

# Vinyl Ester Resin Modified With Silicone-Based Additives: II. Flammability Properties

Cristiana A. Ittner Mazali, Maria Isabel Felisberti

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13084-971 –Campinas, SP, Brazil

Received 29 December 2004; accepted 8 April 2005

DOI 10.1002/app.22496

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Silicone-based additives have been used as fire retardants for thermoplastics, presenting the advantages of improving processing and impact resistance of the polymers. In this work we used three different silicone-based additives as modifiers of a thermoset based on a vinyl ester resin. The additives are fine powders made up of about 50 wt % ultra high molecular weight polydimethylsiloxane and 50 wt % silica. The differences between them are the functional groups inserted on the additives and the size and size distribution of the particles. The additives were dispersed in resin containing 35 wt % of styrene. For curing the mixture a conventional catalyst and initiator were used and the reaction was carried out in two ways, differing in the curing temperature, the post curing temperature, and the time, and in the addition of dimethylaniline (DMA) as a promoter of the polyaddition reaction. The samples were characterized by thermogravimetric analyses and swelling experiments. The fire retardances of the samples were evaluated by the determination of the flash-ignition, self-ignition, and pyro-

lysis temperatures (ASTM D1919–91a), and of the oxygen index (ASTM D-2863–91). The results obtained showed that the silicone-based additives and the methods used in the preparation of the modified resin influence the flash-ignition, self-ignition, and pyrolysis temperatures, but not the oxygen index. Samples cured by different methods present different network characteristics, which influence their thermal decomposition. The volatile species produced by thermal decomposition may be a combination of inert and active species. The network structure may influence only the inert fraction of the volatiles, not the combustibles. These volatile inert species (smoke-black, water vapor, carbon dioxide, etc.) probably dilute the combustibles in the solid and in the gaseous phase, increasing the flash-ignition temperature of the samples. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 644–649, 2006

**Key words:** additives; silicones; swelling; thermal properties; thermosets

## INTRODUCTION

The growth of disposable polymeric materials has been followed by intense divulgation of safety patterns, because during heating a polymer can suffer thermal decomposition at relatively low temperatures yielding volatile and highly flammable organic compounds. These can readily burn, emitting large amounts of heat, which causes further polymer degradation, rapidly accelerating progression of the fire.<sup>1–4</sup>

Flammability estimation of polymeric materials using large scale techniques is very expensive and time consuming. Because of this, laboratory scale techniques have been developed. These techniques are not advantageous with regard to the behavior of materials under real conditions, but they are advantageous in the comparison of different materials or different for-

mulations. Thus, the evaluation of material flammability only can be made comparatively under standardized conditions.<sup>5</sup>

Flame retardation is a process by which the normal degradation or combustion processes of polymers are altered by the addition of certain chemicals. Some plastics are inherently fire retardant or smoke retardant, and their performance is acceptable for certain applications. However, for many plastic materials, it is necessary to improve their performance under combustion conditions by incorporating commercially available flame retardants.<sup>6</sup>

Some fillers have undesirable effects. For example, high loadings of alumina trihydrate can alter the physical properties of the material, while antimony trioxide is toxic and can increase smoke production. The inclusion of halogenated compounds can produce corrosive acidic products.<sup>7</sup>

Generally, the mechanism of action is classified as “vapor phase” if volatile species are produced and interfere with the flame propagation mechanism, and “condensed phase” if interactions before vaporization change the nature of the products of degradation and combustion, making the mixture less flammable.<sup>7</sup>

Correspondence to: M. I. Felisberti (misabel@iqm.unicamp.br).

Contract grant sponsor: FAPESP; contract grant number: 98/13,016–0.

This work concerns the study of a vinyl ester thermoset resin that shows a wide range of applications, such as making pipelines, storage tanks for solvents, pools, and so forth. The vinyl ester resins are generally dimethacrylate esters, obtained from the reaction between a bisphenol A-based epoxy resin and an unsaturated carboxylic acid, such as methacrylic acid.<sup>8,9</sup> This resin does not show satisfactory flammability properties, making the use of additives to improve this property necessary.

