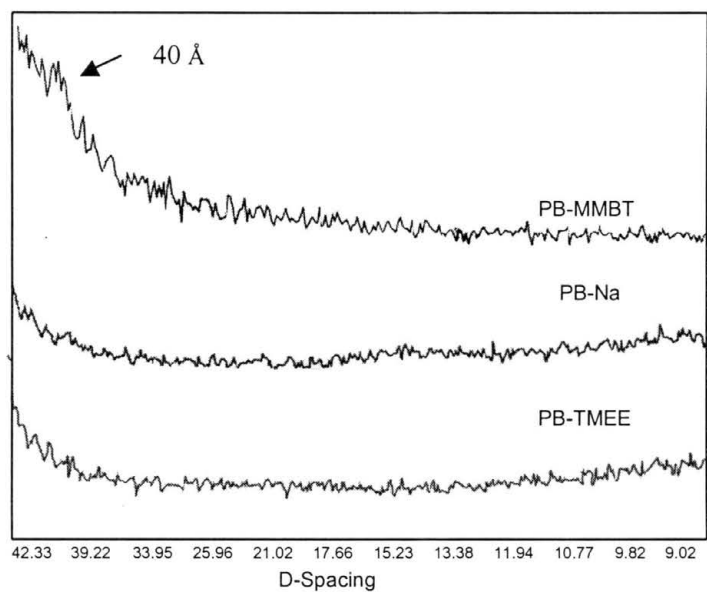


Figure 21. XRD of Clay-Modified Phenolic for PB-MMBT Processed by a Solvent Approach and PB-Na, PB-TMEE Processed by a Melting Approach.

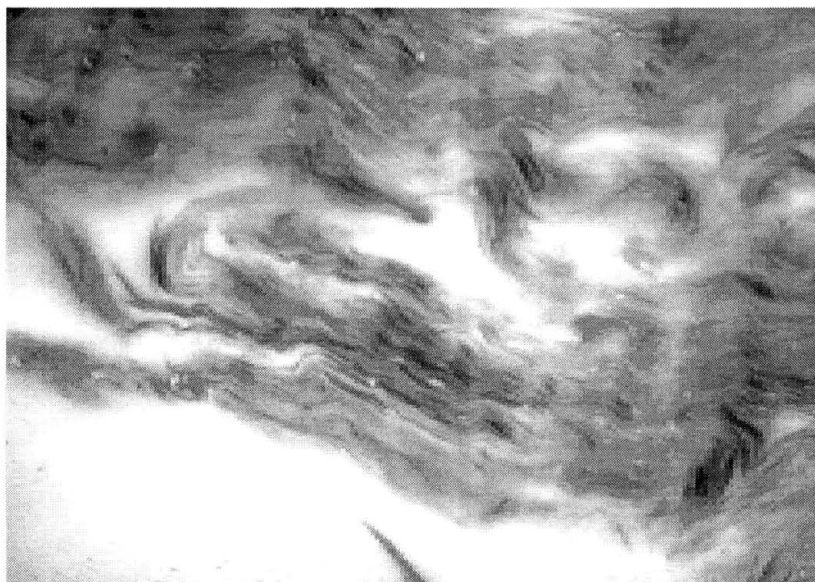


Figure 22. TEM Picture of Intercalate Clay-Modified Phenolics with MMBT Clay at 80,000x.



Figure 23. Exfoliation in Some Regions of the Clay-Modified Phenolic with MMBT at 80,000x.

3.3.1.2 Twin screw Processing Blend

Melt intercalation of polymers has been widely studied for thermoplastics using different clays and a different melt approach.³³ Our first approach was to use a long resident time mixing head that holds 60g for 15 min under 60 rpm and 90°C. This initial effort didn't show any difference from the manual mixing and the samples were very dark. Subsequently, samples were mixed using a higher shear on the twin screw.

The Phenolic was mixed with different compositions of clay (2% and 5% of the phenolic/1,3-BOX) and run in the twin screw extruder. The clay and phenolic were placed in a extruder at a constant feed under 100 rpm and 100°C. The 2% clay composition appeared to be the clearest material coming out of the extruder of all the clays used, but the colors were different depending on the cation modification of the clay.

The TMEE clay, as described in the experimental section, extruded relatively clear material due to the presence of ethanol in the ammonium alkyl and the compatibility with phenolic. Incorporation of clay with a sodium cation also extruded clear material but a little darker than the two clays described above, and the MMBT was the darkest blend.

We experienced some difficulties with the 5% clay composition. The blend TMEE/phenolic was impossible to cast due to the premature crosslinking, while MMBT and Na were easy to cast. XRD (Figure 21) of 2% Na and 2% TEEM showed no peak, which is evidence of interaction with a high d-spacing.

3.3.2 Fire Retardant Properties

Clay/phenolic blends were cured with 1,3-BOX as discussed in Section 2. The cured plaques were cut, and then placed under a heat flux of 75kW/m^2 . Figures 24 and 25 show a summary of average values for peak HRR, and total heat release (THR), based on a burn time of 600s. The experimental HRR and mass remaining were taken from the mass loss calorimeter and are included in Appendix I for all blends. Percent clay composition was varied between 2% and 5% by weight; however, some data were not reported due to the processing difficulties as described in Section 3. The peak heat release rate may decrease slightly for the 2% composition clay; but, because the standard deviation is $\pm 17\text{ kW/m}^2$, we conclude that there is no improvement of the fire retardant properties. The peak heat release rate for 5% clay likewise did not reduce significantly. The solvent-processed blend is even showing an increase for the peak HRR.

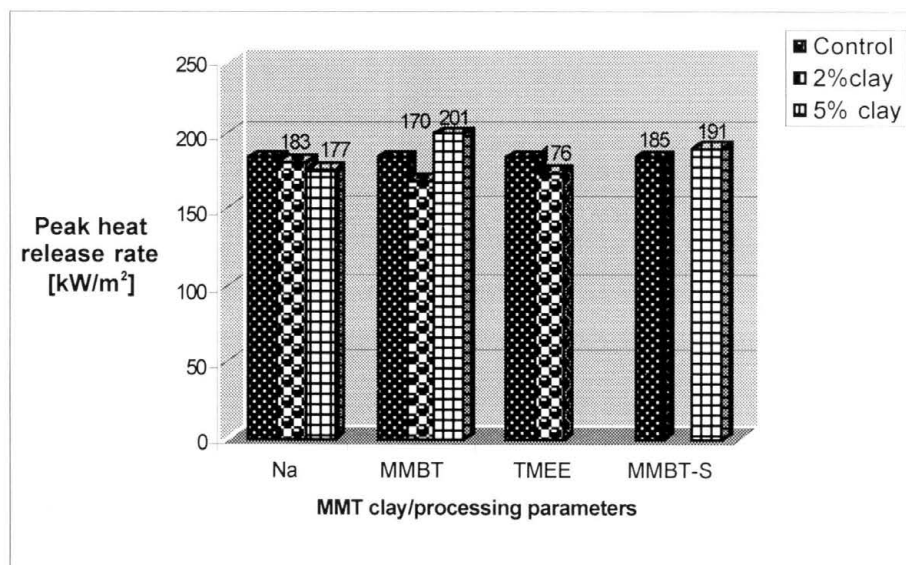


Figure 24. Peak Heat Release Rate of Clay-Modified Phenolic Blends at 75kW/m².

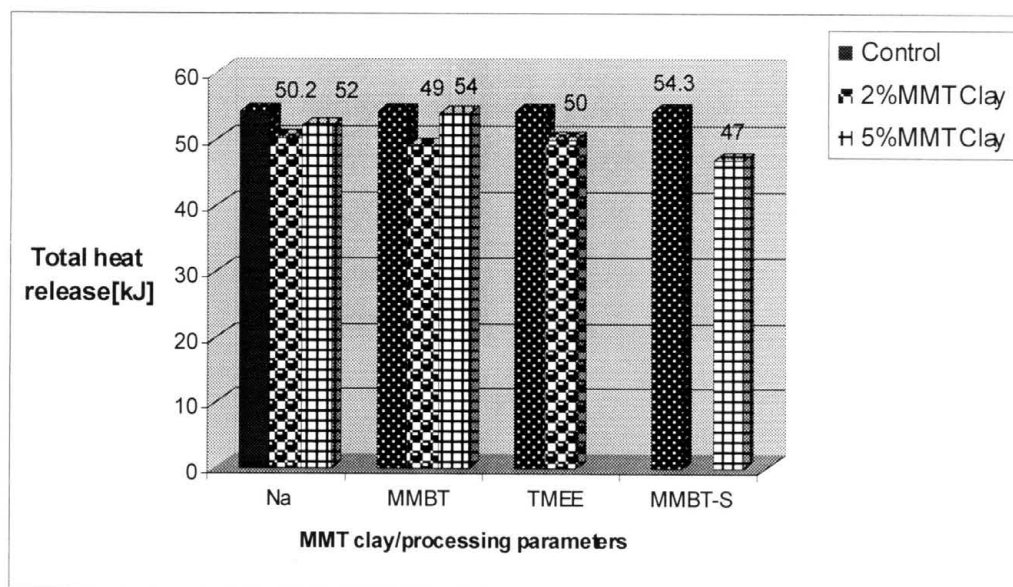


Figure 25. Total Heat Release Rate of Clay-Modified Phenolic Blends at 75kW/m².

Studies of thermoplastics nanocomposites showed that adding 2%-5% composition clay to the polymer improves the fire retardant properties.³³ However, the thermoset system in this study did not perform any better, perhaps due to the low degree of crosslinking. X-ray diffraction and TEM show intercalation and some exfoliation in certain regions. If the polymer is intercalated between the clay layers when the crosslinking occurs, the crosslinker will be hindered approaching the hydroxyl groups hidden in the gallery, and the probability of collision of the 1,3-BOX with the phenolic chains is decreased. As a result, the degree of the network crosslinking is reduced. If we were to obtain a higher degree of exfoliation, perhaps fire retardancy might be improved. Another concern is that the peak HRR of these phenolic materials is already very low; and there may be a lower limit to the enhancement in PHRR one can expect from this additive.

