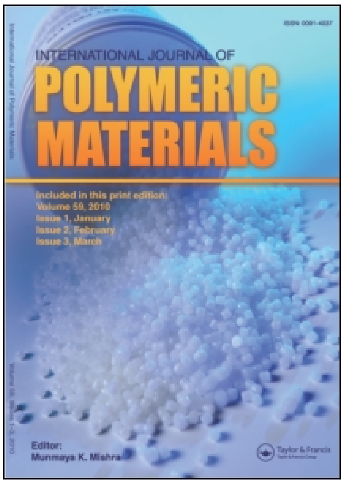

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Flammability Evaluation of Spectra® Composites Under Exposure to a Turbo-Torch Flame

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Because of an outstanding capability of absorbing mechanical energy, Spectra® fibers are frequently used in damage tolerant composite materials to protect equipment, blast proof aircraft luggage containers, armor, apparatus and/or people against blast and debris of explosion or projectiles. Since Spectra® fiber is made of polyethylene which is one of the most thermally stable polymers in the absence of oxygen, it is possible to design composite structures that are suitable for use in applications where prolonged exposure to flame is anticipated. In this paper, we report the findings obtained in a recent study on the development of the flame barrier materials for constructing the turbo-torch flame resistant Spectra® composites. A heat transfer analysis was conducted to achieve a better understanding of the dynamics of the flame resistance. It is shown that the general trend in flame resistance behavior of the composite can be predicted from the component material properties and composite construction parameters.

KEY WORDS Polyethylene fibers, composites, flammability

INTRODUCTION

Recently, Spectra® fiber composite has demonstrated its unsurpassed weight effectiveness in many armor applications including blast proof aircraft luggage containers,[1] damage tolerant structures[2] and a variety of armor systems.[3] Spectra® fiber is made of polyethylene and has excellent resistance to moisture and chemicals, very low dielectric constant, high cut resistance, and extraordinary strength (and stiffness) to weight ratio. It is one of the most thermally stable polymers in the absence of oxygen. In a typical thermogravimetric analysis test, its decomposition temperature is approximately 400°C in argon, and about 280°C in air.[4] In applications of Spectra® composites, however, flame resistance is frequently required and several flame resistant Spectra® composite systems have been developed to meet this need.[5]

The thermal stability of a Spectra® composite is enhanced by the fact that Spectra® fiber is a highly oriented, high molecular weight polyethylene. In the construction of Spectra® composites, e.g., Spectrashield® composites, each filament is embedded in a resin matrix and exposed only at the fiber ends. The flammability of the resin is therefore the controlling factor in potential ignition of the Spectra® composite except at the edge where fiber ends may be exposed. The ignition of the fiber from the edge is further inhibited by the unique property of Spectra® fiber filaments to retract into the matrix upon exposure to high temperature. This retraction reduces the fiber end exposure to the high temperature environment. It is noted that, except at the edge where the ends are exposed to atmospheric oxygen, the fibers are positioned in an oxygen-free environment. Thus, their decomposition temperature should be around 400°C as that obtained in an inert atmosphere. Therefore, it should be possible to develop Spectra® composite structures that meet a variety of flame resistance specifications.

This assertion was verified experimentally in a recent study on the flame resistant behavior of the unprotected (without addition of any flame retardants or incorporation of flame resistant barrier material) Spectra® composites by the standard flammability tests for automotive interior materials (the Motor Vehicle Safety Standard No. 302 test,[6] and the Ford Laboratory MD/MF-MH BN 24-2 test[7] in Springborn Laboratories, Enfield, Connecticut). The unprotected Spectra® composites were rated as not ignitable materials.[8-10]

Based on the thermal and thermo-physical behavior of Spectra® fiber, these results are not surprising. We observed that, during the test, as soon as the flame was brought in contact with the Spectra composite kept at a FIXED position, the Spectra fibers contracted and escaped ignition. Also, no dripping of low viscosity materials was observed during the test. Since the matrix concentration was about 20 wt%, this finding indicated that Spectra fibers did not melt into a low viscosity fluid but rather formed a leathery material upon melting. Furthermore, regardless of the thickness and the type of Spectra composite evaluated, no ignition, burning and very little visible smoke were observed during the burning tests.[8-10]

In recent years, a torch flame test has been used by the U.S. Army Materials Technology Laboratory (MTL) to screen and assess flammability of polymers and composites.[11] In this test, the flame is directed to the materials for a 600 second exposure. This test is the most demanding flammability test for evaluating polymeric materials compared to other methods described in the literature.[12-15]

Although various systems have been developed in recent years to improve the high temperature and flammability characteristics of the Spectra® composites,[5] a special design was needed to construct the Spectra® composite in order to withstand the torch flame test. In earlier studies, we reported the flammability characteristics of specially constructed Spectra® composites that can withstand the turbo-torch flame for 10 minutes.[4,16-18] The flammability behavior of Spectra® composite when used as a spall liner in armor against chemical energy warheads was also studied. In addition, we reported that the smoke generation and toxic gas emission from the Spectra® composites in contact with high temperature metal debris are far below the limits set in the standard for current commercial aircraft interior materials.[4,16-20]

In this paper, we discuss various factors which affect the flame resistant behavior of these specially constructed composites.

DESIGN OF THE FLAME RESISTANCE BARRIER

A flame resistance barrier material was designed in such a way that the transfer of heat (from the turbo-torch flame) across the composite will be regulated by heat absorption of certain compounds resulting from a set of endothermic reactions (i.e. heat of decomposition, heat of evaporation, etc.). On heating or exposure to flame, the compounds produce non-flammable gases such as carbon dioxide and steam. As a result, the compound is converted into a porous structure with a low thermal conductivity and increase in thickness due to the foaming action of the volatiles.

Figure 1 is a schematic diagram of the flame resistant Spectra® composite construction, showing the details of the three-layer structured flame resistant barrier. This type of barrier material was tested experimentally and found to be very effective in protecting the Spectra® composites against the turbo-torch flame.[4]

In the flame resistant barrier, the first layer is a refractory coating which protects the second layer against severe heat. An intumescent coating is preferred because when this type of coating is exposed to an open flame, it foamed and produced char. Once this occurs, the thermal conductivity of this layer is expected reduced markedly.

The second layer consists of glass fabrics impregnated with a thermoplastic resin filled with flame retardant. The role of this layer is to protect the third layer so that its thermal stability can be fully utilized against the heat from the flame.

The third layer consists of glass fabrics impregnated with the compound which is required for the flame resistant barrier. This compound normally is a partially cured high temperature resin filled with flame retardant. Additional chemical reactions (i.e., curing reactions) will take place when this layer is subjected to heat and this also helps to improve heat resistance.