Silicone based additives were developed by Dow Corning with the purpose of changing the flammability of polymeric materials through reduction of the rate of heat release, carbon monoxide generation, and smoke evolution, without affecting their processing characteristics and mechanical properties, such as impact resistance, tensile strength, and modulus, often affected by some retardant additives.<sup>10–13</sup> These additives are a combination of ultra high molar mass polydimethylsiloxane with fumed silica filler and other additives. The resulting additive is a free flowing agglomerate, with a particle size range of 6 to 600  $\mu\text{m}$ .<sup>10,12,13</sup> These powders can be further modified to present chemical groups, such as epoxy and methacrylate, to enhance compatibility of the powders with various organic resins.<sup>12</sup>

The siloxane powders, when compounded into an organic resin using some types of mixing equipments, can break down into smaller sizes. The additives have the capability of improving processability and mechanical properties, and show synergistic behavior with conventional flame retardant additives.<sup>14</sup> Jayakody et al.<sup>14</sup> studied polyurethanes modified with powdered siloxanes. The exact mechanism of the flame retardancy of powdered siloxane modified polyurethanes has not been determined. However, the siloxane additives are a combination of PDMS and silica that contains many acidic silanol sites that can form crosslinked networks during the burning process. These act as a thermal barrier and prevent the feedback of heat to the substrate.<sup>14</sup>

The effect of a siloxane powder as a processing aid in polypropylene was demonstrated by torque rheometry.<sup>12</sup> Polypropylene containing typical fire retardants is very difficult to process because of the high filler content and nonlubricating nature of the additives. With the addition of 1% of methacrylate-functionalized silicone powder, the extrusion torque was reduced over 50%. Silicone-based additives also improved the mechanical properties of polypropylene. The addition of 1% of the same silicone based additive increased the impact strength of the polypropylene about 100% over the fire retardant system, restoring mechanical properties lost from the use of the fire retardant additives.<sup>12</sup>

The effect of silicone powder as a processing aid in polyphenylene oxide (PPO) was demonstrated by dy-

namic mechanical analysis.<sup>10,13</sup> PPO is very difficult to process and, for commercial applications, is blended with high impact polystyrene (HIPS) to give a resin that can be processed more easily. If HIPS is replaced with as little as 1% of epoxy-functional silicone powder, PPO can then be processed easily. The HIPS-free resin has improved fire and mechanical properties and higher thermal stability in comparison to PPO and its blends with HIPS. The impact strength as well as the flammability properties were improved by addition of 10 to 15% of this powder.<sup>10,13</sup>

The effects of these additives on the flammability properties of thermoset resins have not been described in literature. The aim of this work is the study of the flammability behavior of a vinyl ester resin modified with silicone-based additives.

## EXPERIMENTAL

### Materials

The commercial materials used in this study are summarized in Table I.

The resin used was a vinyl ester resin (VER), Resapol 10–500, based on bisphenol A epoxy resin, containing 35 wt % of styrene monomer. The resin was supplied by Reichold S/A (São Paulo, Brazil) as a yellow liquid. Silicone based additives were supplied by Dow Corning Ltd. (Hortolândia, Brazil) in powder form. The additives are fine powders made up of about 50 wt % modified polydimethylsiloxane and 50 wt % silica. The differences between them are the functional groups inserted on the additives, such as epoxy, methacrylate, vinyl, and other groups<sup>11</sup> (Table I) and the size and size distribution of the particles.<sup>15</sup> Additive 05 shows a bimodal size distribution, with a major fraction in the range of 0.250 and 0.850  $\mu\text{m}$  and a minor fraction between 0.074 and 0.250  $\mu\text{m}$ . Additive 51 shows a trimodal distribution, with the major fraction between 0.074 and 0.250  $\mu\text{m}$ . Additive 81 shows particles with diameters between 0.074 and 0.250  $\mu\text{m}$ .<sup>15</sup>

### Sample preparation

Three different additives were used to modify the resin (Table I). For this purpose 5 wt % of additives were dispersed in the resin using a mechanical stirrer at 2300 rpm for 4 h. Reaction curing was conducted using two different curing systems. In one, 0.5 wt % of a cobalt-II octanoate (CoOo) solution was added. In the other, 0.5 wt % of a cobalt-II octanoate solution and 0.05 wt % of *N,N*-dimethylaniline (DMA) were added to the dispersion. All the resulting mixtures were stirred at 2300 rpm for 15 min, and then the stirring rate was decreased to approximately 140 rpm and the mixture was maintained in an ultrasonic bath at

TABLE I  
Characteristics of the Vinyl Ester Resin and the Silicone-Based Additives