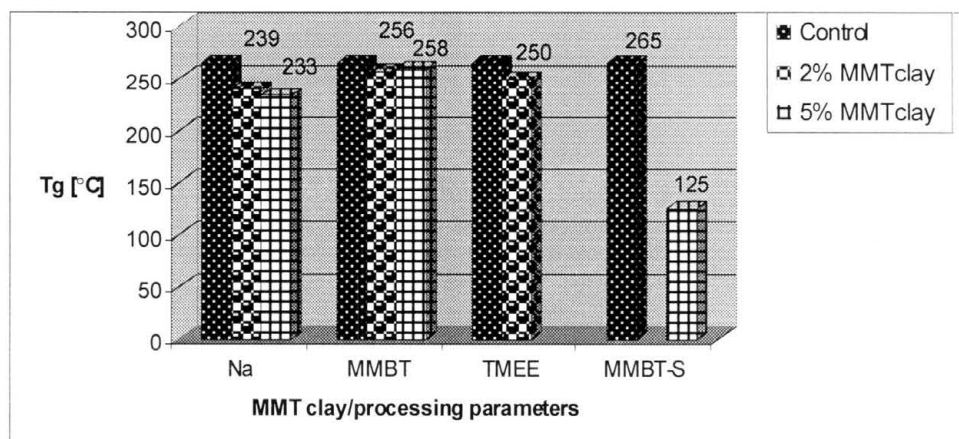
3.3.3 Thermal Properties

Important factors that may determine the extent of the thermal stabilization in nanocomposites arise from the nature of the thermal degradation mechanism as measured by TGA. For this system no improvement was obtained in the 10% mass loss; however, the average char yield for all the clay-modified phenolics is higher than the neat phenolic. These data are presented in Table V; the standard deviation for the TGA data is ± 5 °C and for DMTA is ± 3 °C.

Table VI. Summary of Thermal Properties of clay/phenolic blends.

Material	T _g (°C)	Temp (°C) 10% mass loss Air	Temp (°C) 10% mass loss Argon	% Char Air at 900 °C	% Char Argon at 900 °C
PB	265	405	402	4	37
PB-MMBT-5%-S	126	393	390	3	32
PB-MMBT-5%	258	401	404	4	32
PB-MMBT-2%	256	405	404	3	32
PB-Na-5%	233	400	401	5	41
PB-Na-2%	239	398	399	4	37
PB-TEEM-2%	250	402	395	3	37

Glass transition data are compared in Figure 26, and show an increase for the clay-modified phenolics. The phenolic–MMBT solvent blend, however, showed a 52% decrease compared to the control. Undoubtedly this decrease indicates that the solvent is still present in the matrix even after drying and curing the material.

**Figure 26. Glass Transition Temperatures of Clay-Modified Phenolic Blends.**

3.3.4 Flexural Properties

The flexural modulus, expressing the stiffness of the phenolic-clay blend, actually decreased when the nanocomposite was formed. The flexural modulus decreased dramatically for the phenolic which was modified with 5% MMBT (Figure 27). As described before, we attribute this decrease to less crosslinking. When intercalation is obtained for a thermoset resin as in this system, the probability of the interaction of the 1,3-BOX with hydroxyl groups of the phenolic is low, which reduces the degree of crosslinking, and subsequently will cause a weakened polymer matrix. Some studies reported for epoxy resin-based nanocomposites that neither intercalation nor exfoliation of the nanosilicate lead to an improvement in modulus, instead, they make the material more brittle.^{35,36}

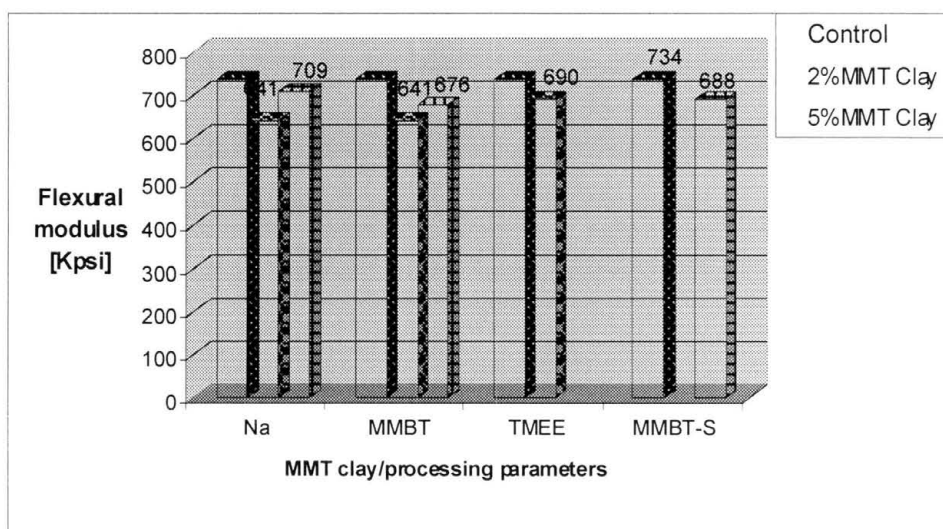


Figure 27. Comparison of Neat Phenolic Flexural Modulus with Clay-Modified Phenolic Blends.

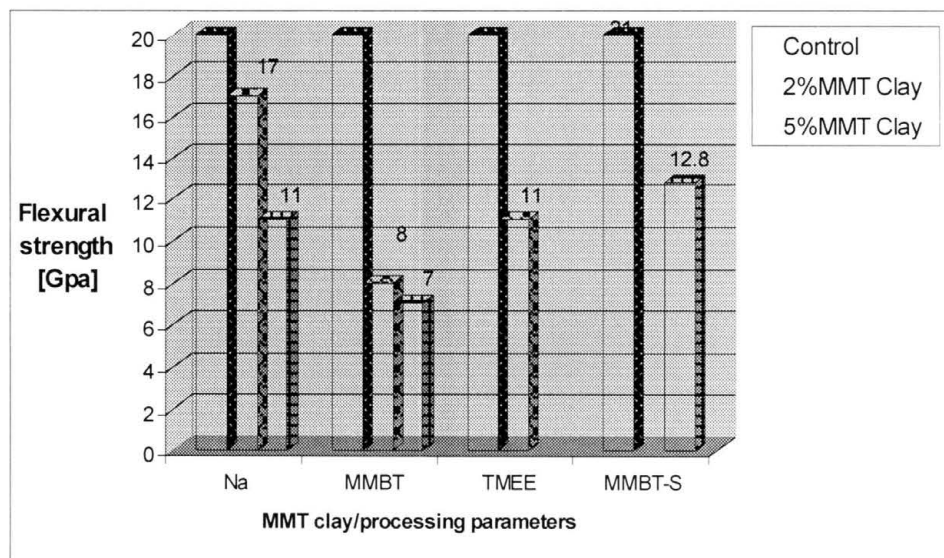


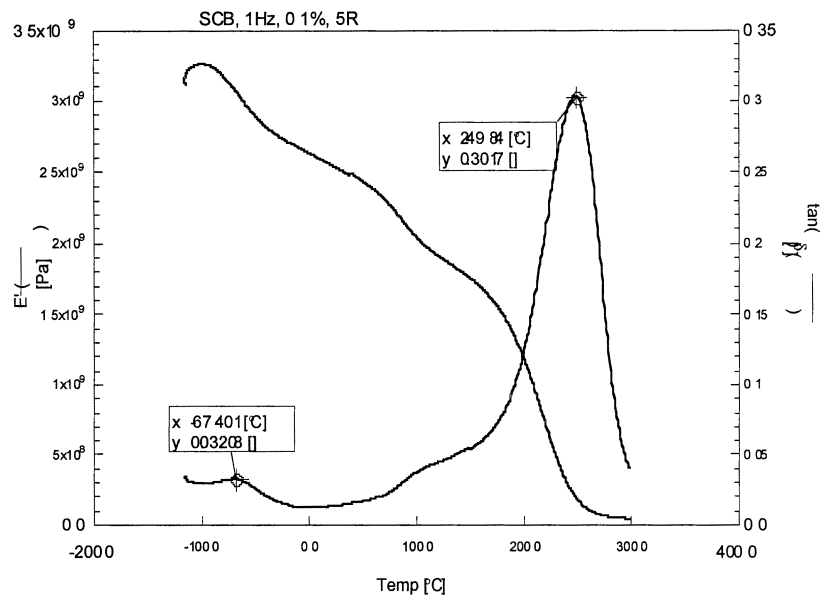
Figure 28. Comparison of Neat Phenolic Flexural Strength with Clay-Modified Phenolic Blends.

4.0 CONCLUSION

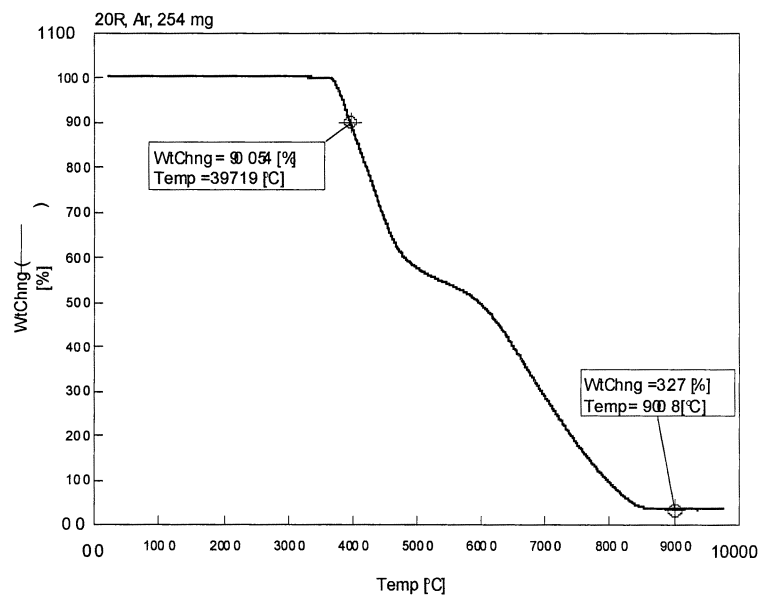
A new method of solvent processing novolak phenolic crosslinked with 1,3-BOX was developed. The addition of the different compositions of dimethylsiloxane did not improve the fire retardancy or the flexural properties of the crosslinked phenolic resin. Furthermore the addition of clay montmorillonite to this system showed a decrease in the flexural modulus and strength, when processed by either twin-screw or by a solvent method. X-ray diffraction and TEM showed an intercalation of phenolics in the montmorillonite clay galleries; however, the fire retardant properties were not substantially improved.