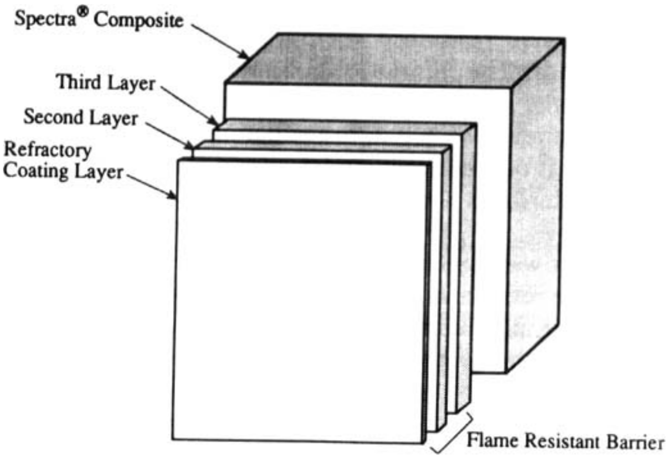

FIGURE 1 Schematic diagram of the flame resistant Spectra® composites construction.

In a recent study, we investigated the effect of critical parameters such as configuration of arrangement of component layers and relative ratio of thicknesses of among these three layers in the flame resistant barrier on the flame resistant performance of the Spectra® composite when it is exposed to the torch flame.[4,16–18] In this study, we investigated the role of matrix resins and the flame retardants in the flame resistant barrier on the flame resistant performance of the Spectra® composite subjected to a turbo torch flame.

Matrix Resins

Since the Spectra® composite must face a temperature of 1200°C during the turbo-torch flame test, the matrix resin therefore should have: (1) high temperature performance, (2) high char yield, (3) preferably a reactive system by which the performance can be improved through absorption of heat when subjected to severe heating or exposed to flame, (4) simultaneous conversion of the system into porous structure maintaining to a large degree its dimensions, (5) sufficient mechanical integrity, (6) very low heat transfer conductance, (7) very efficient endothermic characteristics during fire situation.

High temperature resins such as phenolics, PMR-15, vinyl ester, and epoxy resins which were available commercially were evaluated. In addition a new entry, the Primaset™ resin, was also considered because its salient properties may help to meet the requirements. This resin can be used continuously at temperatures higher than 500°C. Unlike other high temperature resins, these resins are easily processable using conventional equipment.[21]

Flame Retardants

Although the use of inorganic fillers as flame retardants and smoke suppressants in polymeric materials has been increasingly gaining technological importance in the past decades, the application of these materials is still somewhat limited because of generally poorer flame resistance compared to halogenated (brominated or chlorinated) compounds. The inferiority becomes even more subtle due to synergistic effects when the halogenated compounds are used in conjunction with antimony trioxide. However, in a real fire situation, the smoke generated by the halogenated materials is of great concern because it is highly toxic. Therefore, the halogenated flame retardants are of little use for the flame resistant Spectra® composites.

Consequently, effort was directed toward development of novel formulations of non-halogenated flame retardants. Specific attention was paid to those fillers which decompose endothermically emitting water and/or gases, such as carbon dioxide, to absorb heat and alter the heat transfer behavior. Water is an excellent heat sink because it has a sizable latent heat of evaporation (about 9.7 kcal/mole). The foaming actions of gases being generated greatly reduces the thermal conductivity and thus further lowers the rate of heat transfer across the composite during exposure to a fire.

HEAT TRANSFER ANALYSIS

A heat transfer analysis was conducted to identify the critical parameters affecting the performance of flame resistant barrier structures. The use of the flame resistant barrier is to prevent the fire and to absorb as much heat as possible so that the Spectra® composite would not suffer any adverse effect of excessive heat due to excessive high (local) temperature, $T_{(x,t)}$, during the torch flame test.

Two approaches were taken to develop an effective flame resistant barrier material for minimizing the temperatures which the Spectra® composite would experience: (1) maximize the rate of heat removal and (2) minimize the thermal properties such as thermal diffusivity.

Equation (1) represents the overall energy-balance for a small control volume of the Spectra® composite subjected to a turbo-torch flame.

$$\mathrm{div}[\lambda \nabla T_{(s,t)}] = \rho C_p \partial T_{(s,t)}/\partial t + Q_{(s,t)} \tag{1}$$

where s is a spacial position in a solid body, ρ is the density, C_p the heat capacity, λ the thermal conductivity, and $Q_{(s,t)}$ the rate of heat removal.

In this analysis, we are interested in estimating the maximum temperature rise at various depths from the surface. Also, the thermal properties of the fiber and matrix resin are not greatly different. Furthermore, the fiber and matrix resin are intimately mixed. Therefore to simplify the analysis in obtaining conservative results, we assume a one-dimensional heat transfer system and use the average thermal properties of the composite material in the computation. Also, to be realistic, we are using a four-layer composite model to calculate the temperature rise in the flame resistant composite. The details of this model are discussed later in Section E of this paper.

Equation (2) describes the one-dimensional heat transfer process for the stationary solid with heat removal within the solid

$$\rho C_p \partial T_{(x,t)}/\partial t = \partial/\partial x[\lambda \partial T_{(x,t)}/\partial x] - Q_{(x,t)} \tag{2}$$

$Q_{(x,t)}$, described in Equation (1) can be expressed in terms of the product of rate of chemical reactions and the heat removal from the reaction.[22]

$$Q_{(x,t)} = R_a \Delta H \tag{3}$$

where R_a is the rate of reaction and ΔH is the heat of reaction.

If the decomposition reaction of flame retardants is assumed to follow a first-order kinetic mechanism, we obtain

$$\rho C_p \partial T_{(x,t)}/\partial t = \partial/\partial x[\lambda T_{(x,t)}/\partial x] - \Delta H(dC_a/dt) \tag{4}$$

Defining the following variables,

$$\Theta = T/T_i \tag{5}$$

$$\alpha = (C_{ao} - C_a)/C_a \tag{6}$$

$$X = x/D \tag{7}$$

$$\tau = (t/D^2)(\lambda/\rho C_p) \tag{8}$$

Two dimensionless equations can be easily derived as follows[4]:

$$d\alpha/d\tau = -k_1\lambda(1 - \alpha)/(\rho C_p D^2) \tag{9}$$

$$\partial\Theta_{(X,\tau)}/\partial\tau = \partial^2\Theta_{(X,\tau)}/\partial X^2 - (\Delta H)D^2k_1(1 - \alpha)/(\lambda T_i) \tag{10}$$

where C_a is the flame retardant concentration, k_1 is the reaction rate constant, ΔE is the activation energy, R the gas constant, T absolute temperature, T_i is the initial (ambient temperature), C_{ao} the initial concentration of endothermic additive (such as magnesium hydroxide), D the thickness of the sample to be evaluated, and λ the thermal conductivity of the material.