Materials	Code	Composition	Reactive groups
Vinyl ester resin	VER	<p>The structure shows a repeating unit of a poly(vinyl siloxane) backbone. The backbone consists of alternating silicon and oxygen atoms. Each silicon atom is bonded to two methyl groups and a vinyl group. The oxygen atoms are part of the backbone and are also bonded to methyl ester groups and hydroxyl groups. The structure is shown as a chain of units connected by oxygen atoms, with a vinyl group at the end.</p>	hydroxyl; epoxy; acrylic; vinyl
Additive 4-7105	05	Poly(dimethyl-co-methylvinylsiloxane) with terminating hydroxyl groups and fumed silica	hydroxyl; vinyl
Additive 4-7081	81	Poly(dimethyl-co-methylvinylsiloxane) with terminating vinyl groups, poly(dimethyl-co-methyl-co-methylvinyl phenylsiloxane) and fumed silica	hydroxyl; vinyl; methacryl
Additive 4-7051	51	Poly(dimethyl-co-methylvinylsiloxane) with terminating vinyl groups and fumed silica	hydroxyl; vinyl and epoxy

room temperature for 30 min for degassing. Methyl-ethylketone peroxide (MEKP) (1.0 wt %) was added to the mixture, and it was stirred for another 15 min at 140 rpm. The mixture was then quickly transferred to appropriate polytetrafluorethylene molds and cured by two different methods. In the first, the samples were cured at 25°C for 24 h and postcured at 65°C for 48 h. In the second, the samples were cured at 25°C for 24 h and postcured at 130°C for 4 h under vacuum. Table II describes the curing conditions related to the methods A and B.

### Characterization

#### Thermogravimetric analysis

A TA Instruments 2050 Thermal Analyzer was used to study the thermal behavior of the resin, the additives, and the modified resins. The measurements were conducted in an argon atmosphere (100 mL/min), at a heating rate of 10°C/min, in the temperature range from 30 to 950°C. A sample weight of 10 mg was used.

TABLE II  
Compositions and Curing Conditions of the Composites

Curing method		A	B
Curing temperature and time	25°C/24 h	X	X
Postcuring temperature and time	65°C/48 h	X	—
	130°C/4 h	—	X
Curing system	0.5 wt % CoOc	X	X
	1 wt % MEKP	X	X
	0.05 wt % DMA	—	X

#### Swelling behavior

Sample bars of unmodified and modified cured resin with mass  $m_o$  were submerged in ethanol. The mass gain was monitored until constant mass (around 60 days), when the samples were dried on absorbent paper and weighed ( $m_s$ ). Then, the samples were dried at 100°C and weighed ( $m_d$ ). The difference between  $m_s$  and  $m_d$  gives the solvent mass ( $m_{\text{solv}}$ ) sorbed in the material. The ratio of  $m_{\text{solv}}$  and  $m_d$  is the swelling coefficient ( $q$ ). The difference between  $m_d$  and  $m_o$  is used to calculate the fraction of free chains in the network ( $f_s$ ).

#### Flash-ignition and self-ignition points

The flame retardant properties of the cured vinyl ester resin and the modified resin were evaluated according to ASTM D1919–91a. This method allows determination of the flash-ignition and self-ignition temperatures of plastics using a hot air ignition furnace. At least 3 samples of each composition with dimensions of 3.0 × 12.5 × 20.0 mm were tested. Table III presents

TABLE III  
Experimental Details to Determine the Flash-Ignition and Self-Ignition Points

Experimental details	Flash-ignition point	Self-ignition point
Air flow (L/min)	3.30	6.60
Heating rate (°C/min)	10	20
Dimension of the samples (mm)	3.00 × 12.5 × 20.0	3.00 × 12.5 × 20.0
Flame pilot	yes	no

the experimental conditions used to determine flash-ignition, self-ignition, and pyrolysis temperatures.

### Oxygen index

The flame retardant property of the cured vinyl ester resin and composites was also evaluated by measuring their oxygen index values. Oxygen index is defined by ASTM D-2863-91 as the minimum concentration of oxygen, expressed in percentual volume in a mixture of oxygen and nitrogen, that will just support flame combustion of the material in an environment with controlled temperature. The oxygen concentration of the mixture used in each successive test is increased or reduced by a small amount until the required concentration is reached.<sup>6</sup>

According to ASTM D2863-91, vinyl ester resins are classified as rigid samples. In this case, the specimen dimensions should be 6.5 mm in width, 60 mm in length, and 3.0 mm in thickness, with a fired zone of 6.5 mm wide, 40 mm long, and 3.0 mm thick. The samples were fixed at about 135 mm from the column bottom.