Appendix I
TGA and DMTA

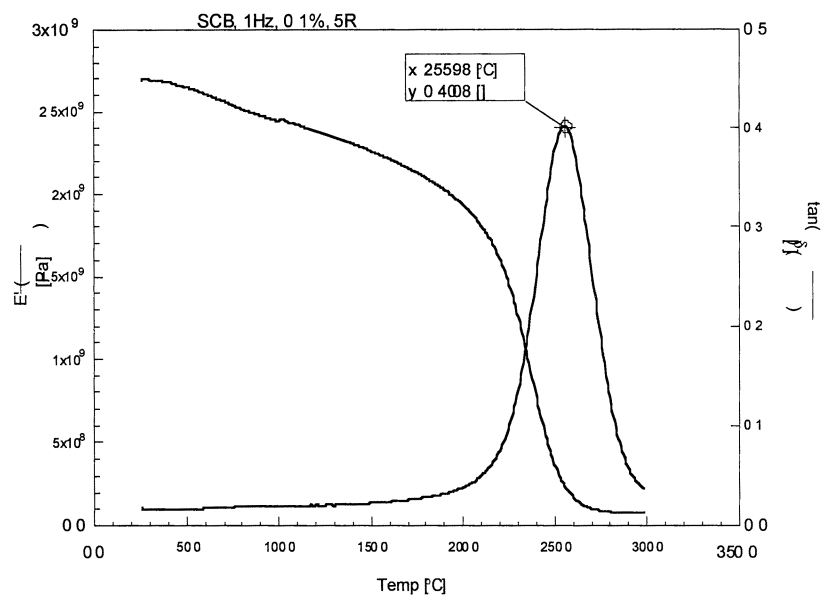
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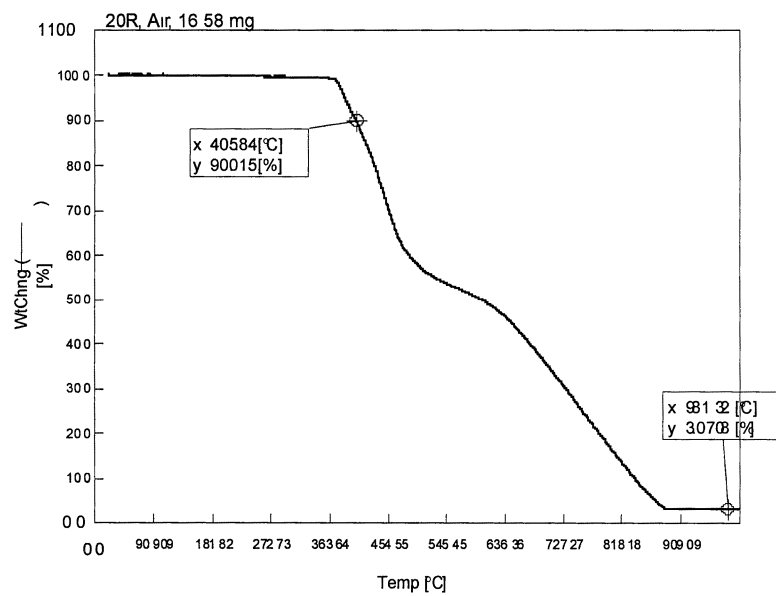
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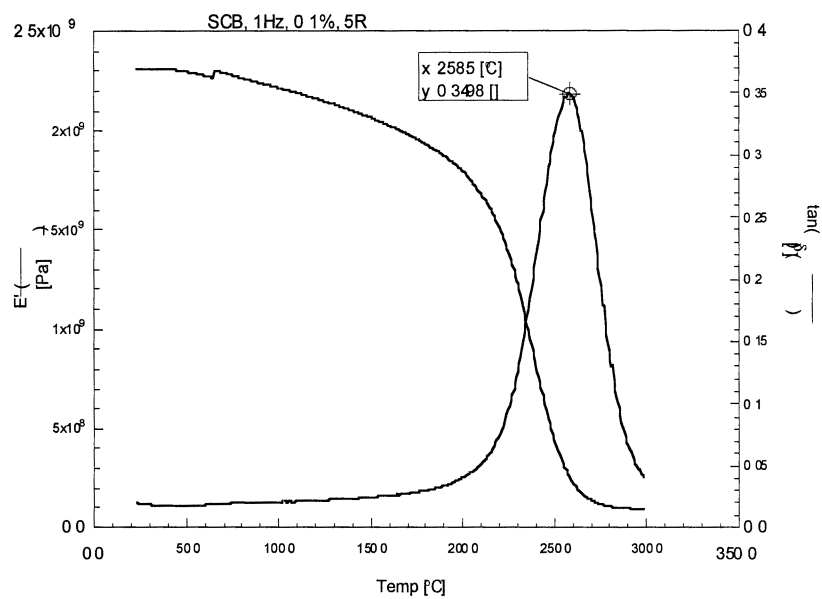
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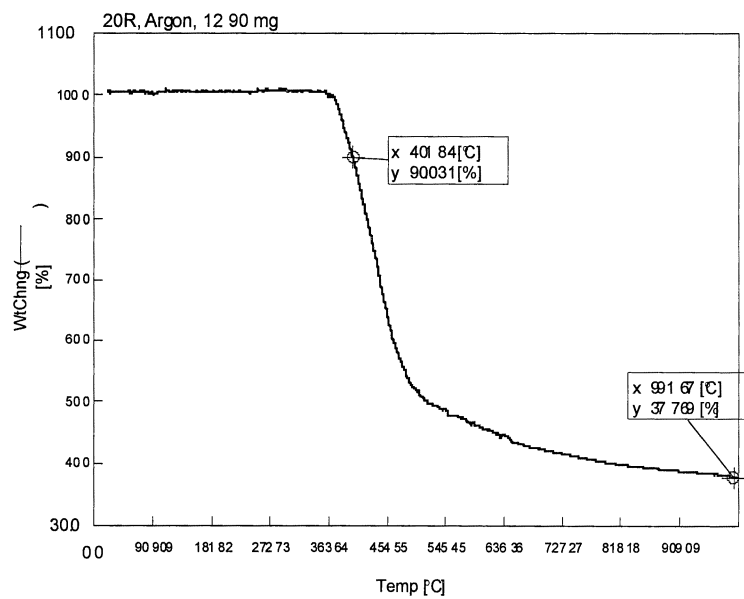
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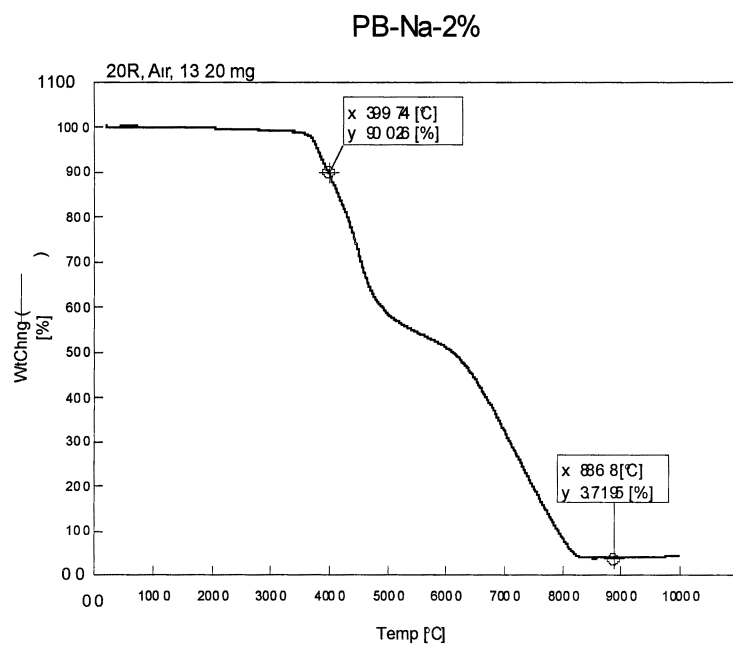
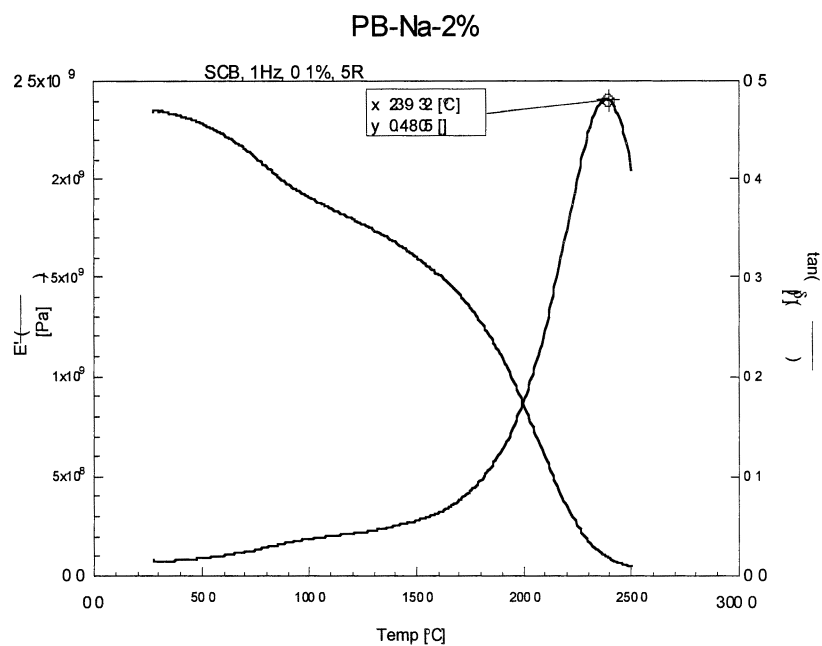


