Abstract

With glass being heavy, expensive, and fairly brittle, there is a market for flame-retardant acrylic (PMMA). Acrylic has optimal transparency, mechanical properties, and cost of production; therefore, adding flame retardant capabilities would be valuable for glass replacement applications. Blends of monomer and polymer PMMA, a unique nanostructured chemical Polyhedral Oligomeric Silesquioxane (POSS), and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (DOPO) were prepared to obtain transparent flame retardant acrylic. The results show that the synergistic additives had significant effect on the flame retardancy of the acrylic, with minor effect on optical and mechanical properties.

Introduction

Acrylic, like most polymers, is known for its relatively high flammability that is accompanied by toxic gases and smoke during combustion. Because of this behavior, it can be challenging to use acrylic for many applications that typically require a certain level of flame retardancy.

Due to the transparency of acrylic, it became a main interest to find a flame-retardant additive that is compatible with the optics of the material. There is a vast market for architectural and structural applications using flame retardant acrylic as a glass replacement. Replacing glass with acrylic allows for weight and cost reduction, tinting, designs, and formability.

Several flame-retardant additives are available for acrylic; however, some tend to make the material opaque, alter the mechanical properties, or cause toxic gas while burning. Fumed silicas are common additives for opaque material, but are incompatible for transparent applications. Halogenated flame retardants have been used in the past, but brought up health and environmental concerns. Other additives can be used; however, it can be necessary to increase loading levels to retain flame retardancy. This often negatively affects the mechanical properties of the material. It becomes very difficult to create transparent flame retardant acrylic when most known additives have at least one downfall.

The interest in transparent flame retardant acrylic is nothing new in this industry. Many experiments have been performed with numerous additives and polymer combinations to achieve this goal. In recent years, POSS has been revived and made enormous progress due to new analytical methods [1]. POSS is a nanostructured hybrid intermediate between silica (SiO$_2$) and silicone (R$_2$SiO). Because the POSS molecule (RSiO$_{1.5}$) is a combination of both ceramic and organic chemicals, it can be used for many applications, but flame retardancy has not been perfected [2].

Typical POSS materials are colorless, oily, semi-solid filling materials that can affect light transmittance. To counteract this effect, a derived form of POSS that contains either methacrylate or acrylate end groups (R) were used for this application (Figure 1). The flame retardancy varied with both forms of POSS due to the reactivity of the substituents.

![Figure 1. The general structure of POSS (left), the methacrylate R group (top) and acrylate R group (bottom).](image1)

The synergist, DOPO, is a solid white powder that contains phosphorous; a common halogen-free flame retardant alternative (Figure 2). Because the molecule contains aromatic rings, they are known to add a yellow tint to plastic materials. However, since DOPO was used as a synergist, the loading levels were low enough that the yellowing did not affect the transparency of the acrylic for the thicknesses needed.

![Figure 2. The structure of DOPO.](image2)
Experimental

Materials

Three flame retardant additives were used for the experimental work: both Methacryl and Acrylo POSS additives were supplied by Hybrid Plastics and DOPO was supplied by TCI America. The flame-retardant additives were added to a mix of PMMA monomer and polymer supplied by Lucite International. The only additional additive was premix containing a cross linker.

Sample Preparation

POSS (1.5%) and DOPO (1%) were added to the PMMA blend and mixed in a hot water bath until thickened. The samples were refrigerated overnight and then placed in an autoclave for 5-10 days under nitrogen at 6.89 KPa.

The acrylic is created via continuous cell cast in an autoclave. A polymerized acrylic slush is poured into a steel mold with desired thickness and then continually heated and cooled until the acrylic has fully reacted and cured. The amount of time the slush mold is placed in the autoclave is based on the thickness of the panel. This process creates transparent acrylic with uniform high molecular weight polymer.

After the samples come out of the autoclave, they are machined down to the dimensions required. In this case, the dimensions were based on various ASTM test methods and in-house mechanical testing requirements. The acrylic is then annealed to reduce stresses caused by fabrication.