In the beginning, several oxygen concentrations in the nitrogen/oxygen mixture were tested to obtain a concentration in which the material would burn at a slow and uniform rate.<sup>6</sup> The flow valves were adjusted to obtain a volumetric flow of 8.6 L/min. The entire top of the specimen was ignited with the ignition flame so that the specimen was well ignited, and then the flame pilot was removed and the timer started.

If the oxygen concentration is not enough, the flaming of the specimen extinguishes before reaching the delimited area. The oxygen concentration in the mixture was then increased. This method was repeated until the limiting oxygen index was determined.

## RESULTS AND DISCUSSION

### Swelling behavior

The flame retardancy of a resin is determined by its structure. For crosslinked resins, the crosslinking density and the fraction of free chains strongly influence the thermal stability and the evolution of volatile products that can react with oxygen, catching fire and burning.

To characterize the modified and unmodified resins with respect to crosslinking density and fraction of free chains, swelling experiments were conducted. Two parameters were determined in the swelling experiments: swelling coefficient ( $q$ ), defined as the fraction of solvent sorbed for the polymer at equilibrium, and the free or soluble fraction ( $fs$ ). Both parameters are directly related to the network structure of the resin. Table IV shows the values of  $q$  and  $fs$  in ethanol. For the same curing method, it was observed that the

**TABLE IV**  
Swelling Coefficients ( $f$ ) and Fractions of the Soluble Material ( $fs$ ) in Ethanol for Unmodified and Modified Resins, Obtained by Methods A and B

Samples	Curing method	Ethanol	
		$q$ (%)	$fs$ (%)
VER	A	$32 \pm 6$	$1.1 \pm 0.1$
VER + 5 wt % 51		$33 \pm 3$	$1.6 \pm 0.6$
VER + 5 wt % 81		$35 \pm 2$	$1.6 \pm 0.4$
VER + 5 wt % 05	B	$42 \pm 5$	$1.03 \pm 0.01$
VER		$9 \pm 1$	0
VER + 5 wt % 51		$10 \pm 0$	0
VER + 5 wt % 81		$10 \pm 0$	0
VER + 5 wt % 05		$13 \pm 1$	0

swelling coefficients are approximately equal, except for samples containing the additive 05.

For the same composition, the swelling coefficients obtained in ethanol of samples cured by method B are smaller than those obtained by method A. This result showed that samples obtained by method A present smaller crosslinking densities than those obtained by method B. However, the soluble fraction is practically equal for all samples.

### Pyrolysis temperature

The pyrolysis temperature is defined as the temperature at which it is possible to observe the release of combustible gases deriving from the pyrolysis stage. It is difficult to affirm that this temperature corresponds to the beginning of pyrolysis, however, because invisible gases can be exhausted before the visible gases can be perceived. Table V shows the pyrolysis temperatures obtained under conditions used in the flash-ignition and self-ignition determinations (see Table III). It is important to reiterate that, with the experimental conditions used, the pyrolysis temperatures obtained were only slightly different, because different experimental conditions were used in each test.

The increase of the heating rate has been related to the increase of the pyrolysis temperature, as observed for most samples. The pyrolysis temperature was higher for modified resins, independent of the curing method. The increase of heating rate and volumetric air flow enhanced the differences of behavior among the samples.

### Flash-ignition and self-ignition temperatures

The flash-ignition temperature is defined as the lowest temperature at which the gas from a material will burn if a flame is put near it, and the self-ignition temperature as the temperature at which the material burns without the presence of a flame.



TABLE V  
Pyrolysis Temperatures, Flash-Ignition, and Self-Ignition Temperatures of the Unmodified and Modified Resins, Obtained by Methods A and B

Samples	Curing method	Pyrolysis temperature (°C)		Flash-ignition temperature (°C)	Self-ignition temperature (°C)
		Self-ignition conditions	Flash-ignition conditions		
VER	A	430 ± 3	430 ± 3	435 ± 1	453 ± 1
VER + 5 wt % 51		441 ± 4	431 ± 2	461 ± 4	479 ± 6
VER + 5 wt % 81		443 ± 4	443 ± 1	456 ± 1	462 ± 6
VER + 5 wt % 05		445 ± 1	444 ± 4	459 ± 1	483 ± 2
VER	B	436 ± 4	425 ± 2	428 ± 2	456 ± 3
VER + 5 wt % 51		441 ± 2	432 ± 4	439 ± 3	455 ± 3
VER + 5 wt % 81		434 ± 9	432 ± 3	446 ± 1	466 ± 1
VER + 5 wt % 05		449 ± 5	429 ± 4	439 ± 4	460 ± 3