The dimensionless Equations (9) and (10) were solved numerically using the Crank-Nicholson method with the following initial and boundary conditions.

$$\tau = 0; \quad X < 1, \quad \Theta = 1 \tag{11}$$

$$\tau = 0; \quad \alpha = 0 \tag{12}$$

$$X = 1; \quad \tau > 0, \quad \Theta = 1 \tag{13}$$

EXPERIMENTAL

Materials

The Spectra® fibers in the Spectrashield® which was used to prepare the composites were Spectra® 1000 fibers (AlliedSignal Inc., High Performance Fibers Division). The concentration of matrix resin was about 20 wt%. In preparing the Spectra® composites, no other additives such as flame retardants or fillers were added to the matrix.

In constructing the Spectra® composite for the torch flame test and hot metal ball contact test, layers of glass fibers were used to protect the Spectra® composite. The resins used as matrix material in the construction of the glass layer composite

TABLE I

A summary of matrix resins

No	Resin	Trade Name	Manufacturer
1	PT Resin	Primaset™	AlliedSignal
2	Vinyl Ester	Derakane 8087	Dow Chemical
	(catalyst)	Lupersol Peroxide	Lucidal Chemical
3	Epoxy Resin	DER 331	Dow Chemical
	(curing agent)	Methylene Dianiline	Aldrich Chemical
4	Resole Phenolic	SP-6842 Clear	Schenectady Chemicals
5	Polyimide	PMR-15	Dexter (Hysol)

were a poly(vinyl acetate) (PVAc) emulsion and several types of high performance matrix resins. The PVAc emulsion was a product of Air Products (tradename VINAC® XX210). The type, trade name, and manufacturer of the high performance resins used as the matrix resin in the third layer are given in Table I. All the resins were used without further purification.

The information pertinent to the several types of flame retardants investigated are given in Table II. The ratio between the matrix resin and flame retardant in the formulation is 1 to 2 by weight. The molecular weight ratio given in Table II is the ratio of the molecular weight of $Mg(OH)_2$/flame retardant. The refractory coating NO FIRE® made by No Fire Engineering, Inc. was used to coat the surface. The glass fabric used was a S-2 glass fabric made by Clark Schwebel.

Thermal Characterization

A DuPont Thermal Analyzer equipped with a DuPont 900 DSC cell was used. The scanning rate used was 20°C/Min in Argon. The temperature used was from 25 to 600°C. The sample size ranged between 5 to 12 mg.

Thermogravimetric Analysis

The weight retention of resins and the mixture of resins and flame retardant was determined by using a DuPont Thermogravimetric Analyzer (TGA). The sample size ranged from 15 to 25 mg. The scanning rate used was 20°C/min and the sample was heated from 25 to 1000°C in argon atmosphere. The weight retention is the remaining weight of the sample after it has been heated to 850°C.

Preparation of Spectra® Composites for Torch Flame Test

Various flame resistant barriers of different composition were evaluated to determine their role on the temperature profile of Spectra® composites to be exposed to a turbo-

TABLE II

Fillers

	Alumina Trihydrate	Magnesium Hydroxide	Zinc Borate	Basic Magnesium Carbonate
Molecular formulas	$Al(OH)_3$	$Mg(OH)_2$	$2ZnO.3B_2O_3.5H_2O$	$Mg_4(CO_3)_3(OH)_2.4H_2O$
Molecular Weight	78.0	58.3	461.6	383.3
Molecular Weight Ratio	0.747	1.0	0.126	0.152
Water Content (wt %)	34.5	31.0	14.0	20.0 36% (CO_3)
Decomposition Temp,°C	200	330	300 - 450	230
Enthalpy of Decomposition (kcal/gm)(24)	-0.28	-0.328	---	-0.295
Type of Volatile	Water	Water	Water	Water and CO_2

torch flame. The thickness fraction of the third layer of the flame resistant barrier with respect to the total thickness of the flame resistant barrier was about 0.65. This was found to give the best flame resistance performance.[4] The sample dimensions which were used in this experiment were 0.15 m × 0.15 m × ~0.047 m thick.

In the preparation of Spectra® composites for the torch flame test, one side of a 0.047 m thick Spectrashield™ composite was laminated with the flame resistant barrier. A K-type thermocouple was placed at the center of the panel (where the torch flame is directed) at a depth of 3.174 mm (~$\frac{1}{8}''$) from the surface for temperature monitoring. The composite panel was molded at 125°C for two hours under 96 kN/m^2 pressure. The refractory coating was applied on the outside glass layer of the composite. The thickness of the refractory coating layer (the first layer) was about 0.1 mm.

A control sample (Control Composite) was made in a similar fashion. One side of a 0.047 m thick Spectrashield™ composite was laminated with a flame resistant barrier which consisted of glass fabric prepregs. These prepregs were impregnated with a poly(vinyl acetate) emulsion without any flame retardants. The total thickness of the glass fabric layers was 3.174 mm. A K-type thermocouple was placed at the center of the panel between the Spectra® and glass layer for temperature monitoring. The composite panel was molded in a press at 125°C for two hours under 96 kN/m^2 pressure. The refractory coating was applied on the glass fabric layer and its thickness was about 0.1 mm.

Flammability Evaluation

The flammability of the Spectra® composites constructed with a flame resistant barrier material was evaluated by a turbo-torch flame test in accordance with the MIL-L-46197(MR)[11] test designed by the U.S. Army Laboratory Command, Ma-