Evaluation

Mechanical properties were evaluated in-house using Dynamic Mechanical Analyzer (DMA) and Differential Scanning Calorimeter (DSC) methods. Flame retardancy was evaluated in accordance with ASTM test methods; performed by Intertek. The test methods used were based on fenestration (architectural) IBC fire rating requirements.

Results and Discussion

Mechanical Properties

In addition to having optimal transparency, acrylic is known for being strong and stiff. Some flame-retardant additives can negatively affect these properties. Because of this, DMA and DSC tests were performed for each sample in order to compare standard acrylic with both forms of the flame-retardant acrylic (Table 1). The materials were tested before and after a high temperature anneal.

| Table 1. DMA and DSC results for standard and POSS/DOPO acrylic, both before and after being annealed. |
|---|---|---|---|
|  | Standard Acrylic | Methacryl POSS/DOPO Acrylic | Acrylo POSS/DOPO Acrylic |
| E’ (MPa) Pre-Anneal | 1550-1700 | 1778 | 1205 |
| E’ (MPa) Post-Anneal | 1850-2100 | 1714 | 1783 |
| DMA Tg (°C) Pre-Anneal | 125-133 | 124.7 | 119.8 |
| DMA Tg (°C) Post-Anneal | 125-133 | 125.6 | 130.1 |
| DSC Tg (°C) Pre-Anneal | 118-125 | 118.3 | 117.1 |
| DSC Tg (°C) Post-Anneal | 118-125 | 117.4 | 117.1 |

Both the Methacryl/DOPO and Acrylo/DOPO combinations had unusual results. Initially, a lower modulus and Tg is not a problem because annealing the material should relieve the stresses caused by machining. Once annealed, the modulus and Tg generally increase. The results above proved slightly different, but suggest a few possibilities.

The degree of crosslinking is predicted to increase because the POSS molecules have eight substituents that are able to react into the polymer backbone, keeping in mind steric hindrance. The high level of crosslinking should raise the storage modulus and lower the loss modulus. This explains why the Tg is within range for both post-annealed combinations. When crosslinking is increased, it can cause the material to be more brittle; this can be tested via tensile and flex tests.

POSS materials are commonly used as toughening agents. Toughening agents are slightly rubbery because they are able to absorb and disperse applied energy. The energy is absorbed by the caged nanostructure that is easily able to contract when in contact with forces. The silica nanostructures work together to disperse the energy. Because of the toughening mechanism of POSS molecules, the modulus should be lower than typical acrylic.

It is predicted that the Acrylo POSS requires a higher temperature to kick off; therefore, the modulus was not representative until after the high temperature anneal. Oddly, the modulus decreased for the Methacryl POSS
after the anneal. The Methacryl/DOPO modulus for both pre and post anneal were irregular in that they both exhibited secondary transition peaks. Whether or not the peaks were β transitions is unclear at this time. More tests are required to ensure the average modulus for this material, both before and after annealing.

The unusual results may also have something to do with the DOPO. DOPO contains phosphoric acid and aromatic rings that are both fairly bulky. The bulkiness could restrict the polymer chains from arranging as close as they do for standard acrylic.

Although the modulus is lower for the POSS/DOPO containing acrylic, that is acceptable for flame retardant applications. The reason typical acrylic applications require a high modulus is because they are thick, load bearing panels. The flame-retardant applications will be thin (1/4”-1”) and will be decorative rather than load bearing. Thus, a lower modulus is acceptable. The loading levels can be adjusted in order to meet standard acrylic ranges; however, the flame retardancy capabilities need to remain.