The flash-ignition and the self-ignition temperatures are related to the combustion reaction equilibrium. The material begins to burn (self ignition) when combustible and oxygen concentrations reach a critical value, at which the combustion becomes spontaneous. The oxygen concentration was maintained constant during the experiment. Thus, the self-ignition temperature is a function of the release of combustible volatiles and of the energy provided by the flame. On the other hand, the flash-ignition temperature depends on the oxygen concentration (constant) and the rate of release of combustible volatiles. The latter determines when the instantaneous concentration of the combustibles is enough to ignite.

Table V shows the flash-ignition and self-ignition temperatures of the unmodified and modified resins.

The pyrolysis temperatures are lower than the flash-ignition temperatures or the self-ignition temperatures, when these parameters are determined under the same experimental conditions. This result is expected because volatile product releases are responsible for the combustion of the material.

Samples submitted to the self-ignition test did not reach ignition using volumetric air flowing at 3.30 L/min. So, the volumetric air flow was increased from 3.30 to 6.60 L/min. Even so, samples did not burn. The heating rate was then increased from 10 to 20°C/min.

Samples obtained by method A showed the following increasing order of flash-ignition temperature: REV < REV + 5%81  $\cong$  REV + 5%05  $\cong$  REV + 5%51. Herewith, it was possible to conclude that the additives dislocated the flash-ignition temperature to higher temperatures. However, it was not possible to observe significant differences between the additives. The displacement in the flash-ignition temperature point was about 20°C. With regard to samples obtained by method B, the following increasing order of flash-ignition temperature was observed: REV < REV + 5%51  $\cong$  REV + 5%05 < REV + 5%81. In this case, the additives dislocated the flash-ignition temperatures about 10°C. In general, the flash-ignition temper-

atures of samples cured by method B were lower than those of samples cured by method A.

Thermogravimetric analyses showed that modified resins undergo decomposition starting at temperatures around 300°C and that the mass loss of samples cured in the presence of *N,N*-dimethylaniline, method B, is higher than that observed for samples cured in the absence of *N,N*-dimethylaniline, method A, as shown in Figure 1.

Swelling experiments showed that samples cured by method B present higher crosslinking density. In general, a higher crosslinking density is associated with lower products of thermal decomposition and higher amounts of residue, but this was not observed in this case. Dynamic mechanical analysis<sup>15</sup> and kinetic<sup>16</sup> studies showed that the curing conditions strongly

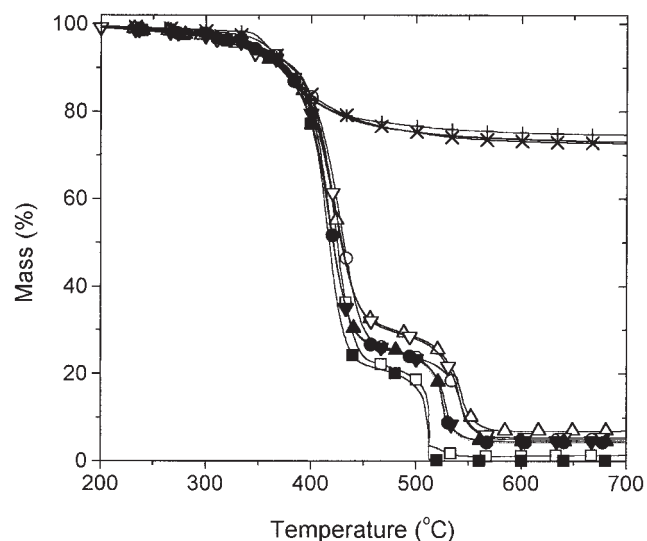


Figure 1 Thermogravimetric curves under an air atmosphere of additives (—) 51, (-x-) 81, and (-+-) 05 unmodified and modified resins cured in the presence of DMA: (■) VER, (●) VER + 5% 51, (▲) VER + 5% 81, (▼) VER + 5% 05; and in the absence of DMA: (□) VER, (○) VER + 5% 51, (△) VER + 5% 81, (▽) VER + 5% 05.