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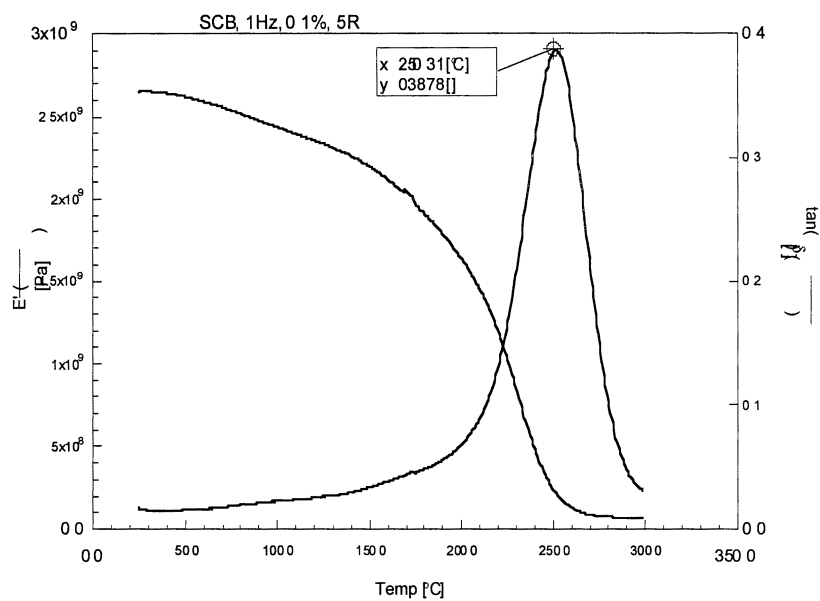


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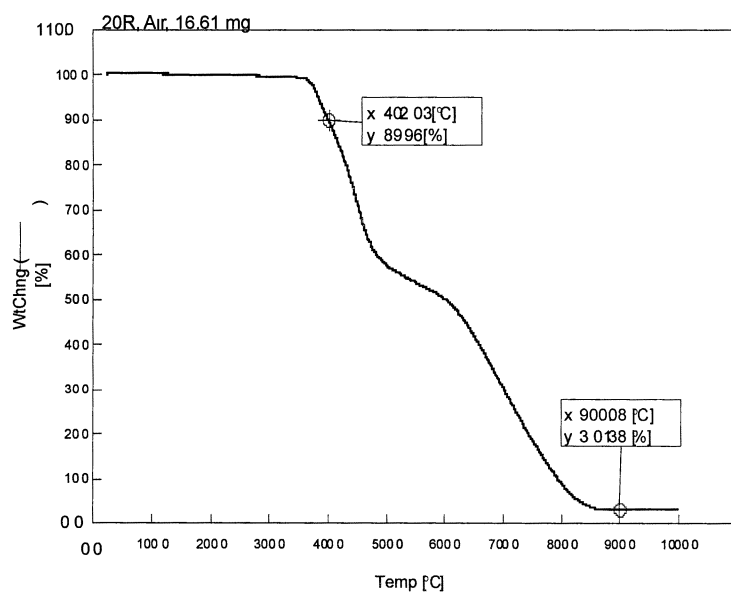


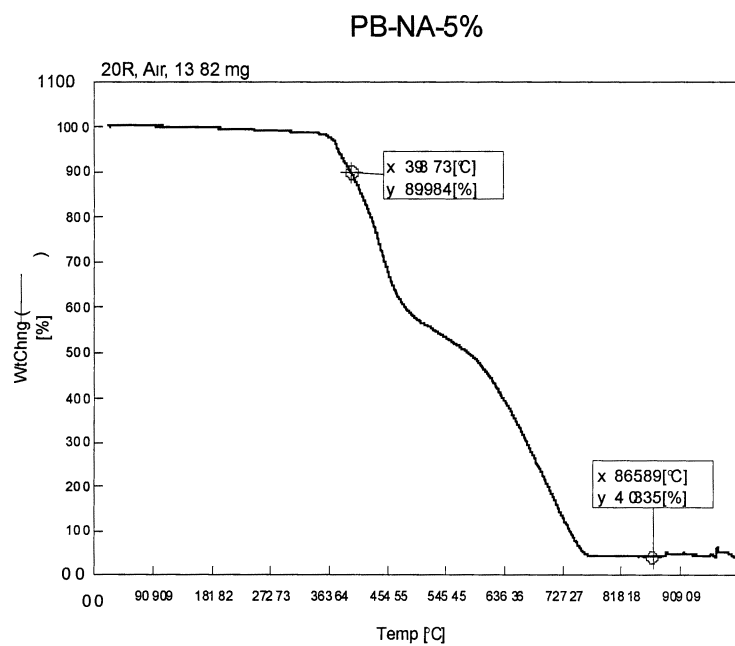
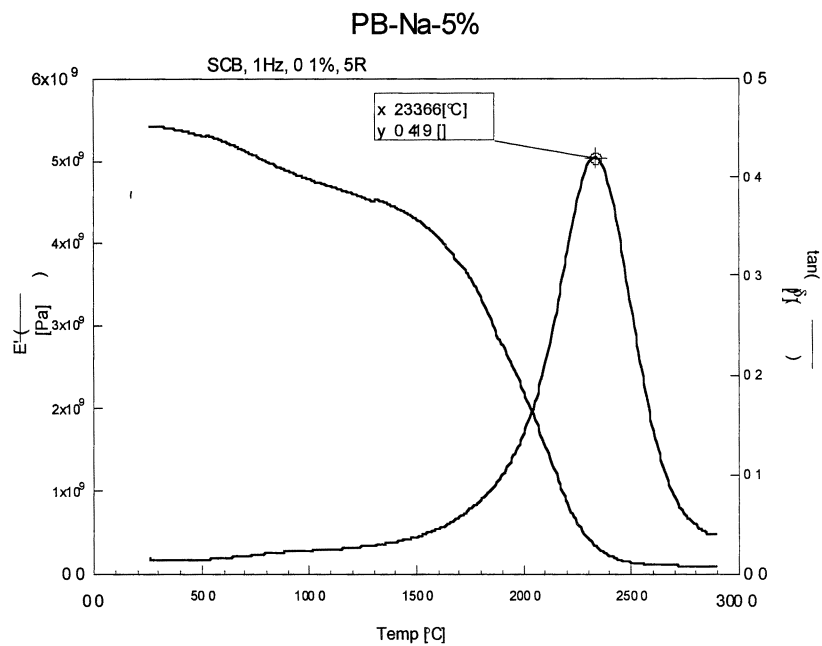