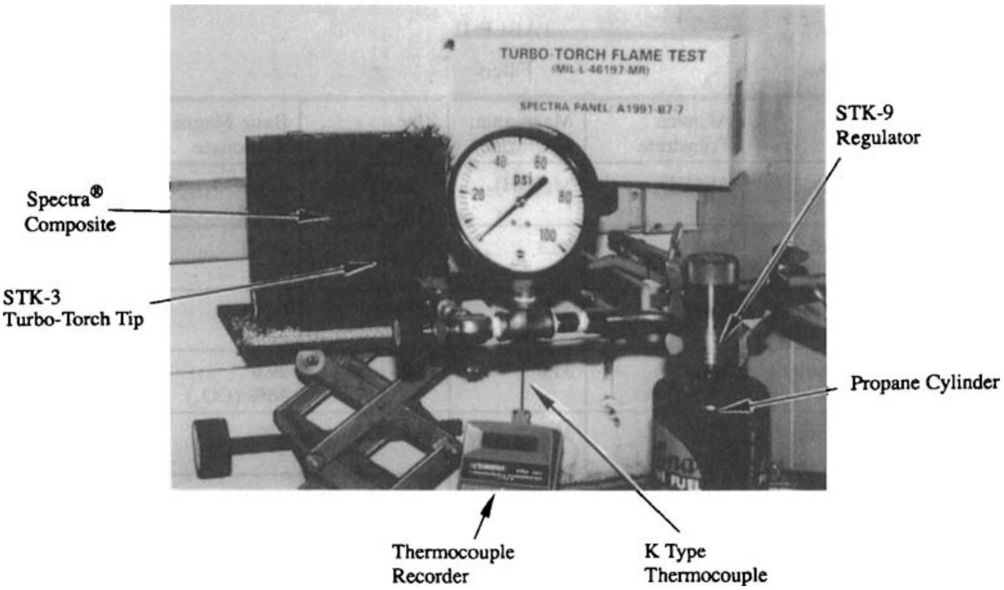

FIGURE 2 A photograph of the turbo-torch flame test set-up.

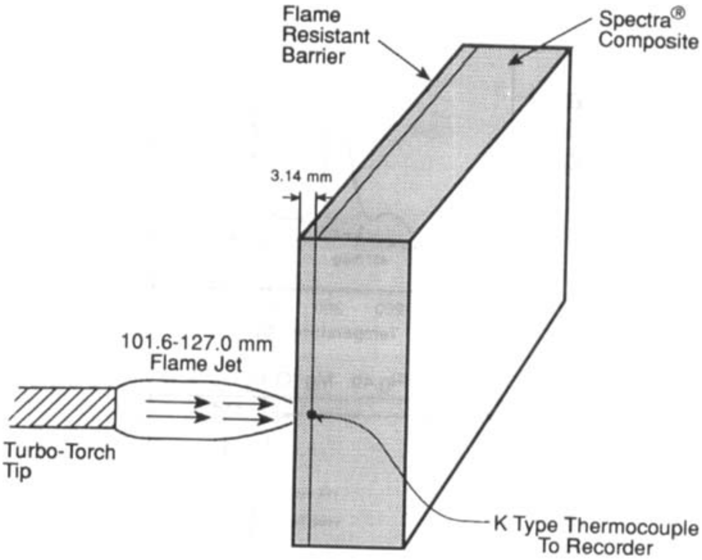

FIGURE 3 A schematic diagram of temperature measurement.

terial Technology Laboratory (MTL) for screening S-2 glass laminates. A Spectra® composite was directly exposed to a torch flame at a temperature of about 1200°C for 600 seconds (10 minutes) by the procedure described in the MIL-L-46197(MR).[11] In this test, a 0.15 m × 0.15 m (6″ × 6″) square test sample of known weight is supported on a standard laboratory jack in a vertical position with layers of thermal insulating materials between the jack and the sample. A commercially available 0.4 kg (14 oz.) propane cylinder equipped with a turbo-torch head, model STK-9 (Victor Equipment, Denton, TX) was adjusted to produce a 4 to 5 inch long flame jet. The STK-9 torch head consisted of a STK-R pressure regulator and a ST-3 tip.[24] A picture of the testing apparatus is given in Figure 2. A schematic diagram of the testing is illustrated in Figure 3. A thermocouple was placed in the Spectra® composite at a depth 3.174 mm from the testing surface. The composite sample was held in contact with the flame jet for ten minutes. The temperature at the sample surface was approximately 1200°C. The temperature increase at 3.174 mm depth from the hot surface was recorded.

RESULTS AND DISCUSSION

A. Thermal Characterization

Figure 4 gives typical differential scanning calorimetry (DSC) thermograms of the matrix resins, flame retardants, and matrix resin/flame retardants systems. Figure 4A is the DSC thermogram for Primaset™ resin, Figure 4B for $Mg(OH)_2$ and Figure 4C for Primaset™ resin/$Mg(OH)_2$. It should be pointed out that the thermal behavior (i.e, onset curing temperature and decomposition temperature, heat content, etc.) depends on the structure of the matrix resin, flame retardant, and

Fig.4a. Primaset™ Resin

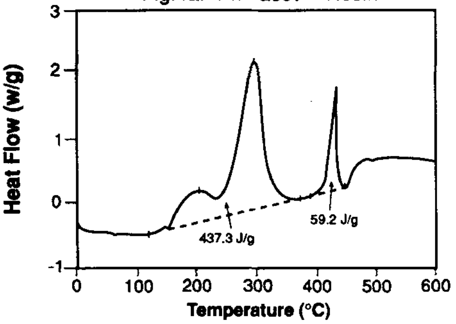

Fig.4b. Mg (OH)$_2$

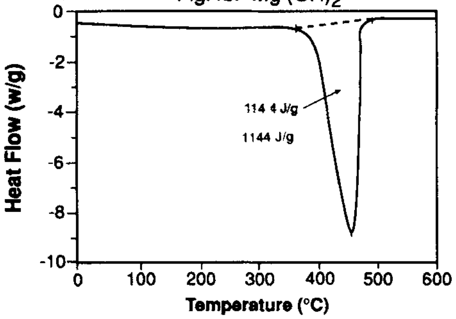

Fig.4c. Primaset™ Resin/Mg (OH)$_2$

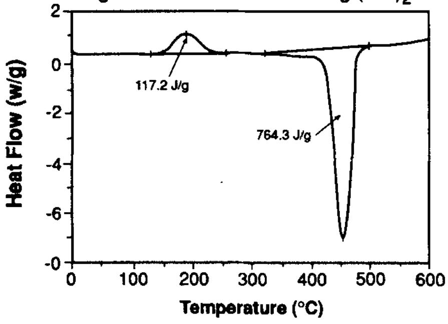

FIGURE 4 DSC Thermograms of Primaset® resin/Mg(OH)$_2$ systems.