**TABLE VI**  
**Oxygen Index of the Unmodified and Modified Resins,**  
**Obtained by Methods A and B**

Samples	Curing method	Oxygen index (%)
VER	A	21 ± 0
VER + 5 wt % 51		22 ± 0
VER + 5 wt % 81		22 ± 0
VER + 5 wt % 05		21 ± 0
VER	B	21 ± 0
VER + 5 wt % 51		23 ± 0
VER + 5 wt % 81		23 ± 0
VER + 5 wt % 05		22 ± 0

affect the network structure of the modified resins. So, the results from thermogravimetric analysis and swelling experiments suggest that the mechanism of decomposition and the volatile products may differ enough from samples cured by methods A and B to change the combustion behavior.

The self-ignition temperature of modified samples was about 10°C higher than for unmodified vinyl ester resin. Samples obtained by method A showed the following increasing order of self-ignition temperature: REV < REV + 5%81 < REV + 5%51 ≅ REV + 5%05. Samples cured by method B showed the following order of self-ignition temperature: REV ≅ REV + 5%51 < REV + 5%05 ≅ REV + 5%81.

Comparison of self-ignition temperature of samples cured by methods A and B did not show any correlation.

### Oxygen index

The oxygen index is a measure of the facility for burning in polymeric materials. As the burn process involves several stages, the oxygen index is a partial measure of the flammability of polymers. Since the oxygen index measures the capacity of the material to burn at a limiting oxygen concentration, a lower oxygen index is associated with higher flammability.<sup>5</sup>

The oxygen index is related to the ability of the materials to produce high energy free radicals, H· and ·OH, which begin the ignition stage. It is considerably affected by increasing temperature.<sup>5</sup>

The flame retardant properties of the neat and modified resin were examined by measuring the oxygen index, and the results are shown in Table VI. The presence of additives in the resin as well as the curing method did not affect the oxygen index values.

### CONCLUSIONS

The results obtained through flammability tests showed that the silicone-based additives and the two different methods used in the preparation of the modified resin influence the flash-ignition, self-ignition, and pyrolysis temperatures, but not the oxygen index. Samples cured by methods A and B present different network characteristics, which influence their thermal decomposition. The volatile species produced by thermal decomposition may be a combination of inert and active species. The network structure may influence only the inert fraction of the volatiles, but not the combustibles. These volatile inert species (smoke-black, water vapor, carbon dioxide, etc.) can dilute the combustibles in the solid and in the gaseous phase, increasing the flash-ignition temperatures of the samples.

The authors thank Reichold SA and Dow Corning Ltd for supplying the materials used in this work.

### References

- Rabello, M. S. Aditivação de polímeros; Artliber Ltda: São Paulo, 2000.
- Pearce, E. M.; Khanna, Y. P.; Raucher, D. In *Thermal Characterization of Polymeric Materials*; Academic Press: Orlando, 1981.
- Porter, D.; Metcalfe, E.; Thomas, M. J. K. *Fire Mater* 2000, 24, 45.
- Hornsby, P. R. *Macromol Symp* 1996, 108, 203.
- Gallo, J. B.; Agnelli, J. A. M. *Polímeros: Ciência e Tecnologia* 1998, VIII, 23.
- Rosa, A. D. L.; Recca, A.; Carter, J. T.; McGrail, P. T. *Polymer* 1999, 40, 4093.
- Atkinson, P. A.; Haines, P. J.; Skinner, G. A. *Thermochim Acta* 2000, 360, 29.
- Martin, J. S.; Laza, J. M.; Morrás, M. L.; Rodrigues, M.; León, L. M. *Polymer* 2000, 41, 4203.
- Pham, S.; Burchill, P. J. *Polymer* 1995, 36, 3279.
- Pape, P. G.; Romenesko, D. J. *J Vinyl Additive Technol* 1997, 3, 225.
- Dow Corning Catalog. *Aditivos Sólidos de Silicone para Indústrias de Plásticos*, São Paulo, Brazil, 1999.
- Ryan, K. J.; Lupton, K. E.; Pape, P. G.; John, V. B. *J Vinyl Additive Technol* 2000, 6, 7.
- Pape, P. G.; Furukawa, H.; Romenesko, D. *J Eng Plast* 1996, 9, 351.
- Jayakody, C.; Nelson, G. L.; Sorathia, U.; Lewandowski, S. *J Fire Sci* 1998, 16, 351.
- Mazali, C. A. I.; Felisberti, M. I. *J Appl Polym Sci* 2004, to appear.
- Mazali, C. A. I. Doctorate Thesis, Universidade Estadual de Campinas, Brazil, 2003.