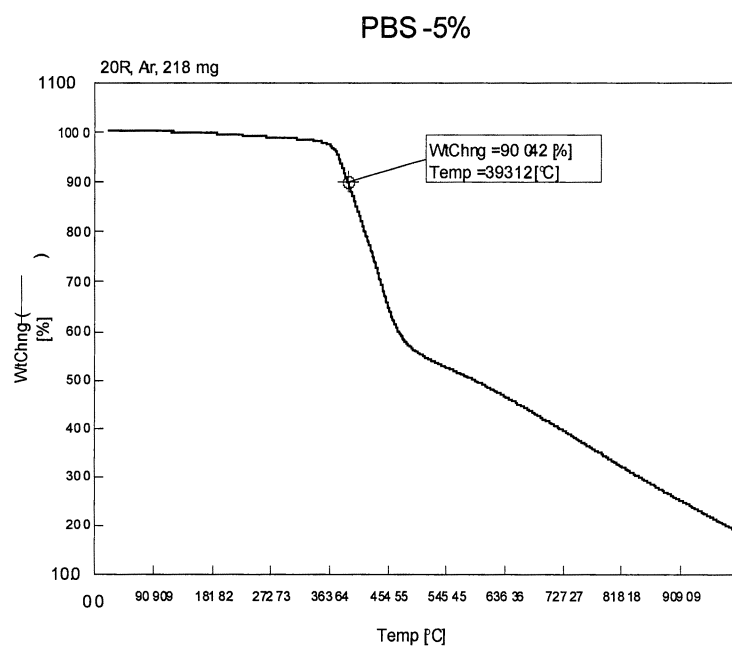
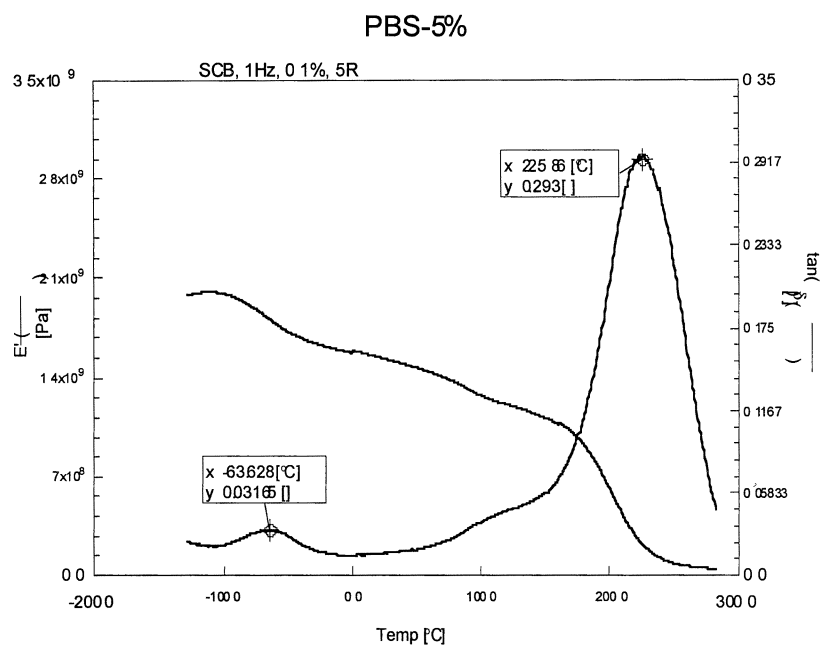
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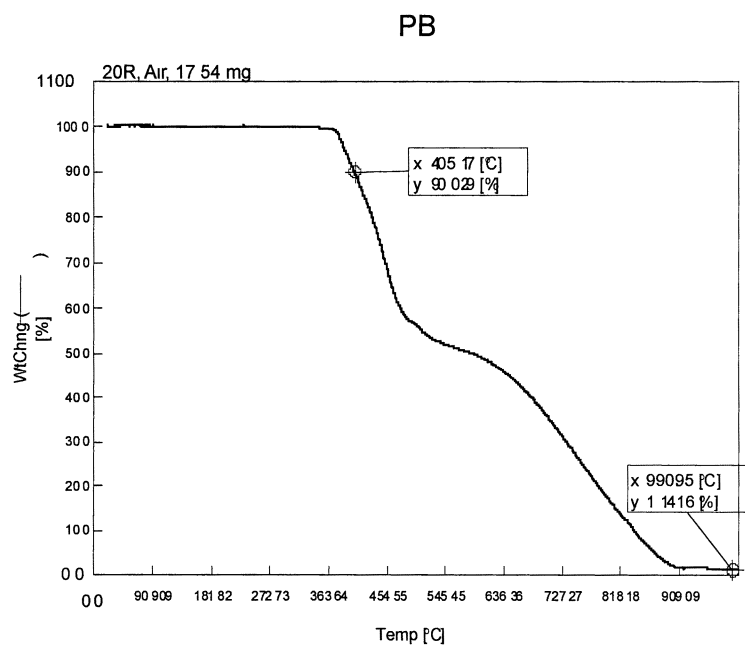
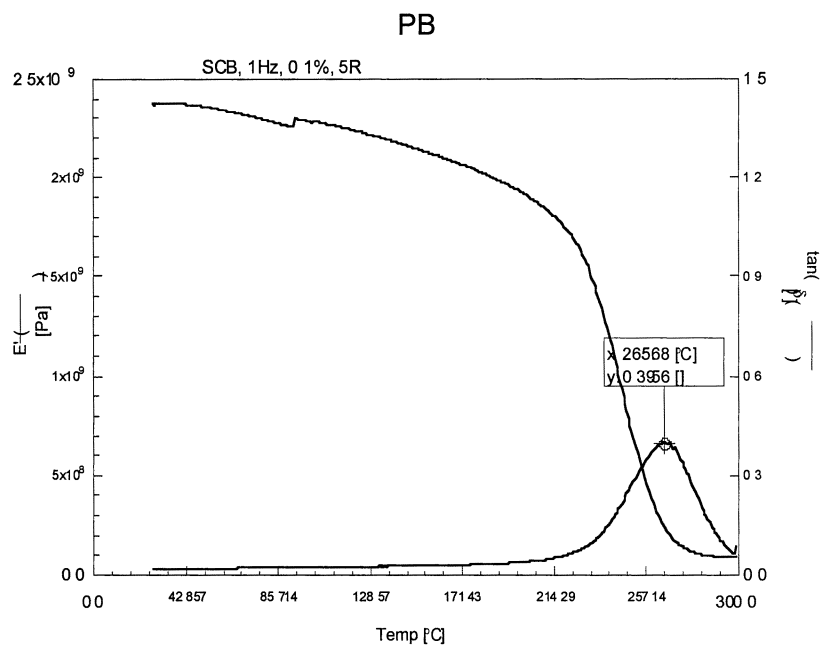


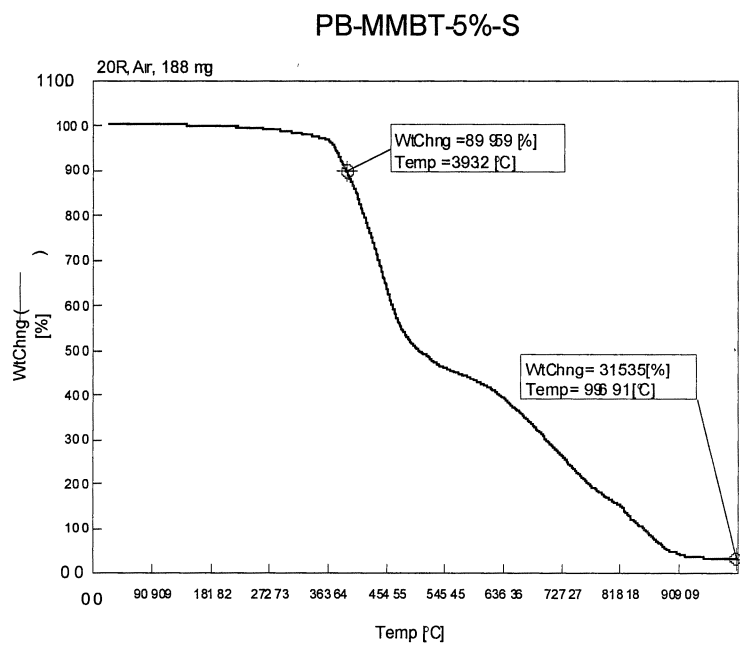
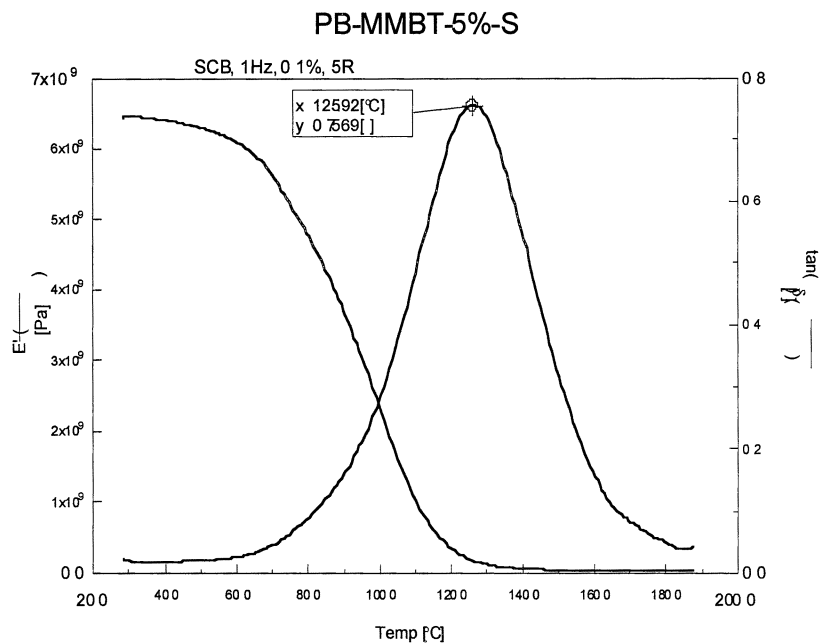
PB-MEET-2%





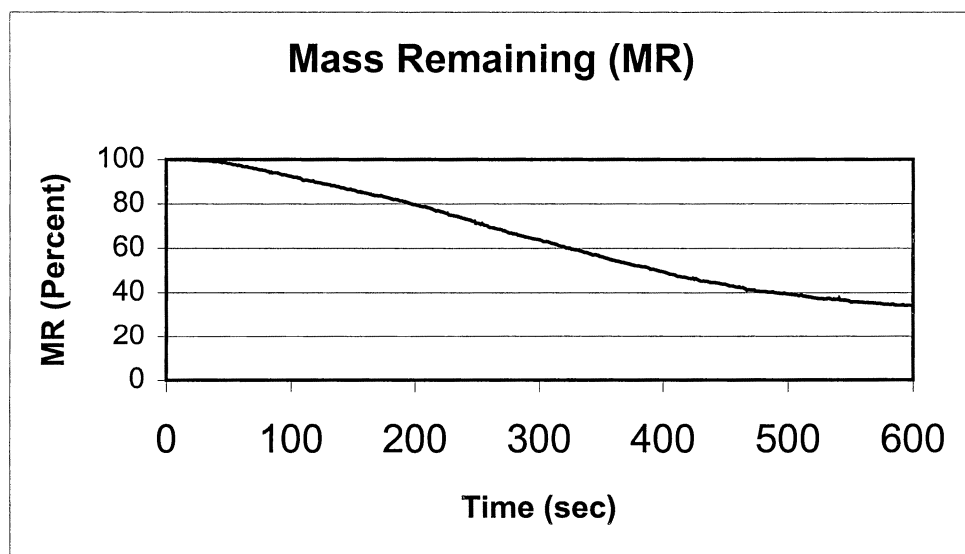
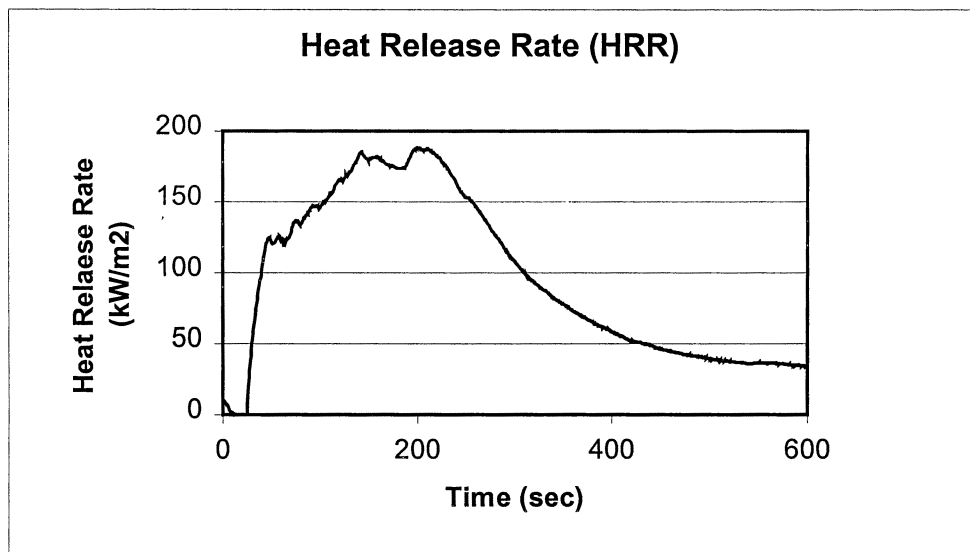