TABLE III

Heat of reaction of matrix resins

Heat J/gm	Matrix				
	Primaset™	VE	Epoxy	Phenolic	PMR-15
Reaction	-437.3	-345.3	-323.3	-452.0	ND
Decomposition	-59.2	+313.4	-54.6	-186.2	ND

TABLE IV

Heat of reaction of the Primaset™ resin/$Mg(OH)_2$ systems

Heat J/gm		Primaset™ Resin/Flame Retardant				
		Primaset™	VE	Epoxy	Phenolic	PMR-15
Reaction	exp.	-117.1	-85.7	-113.2	-47.12	ND
	cal.	-145.7	-115.1	-107.8	-150.6	ND
$Mg(OH)_2$ Decomp	exp.	+764.3	+533.4	+561.4	+410.6	+374.0
	cal.	+764.7	+764.7	+764.7	+764.7	+764.7

TABLE V

Heat of reaction of the Primaset™ resin/flame retardant systems

Heat J/gm	Primaset™ Resin/Flame Retardant Systems			
	Magnesium Hydroxide	Alumina Trihydrate	Zinc Borate	Basic Magnesium Carbonate
Reaction	-117.1 (-145.7)	-120.4 (-145.7)	-101.4 (-145.7)	-122.0 (-145.7)
Flame Retardant Decomposition	+764.3 (+764.7)	+708.3	+298.3	ND

TABLE VI

Weight retention of matrix resins

Weight Retention, %	Matrix				
	Primaset™	VE	Epoxy	Phenolic	PMR-15
Experimental	64.0	5.0	12.0	60.0	38.8

TABLE VII

Weight retention of matrix resins/$Mg(OH)_2$ systems

Weight Retention, %	Matrix/$Mg(OH)_2$ System					
	$Mg(OH)_2$	Primaset™	VE	Epoxy	Phenolic	PMR-15
Experimental	69.0	62.0	44.0	47.5	60.0	55.2
Calculated	69.0	67.4	47.7	50.0	65.9	58.5

TABLE VIII

Results of density measurement of Primaset™/$Mg(OH)_2$ system

	Density (gm/cc)	
	Calculated	Experimental
Cured	1.92	1.86
Decomposed	3.15	1.62

formulation/composition. We discuss the thermal behavior of these materials in the following sections.

Thermal behavior of matrix resin. The heat derived from the thermosetting polymers arises from the heat of reaction/curing and heat of decomposition. The heat of reaction is typically of exothermic nature, whereas the heat of decomposition can be either endothermic or exothermic. Table III summarizes the heat of curing and heat of decomposition of the matrix resin systems which were investigated. The space in the table marked with "ND" indicates that we had difficulties in determining the heat generated from reaction and decomposition due to broad/multiple peaks and/or poor baseline. The "minus" sign indicates the reaction is exothermic and the "positive" sign is for endothermic reactions.

From Table III, first glance, the best choice of the matrix resin is vinyl ester resin, and the worst choice is resole phenolic resin, from the heat content consideration. However, when these resins were compounded with $Mg(OH)_2$, it was observed that the best choice is actually Primaset™ resin/$Mg(OH)_2$ system, as seen in Table IV.

Thermal behavior of matrix resin with magnesium hydroxide. Table IV summarizes the heat of reaction of various flame retardant systems which was measured by DSC in argon. The ratio between the matrix resin and flame retardant in the formulation is 1 to 2 by weight. The calculated values tabulated in Table IV are calculated using the rule of mixtures. Several points are worth noting in Table IV. (1) Under the same test, pure $Mg(OH)_2$ absorbed about 1147 J/gm during its decomposition reaction (this is much lower than the reported value).[24] Therefore, at 66.7% by weight, it absorbs about 763 J/gm. As is seen in Table IV the heat absorbed by $Mg(OH)_2$ during its decomposition reaction is greater with Primaset™ resin than with other resins. (2) The variation in the heat absorbed by $Mg(OH)_2$ may be attributed to many factors. One of them may be chemical reaction between matrix and $Mg(OH)_2$ as in the case of vinyl ester resin, the reaction reduces the concentration of $Mg(OH)_2$. The carboxylic acid group in the vinyl ester resin is known to react with $Mg(OH)_2$ in unsaturated polyester chemistry.[25] (3) Another factor may be the fact that the exothermic decomposition reaction of the resin may take place simultaneously at the decomposition temperature of $Mg(OH)_2$. This would reduce the amount of heat absorbed.

Thermal behavior of Primaset™ resin/flame retardant filler compound. Table V gives a summary of the heat of reaction of the Primaset™ resin/flame retardant systems. The ratio between the matrix resin and flame retardant in the formulation is 1 to 2 by weight. The values in parenthesis are the calculated values which were determined using the rule of mixtures.

From the value of the decomposition endotherm shown in Table V, the choice of the flame retardant is $Mg(OH)_2$.

B. Weight Retention

Table VI gives a summary of the weight retention for the resin and Table VII for the matrix resin/$Mg(OH)_2$ systems evaluated for both calculated (using the rule of mixtures) and experimental values for weight retention. The ratio between the matrix resin and flame retardant in the formulation is 1 to 2 by weight.

As seen from Table VI and VII, Primaset™ resin and Primaset™ resin/$Mg(OH)_2$ system give the highest value of weight retention.

C. Density Measurements

The densities of both cured and decomposed Primaset™/$Mg(OH)_2$ system were measured using the buoyancy method at 23°C. As is seen in Table VIII, in spite of the fact that the decomposed sample should have higher density than the cured sample, the difference is not as one has anticipated. This may be attributed to the sample becoming porous during the carbonization process. The calculated values are based on the densities (gm/cc): 3.580 for MgO, 2.360 for $Mg(OH)_2$, 1.05 for uncured Primaset™ resin, and 2.20 for carbon.

We selected the Primaset™ resin/$Mg(OH)_2$ system as the flame retardant to make the flame resistant barrier because it is the only matrix resin that meets the overall performance criteria. This system exhibits high temperature performance and has high weight retention. It is a reactive system and its high temperature performance can be improved when exposed to flame. As can be seen in Table VIII, this system can be simultaneously converted into a porous structure when exposed to flame, and thus it has very low thermal conductivity after the conversion. Most importantly, this system has the highest endotherm generated from the $Mg(OH)_2$ decomposition among all the resin systems evaluated.

D. Flammability Evaluation by the Turbo-Torch Flame Test

In a previous study, we reported[4] that four regions are observed in the temperature rise profile when a Spectra® composite is exposed to a turbo-torch flame: (1) the initial temperature rise region (Region I), (2) the endothermic action region (Region II), (3) the secondary temperature rise region (Region III), (4) the local melting region (Region IV). Temperature increases rapidly when the torch flame is directed to the Spectra® composites before the decomposition of magnesium hydroxide commences. When the temperature reaches about 320°C, the rate of temperature rise slows down because of a cooling effect due to the decomposition of magnesium hydroxide. Once the decomposition reaction of magnesium hydroxide is completed, the temperature rises rapidly until the composite undergoes local melting. At this point, the temperature then drops.

Also, we discussed the role of the magnesium hydroxide, the roles of the individual layers, the optimum (relative) ratio of thickness among these three layers, and the effect of thickness of the flame resistant barrier on the temperature rise of the Spectra® composite exposed to the turbo-torch flame.[4] In the present study, we discussed the effect of concentration of $Mg(OH)_2$ in the flame resistant barrier on temperature rise behavior.