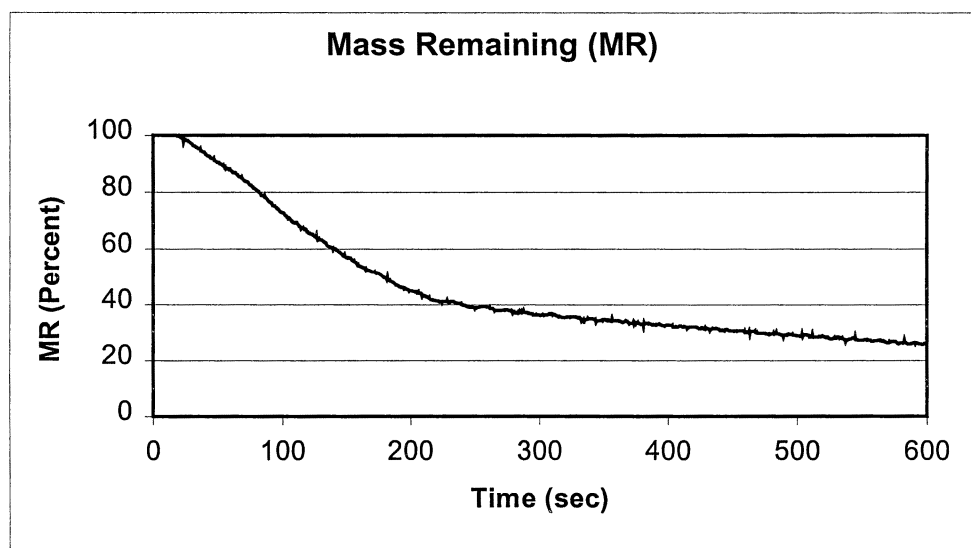
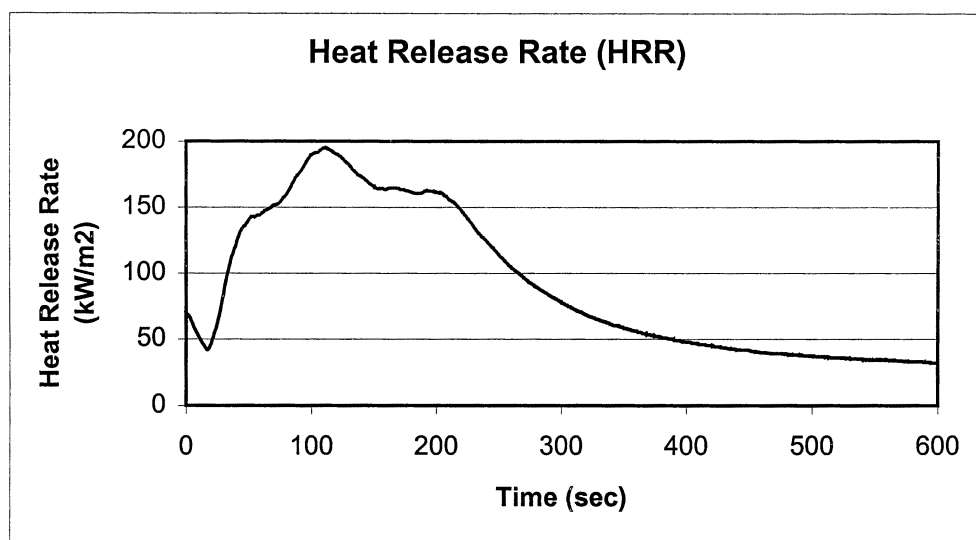


Appendix II
Mass Loss (ML) Calorimeter Data

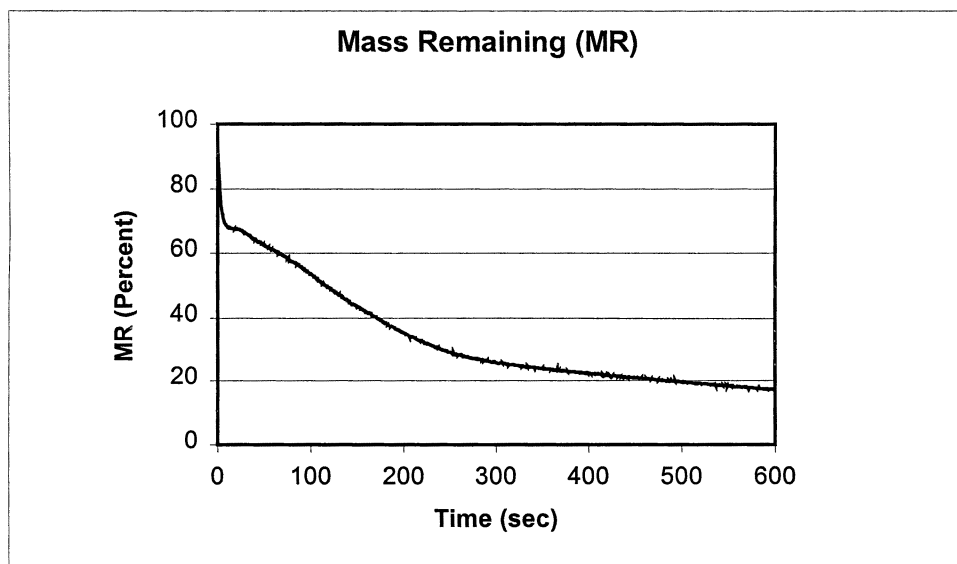
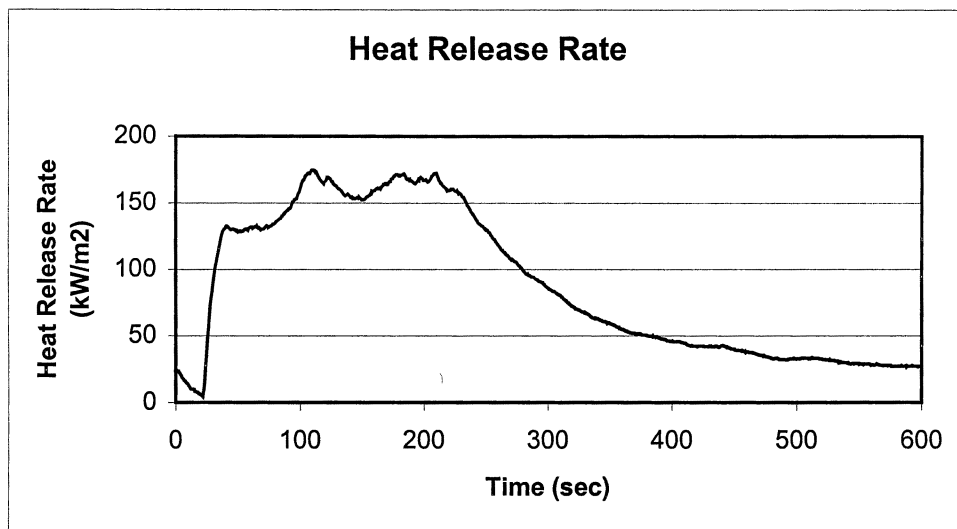
ML Calorimeter Data of PBS-5%



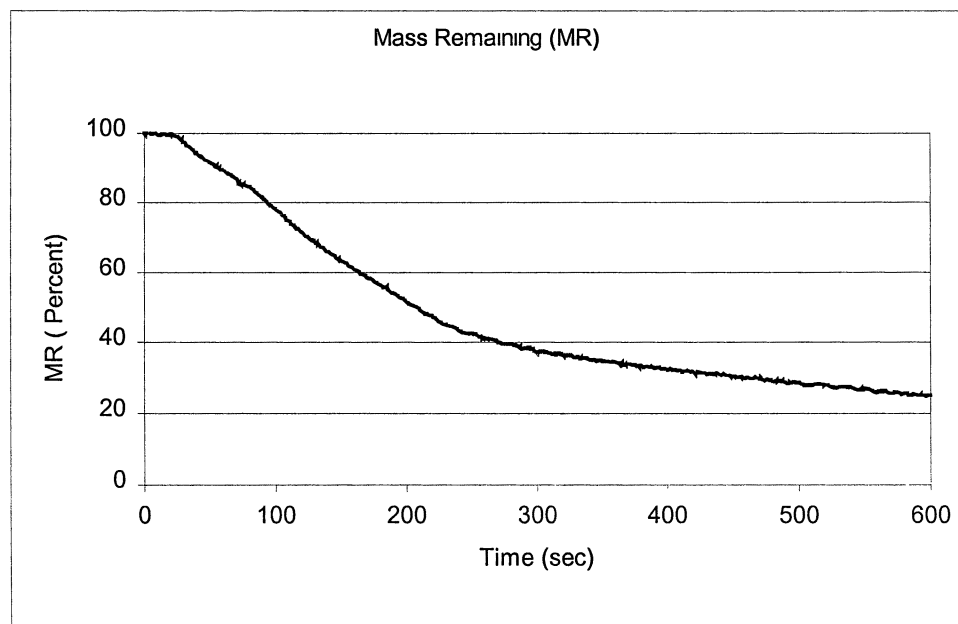
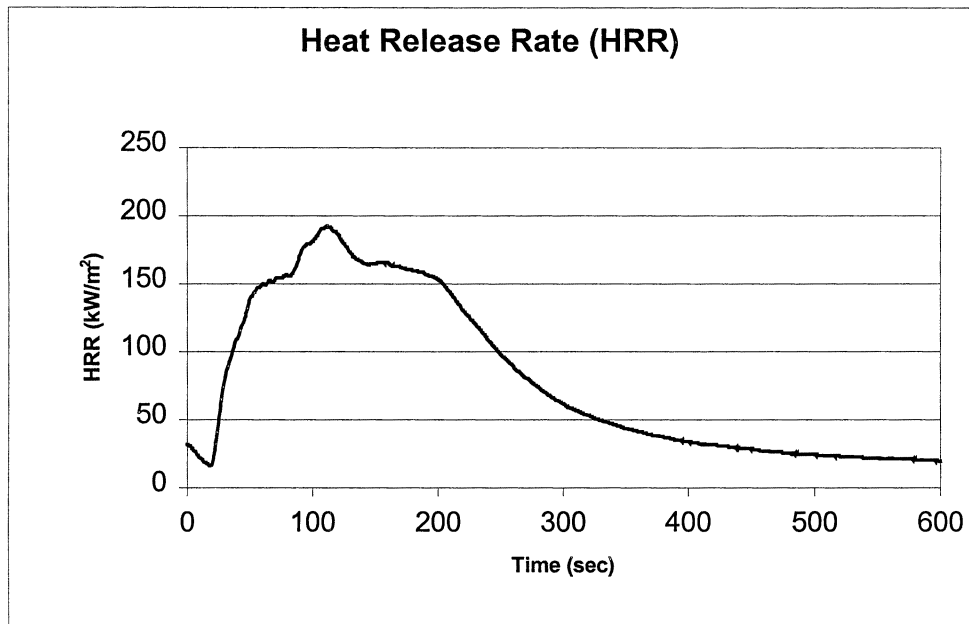
ML Calorimeter Data of PB-MMBT-5%



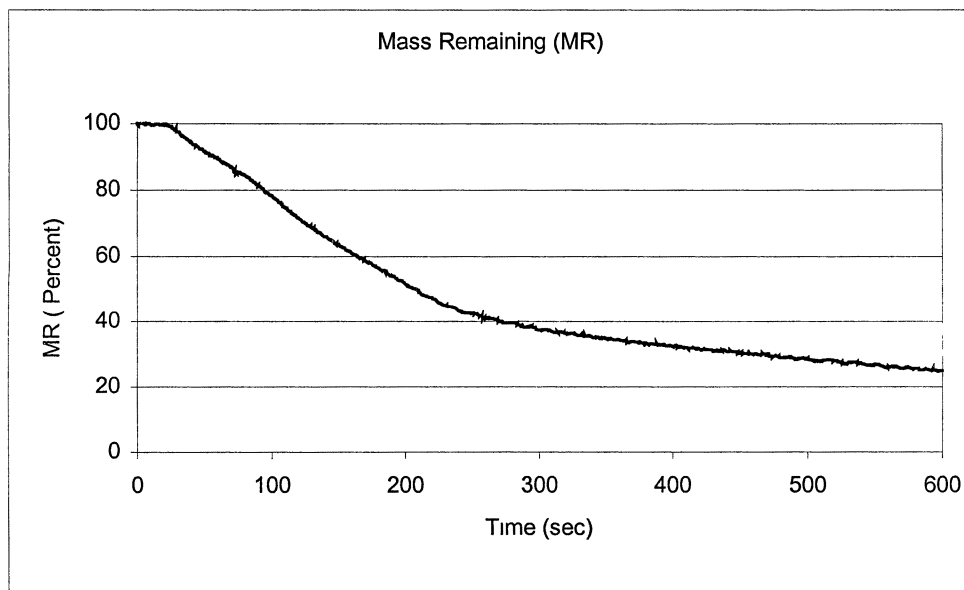
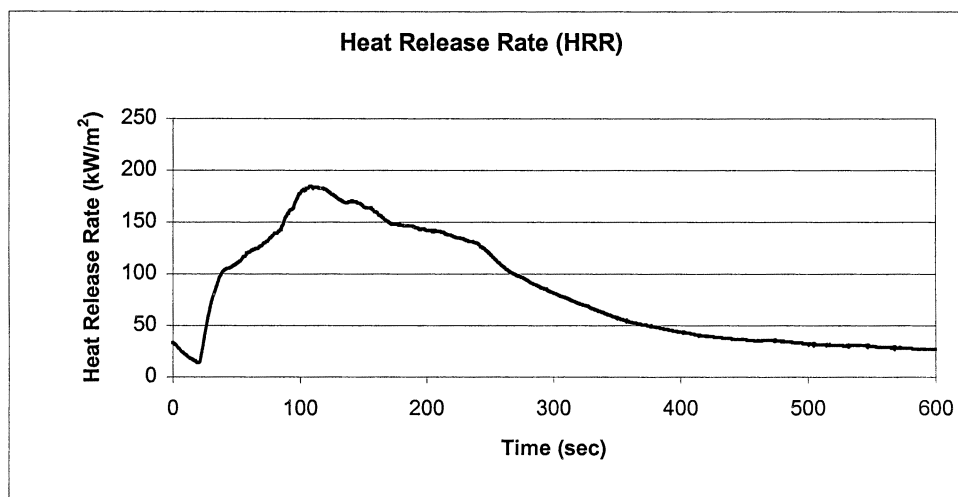
ML Calorimeter Data of PB-NA-5%



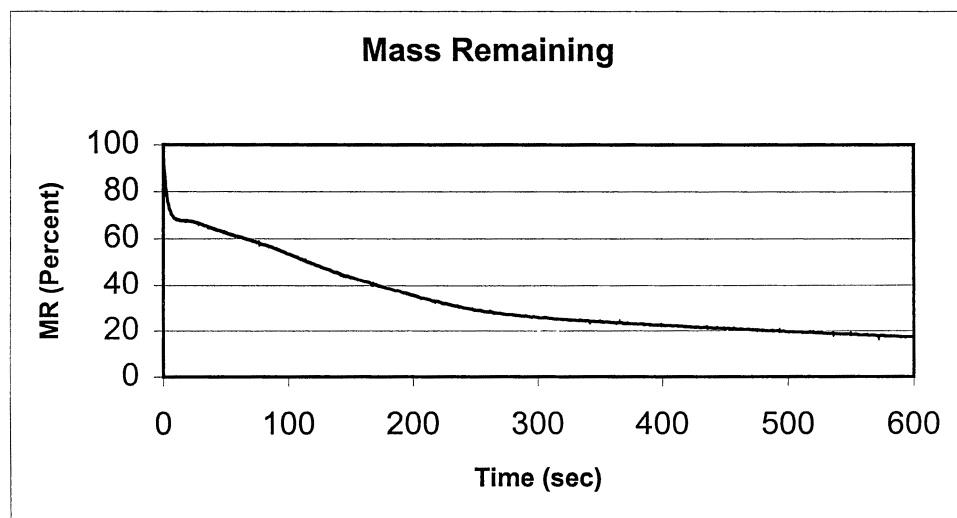
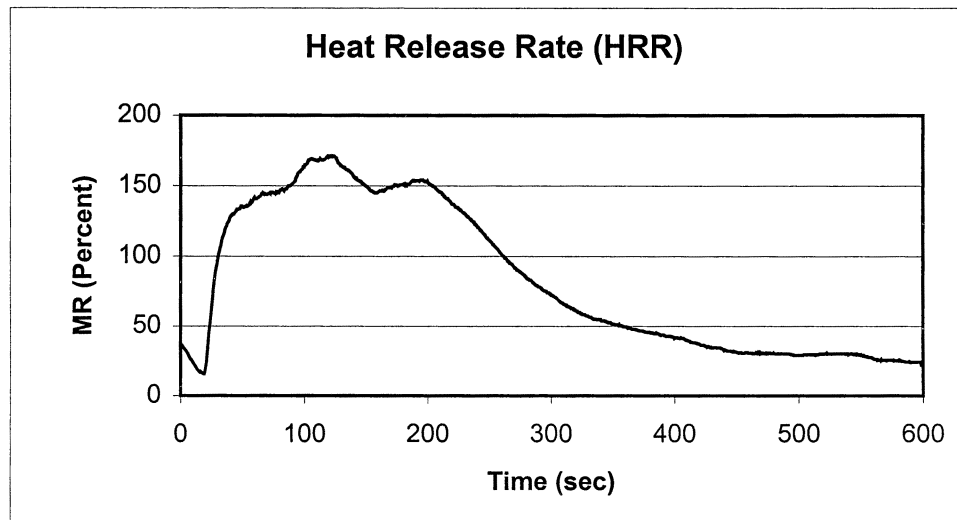
ML Calorimeter Data of PB-MMBT-5%-S