Figure 5 gives the plots of temperature versus exposure time for 5 composite samples: one control composite (whose flame resistant barrier contains no flame retardant) and four composite samples (whose flame resistant barrier has different levels of $Mg(OH)_2$). These composites were prepared with the same construction and the total thickness of the flame resistant barrier was 3.174 mm. The thickness

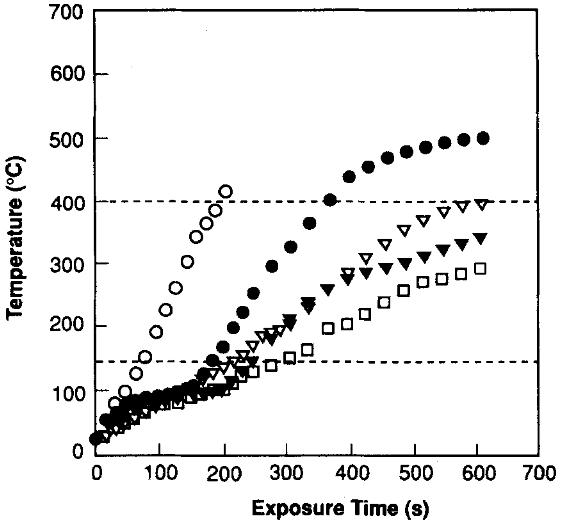

FIGURE 5 Effect of magnesium hydroxide concentration in the flame resistant barrier on temperature profile. (gmol/m^3: (○) 0.0; (●) 2.4 × 10^3; (▽) 4.8 × 10^3; (▼) 9.5 × 10^3; (□) 1.90 × 10^4).

fraction of the third layer of the flame resistant barrier was about 0.65. This thickness fraction was found to give the best flame resistance performance.[4]

As is seen from Figure 5, the presence of magnesium hydroxide in the flame resistant barrier markedly changed the temperature profile in the Spectra® composites. The presence of magnesium hydroxide greatly slows down the temperature rise. As expected, a higher magnesium hydroxide level results in a lower temperature rise.

For instance, the temperature reached 432°C in the control composite after 195 s exposure to the torch flame, whereas the temperature reached about 400°C after 360 s exposure in the composite sample whose flame resistant barrier contained 2.4 × 10^3 gmol/m^3 $Mg(OH)_2$. For the composites whose flame resistant barrier contained more than 9.5 × 10^3 gmol/m^3 $Mg(OH)_2$, the recorded temperature never exceeded 400°C.

Local melting was observed in the control composite after 195 s exposure whereas no local melting was observed after 600 s exposure for the other composite samples. Except for the control composite sample, all composites exhibit an endothermic action region as seen in Figure 5.

The two lines drawn in all the figures of temperature rise represent the melting temperature (~150°C) and decomposition temperature (~400°C) of Spectra® fiber in an inert atmosphere.

E. Heat Transfer Analysis of Temperature Rise Behavior

We have conducted a heat transfer analysis to investigate the effect of $Mg(OH)_2$ on the temperature rise behavior of the Spectra® composites subjected to the turbotorch flame. We compare the experimental temperature data with the calculated temperature to verify the analysis. The temperature which is referred here is the temperature at 3.174 mm (~$\frac{1}{8}$″) depth from the hot surface.

The four-layer composite model. As illustrated in Figure 1, the flame resistant

TABLE IX

Parameters used in the computation

Density (ρ),kg/m3	1st Layer $(\rho)_1$: NOFIRE• coating	0.7 x 10^3
	2nd Layer $(\rho)_2$: Glass Fiber/PVAc/$Mg(OH)_2$	1.50 x 10^3
	3rd Layer $(\rho)_3$: Glass Fiber/PT/$Mg(OH)_2$	2.20 x 10^3
	4th Layer $(\rho)_3$: Spectra• Composite	1.05 x 10^3
Thickness (D), m	1st Layer $(D)_1$: NOFIRE• coating	7.94 x 10^{-4}
	2nd Layer $(D)_2$: Glass Fiber/PVAc/$Mg(OH)_2$	1.06 x 10^{-3}
	3rd Layer $(D)_3$: Glass Fiber/PT/$Mg(OH)_2$	2.12 x 10^{-3}
	$(D)_T$: Total Thickness	2.90 x 10^{-2}
Temp. °C	Ambient Temperature	25.0
	Initial Temperature	1200.0
Heat Capacity J/kg °K	1st Layer $(C_p)_1$: NOFIRE• coating	1.42 x 10^3
	2nd Layer$(C_p)_{g2}$: Glass Fiber/PVAc/$Mg(OH)_2$	1.46 x 10^3
	3rd Layer $(C_p)_{g3}$: Glass Fiber/PT/$Mg(OH)_2$	1.88 x 10^3
	4th Layer $(C_p)_s$: Spectra• Composite	1.88 x 10^3
Thermal Conduct. W/m °K	1st Layer $(\lambda)_1$: NOFIRE• coating	1.62 x 10^{-2}
	2nd Layer$(\lambda)_{g2}$: Glass Fiber/PVAc/$Mg(OH)_2$	3.72 x 10^{-2}
	3rd Layer $(\lambda)_{g3}$: Glass Fiber/PT/$Mg(OH)_2$	8.35 x 10^{-2}
	4th Layer $(\lambda)_s$: Spectra• Composite	2.80 x 10^{-1}
$Mg(OH)_2$ Decomp. Data	Decomposition constant (k_1), s^{-1}	0.1233
	Activation energy (ΔE), kJ/gmol	8.845
	Heat of Decomposition (ΔH), kJ/gmol	-1.03 x 10^2

barrier is made of a 3-layer laminate composite. The first layer is a NOFIRE® refractory coating which protects the second layer against severe heat. The second layer consists of glass fabrics impregnated with a PVAc resin filled with magnesium hydroxide. The role of this layer is to protect the third layer so that its thermal stability can be fully utilized against the heat from the flame. The third layer consists of glass fabrics impregnated with Primaset™ resin filled with magnesium hydroxide. Therefore, we have developed a four-layer composite model to calculate the temperature rise in the flame resistant composite. This model is quite simplified but realistic and the discussion of the parameters used in the calculation is the following.

The first layer is the NOFIRE® coating layer. Although, the thickness of the coating was only about 0.1 mm. This coating is an intumescent coating. When it is exposed to an open flame, this coating foamed and produced char. From measurements, the final thickness of this layer is about 0.794 mm. Without going into a more elaborated analysis in which we must change the stationary boundary conditions prescribed by the set of Equations (11) to (13) into the moving boundary conditions, we assume that the initial thickness of the NOFIRE® layer is 0.794 mm thick. This *assumption* is justified because the coating expands instantaneously as

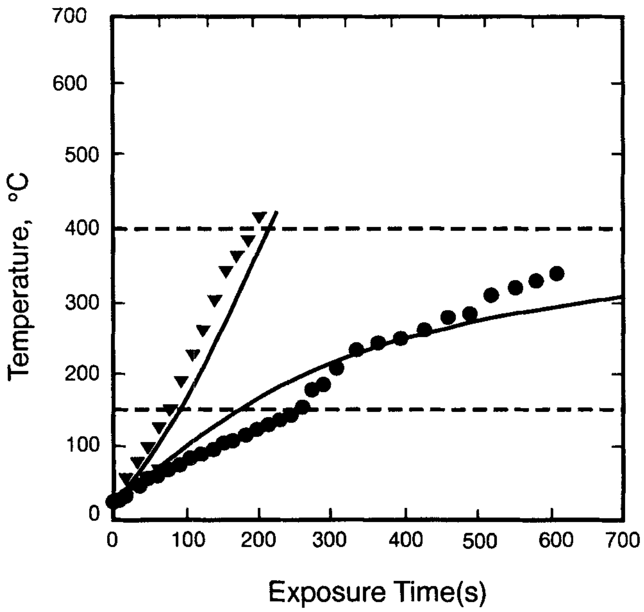

FIGURE 6 Temperature versus exposure time. (Heat transfer analysis: ——; experimental: (●) control composite, (▼) flame resistant composite.)

soon as it exposes to an open flame. We assume the density and thermal properties of this layer are similar to those of the mineral wool.[26]

The second layer is the glass fabric/PVAc resin/$Mg(OH)_2$ layer and its density and thermal properties are assumed to be similar to those of glass blanket.[26]

The third layer are the glass fabric/Primaset™ resin/$Mg(OH)_2$ layer whose density and thermal properties are assumed to be similar to those of glass fiber composite.[26] The fourth layer is the Spectra® composite and the obvious assumption regarding its density and thermal properties are similar to those of polyethylene.[26]

The physical and thermal properties of each layer which are required to solve the Equations (9) and (10) using the Crank-Nicholson method are given in Table IX. We assume that the change of density and thermal properties do not vary with temperature.

In deriving the Equations (9) and (10), we assumed that the decomposition of the $Mg(OH)_2$ in the mixture of Primaset™/$Mg(OH)_2$ follows the first order kinetics. Also, the kinetic parameter such as the decomposition constant and activation energy were determined by thermogravimetry.[27-30] The values of the kinetic parameter are given in Table IX.

Effect of $Mg(OH)_2$. Figure 6 shows the experimental and the calculated temperature rise for the composite samples whose flame resistant barriers were formulated with and without magnesium hydroxide, respectively. The concentration of magnesium hydroxide in the flame resistant barrier was 9.5×10^3 gmol/m^3 $Mg(OH)_2$.

The temperature increase in the control composite was much more rapid than in the flame resistant composite. The temperature reached 432°C after 195 seconds

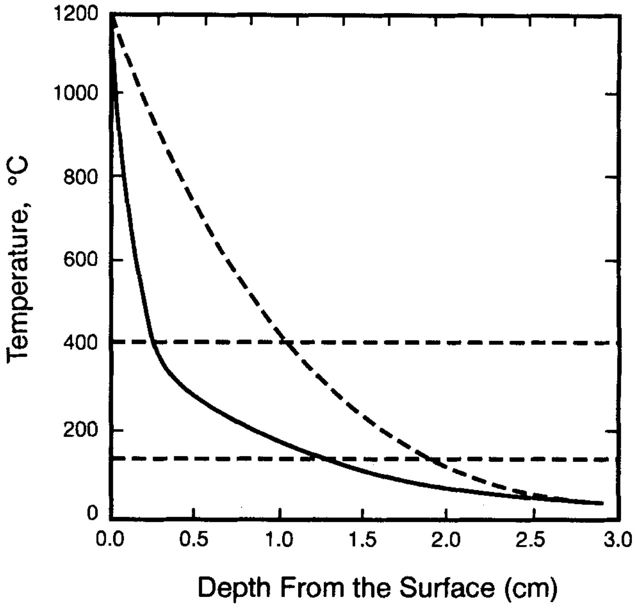

FIGURE 7 Temperature versus position. (Control composite: ——; flame resistant composite: ----.)

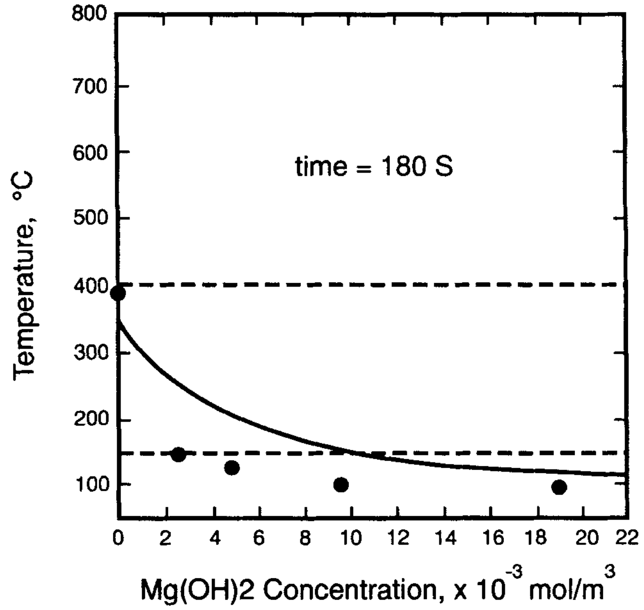

FIGURE 8 Effect of magnesium hydroxide concentration in the flame resistant barrier on temperature profile after 180 s exposure. (Heat transfer analysis: ——; experimental: (●).)