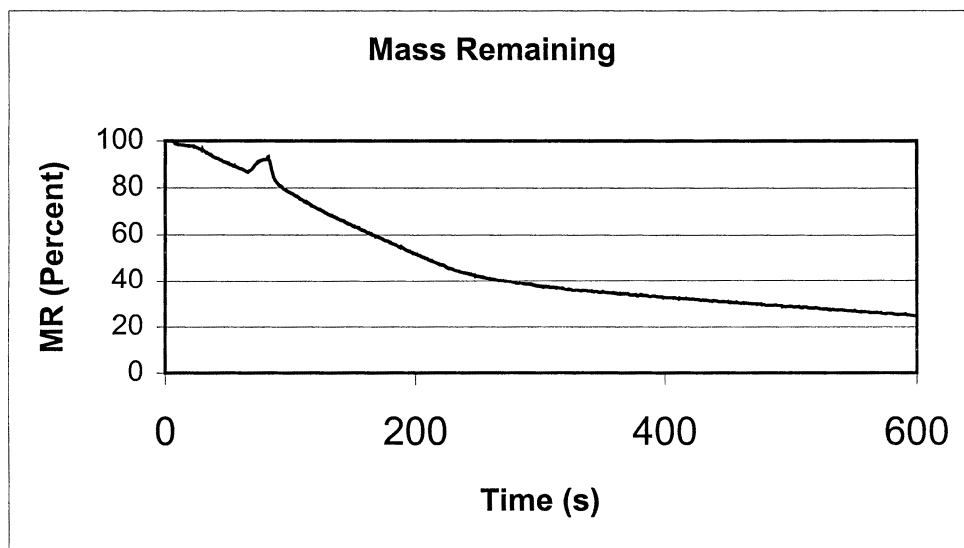
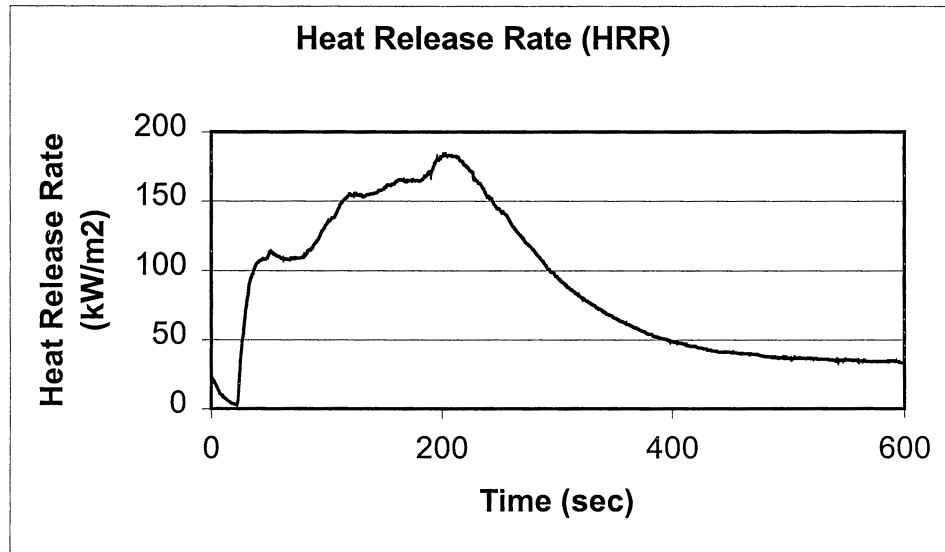
ML Calorimeter Data of PB-NA-2%



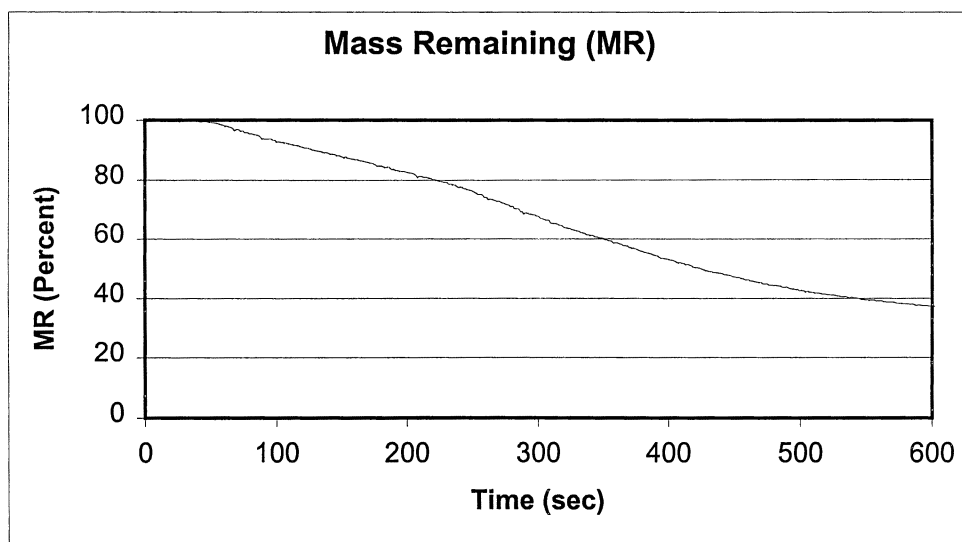
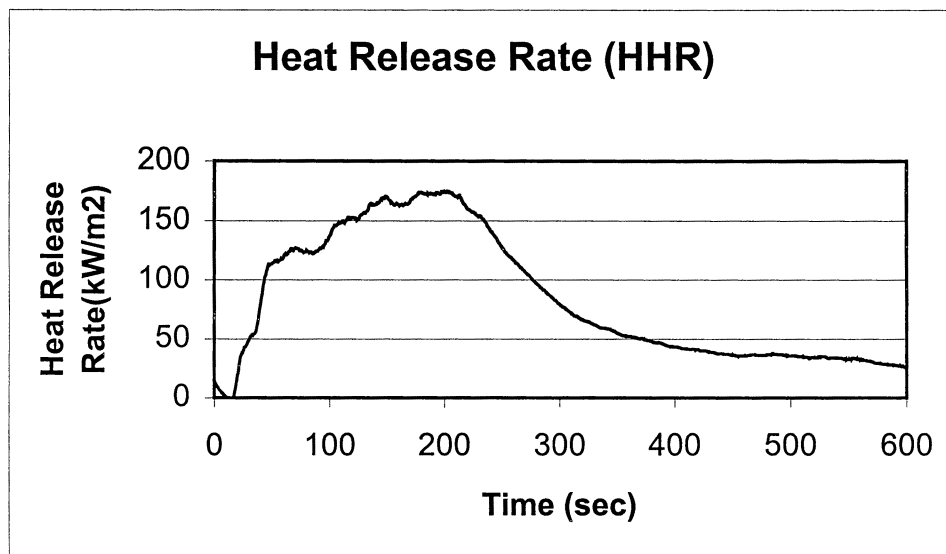
**ML Calorimeter Data of
PB-MMBT-2%**



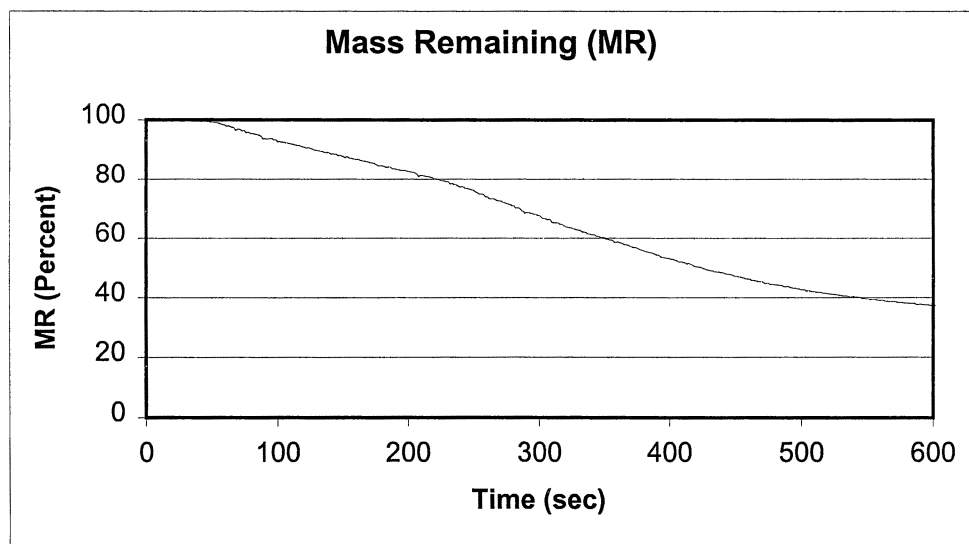
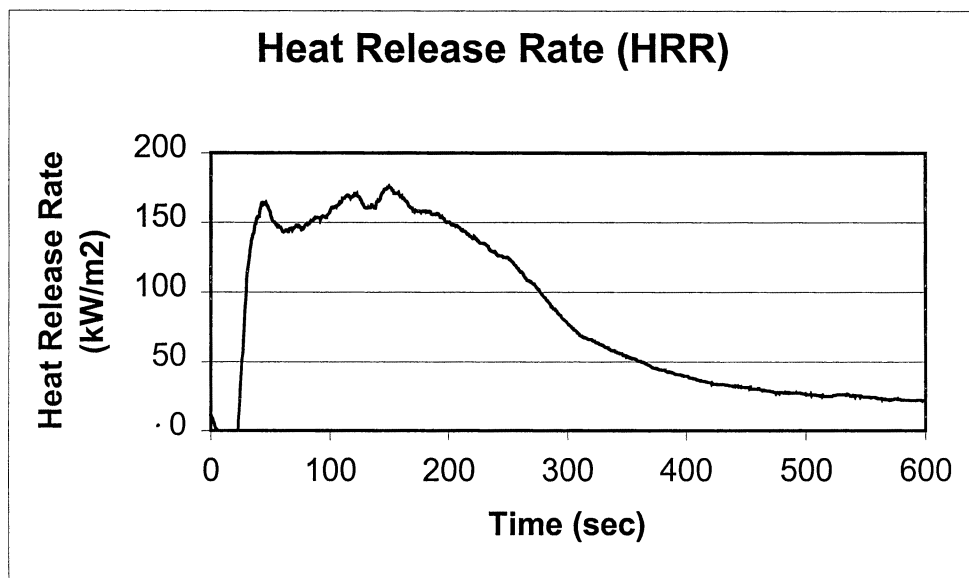
ML Calorimeter Data of PB



**ML Calorimeter Data of
PBS-8%**



**ML Calorimeter Data of
PB-MEET-2%**



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