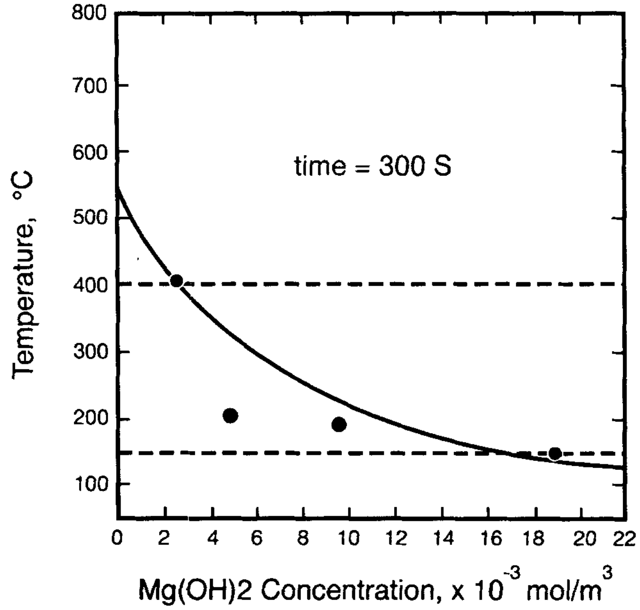

FIGURE 9 Effect of magnesium hydroxide concentration in the flame resistant barrier on temperature profile after 300 s exposure. (Heat transfer analysis: ——; experimental: (●).)

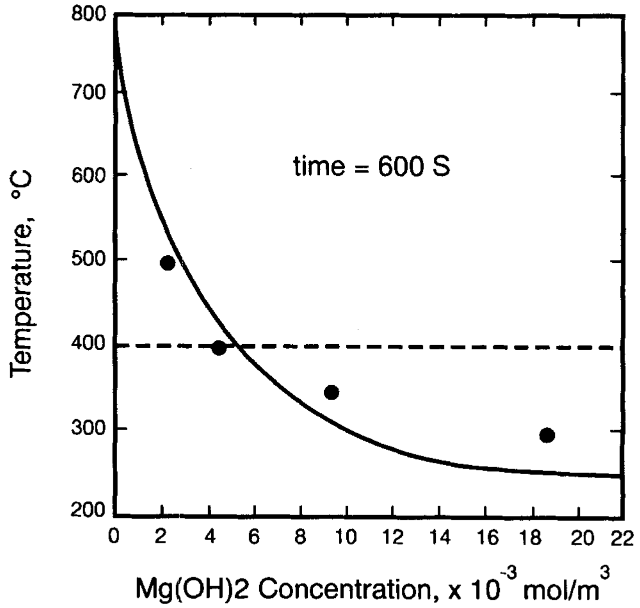

FIGURE 10 Effect of magnesium hydroxide concentration in the flame resistant barrier on temperature profile after 600 s exposure. (Heat transfer analysis: ——; experimental: (●).)

for the control composite. The temperature in flame resistant composite never exceeded 350°C throughout the entire 600 second test.

The data shown in Figure 6 were examined with the heat transfer analysis, showing the calculated values for comparison with the experimental results.

We must point out that, in spite of the fact that the calculated values are close to the experimental data, cautions should be used. In the actual situation, the thermal properties (i.e., λ or $\lambda/\rho C_p$) in Equation (1) may vary from layer to layer. Also their dependence on temperature is not known. Furthermore, the boundary conditions may change due to the volume expansion of the flame resistant layer. Thus, we are not surprised by the differences between the computed results and the experimental temperature data observed in flame resistant composites. In order to establish a more realistic analysis, the kinetics of decomposition should be established more accurately and the effect of the matrix on the decomposition kinetics should be elucidated.

Nevertheless, the model provides qualitative information regarding the temperature profile in the Spectra® composite. Therefore, we have used this analysis to determine the effect of the concentration of $Mg(OH)_2$ on the temperature rise behavior of the Spectra® composites exposed to the turbo-torch flame.

Figure 7 shows the plots of temperature versus distance from the surface (depth) at 600 seconds exposure as calculated by using the same parameters (given in Table IX) which were used in Figure 6 for the two composite samples discussed earlier. In the region facing the torch flame, about 27.3% of the Spectra® composite in the flame resistant composite experienced temperatures greater than 150°C (Spectra® fiber melting point) after its surface was exposed to 1200°C for 600 seconds. Without the flame resistant barrier, approximately 55.5% of the Spectra® composite in the Control Composite experienced temperatures greater than 150°C.

The Effect of $Mg(OH)_2$ Concentration. As is seen in Figures 5 to 7, the addition of magnesium hydroxide in the flame resistant barrier markedly changed the temperature profile in the Spectra® composites. As we have seen from Figure 5, the presence of magnesium hydroxide in the flame resistant barrier has a quenching effect on the temperature rise.

The effect of $Mg(OH)_2$ concentration on calculated and experimental temperature rise of the flame resistant Spectra® composite is shown in Figures 8 to 10 as it is exposed to the turbo-torch flame for 180, 300, and 600 s, respectively. As seen in Figure 8, at short exposure time (e.g., 180 s), the calculated temperature rise is slightly higher than that obtained experimentally. This may be attributed to the exact mechanism of the kinetics of decomposition of the $Mg(OH)_2$ and the matrix is not known and the effect of the matrix (e.g., its interaction) on the decomposition kinetics is not known. Albeit this shortcoming, at higher exposure times (300 and 600 s), the calculated temperature rise is in a better agreement with that obtained experimentally as we can see from Figures 9 and 10.

CONCLUSIONS

We have developed the Spectra® composite structures that survive the turbo torch flame at 1200°C for 600 s without burning and maintain integrity with minimum deterioration after the exposure. The major characteristic feature of this composite structure is the construction of the flame resistant protection layers with glass fiber fabric, matrix resin of high temperature performance and flame resistant filler which has the unique properties of decomposing endothermically to form porous material of low thermal conductivity. To explain and extrapolate the flame resistance behavior of this composite, a heat transfer analysis was conducted. From the results of this analysis, the role of each component in the flame resistant barrier could be explained qualitatively.

In future studies, a more realistic analysis is needed to determine heat absorption behavior during the turbo torch flame test. Experiments should be conducted to establish the kinetics of decomposition, to elucidate the effect of the matrix and the catalyst on the decomposition kinetics, and to determine thermal properties of the flame resistant barrier and their dependence on temperature and physical/chemical changes during the torch flame test.

NOMENCLATURE

C_a: concentration of magnesium hydroxide
C_{ao}: initial concentration of magnesium hydroxide
C_p: heat capacity
D: thickness
D_m: maximum specific optical density
D_s: specific optical density
E: activation energy
H: heat of reaction
h: convective heat transfer coefficient
k_1: reaction rate constant
k_{1o}: preexponential constant
Q: rate of heat removal
q: heat flux vector
R: gas constant
R_a: rate of reaction
s: spatial position in a solid body
T: temperature
t: time
V: volume
x: distance
α: extent of reaction
Θ: temperature
λ: thermal conductivity
ρ: density
τ: time
X: distance

Subscripts

c: composite
f: filler
g: glass layer
i: initial
m: matrix
s: Spectra® layer
1: first layer
2: second layer
3: third layer

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