**Flame Retardancy**

The Methacryl and Acrylo derived forms of POSS were used throughout this experiment which have a unique mechanism for adding flame retardancy to the acrylic. The effect of the substituents (methacrylate and acrylate) is that rather than dispersing throughout the polymer and acting as a plasticizer, the acrylic groups react into the polymer chains. POSS can be thought of as pre-ceramic compound which tends to rearrange to form a hard-ceramic layer instead of forming a char layer, as many flame retardants do. The char formation is thought to be caused by catalysis of the dehydrogenation reaction by the POSS [2].

After ignition, the material undergoes rapid oxidation with the evolution of heat and light. The oxidation creates reactive free radicals that add to the spread of flame. The DOPO was initially added to work in synergy with the POSS as a “radical trap” in the gas phase. At high temperatures, the DOPO molecule degrades and the phosphorous is able to react with the oxygen free radicals in the gas phase. This helps slow the rate of burn because the amount of oxidant is limited.

Thus far, three small scale ASTM test methods have been performed to test the flame-retardant acrylic for fenestration applications. Fenestration includes windows, doors, skylights, curtain walls, and slope glazed systems. Passing these test methods is essential for fenestration glass replacement applications. The POSS/DOPO containing acrylic was able to improve and pass flame retardant requirements for fenestration applications (Table 2).

<table>
<thead>
<tr>
<th>ASTM Standard</th>
<th>Standard Acrylic</th>
<th>Methacryl POSS/DOPO Acrylic</th>
<th>Acrylo POSS/DOPO Acrylic</th>
</tr>
</thead>
<tbody>
<tr>
<td>D635 (mm/s)</td>
<td>0.55</td>
<td>0.28</td>
<td>0.31</td>
</tr>
<tr>
<td>D1929 (°C)</td>
<td>430</td>
<td>404</td>
<td>461</td>
</tr>
<tr>
<td>D2843 rating</td>
<td>10</td>
<td>2.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The ASTM D635 (UL 94 HB) method tests the rate of burn and/or extent and time of burning of plastics in the horizontal position [6]. Both the flame-retardant containing acrylic samples improved the rate of burn compared to standard acrylic. There was a significant decrease in the rate of burn for the Methacryl POSS/DOPO compared to the Acrylo POSS/DOPO. It has been suggested that the methyl containing substituents create a tertiary radical trap which further helps decrease the number of free radicals in the gas phase. Because of this, the rate of burn is decreased further when the substituent contains a methyl group, as does the Methacrylate POSS.

The ASTMD1929 method tests the spontaneous-ignition temperature (SIT) of plastics [7]. The SIT should increase in comparison with the standard acrylic when adding flame retardant additives. The SIT increased for the Acrylo/DOPO acrylic, but decreased for the Methacryl/DOPO acrylic. This suggests a possible interaction between the two flame retardants (Methacryl POSS and DOPO).

The ASTM D2843 method tests the density of smoke from the burning or decomposition of plastics [8]. The smoke density rating, reported above, is based on the average area under the percent light absorption curve of the 3 specimens tested. The smoke density rating was dramatically decreased with the flame-retardant additives. Since the rate of burn decreased, the amount of smoke created was predicted to also decrease.

**Comparison of Failed Flame Retardant Additives**

Before experimenting with POSS materials, fumed silicas, zinc borate, ammonium polyphosphate, and other additives were tested. A few carbonated, brominated and metaborate synergist additives were also tested. Majority
of the additives did not work due to optics or consistency. A few were flame tested, but all were unsuccessful.

Various forms of hydrophilic fumed silica additives were experimented with; both with and without the metaborate synergist. In all cases, the metaborate turned the sample milky yellow and the silica could not all be added to the mixture due to rapid thickening. Hydrophilic fumed silicas are known for thickening quickly; therefore, hydrophobic fumed silicas were tested instead.

The hydrophobic fumed silica additives were able to dissolve in the polymer mix for the most part, but the samples were still milky. The additives would be great for applications using opaque material, but still too milky for transparent material.

The zinc borate additive initially seemed promising because it easily dissolved into the polymer mix with the required consistency, but the samples were slightly opaque. Although opaque, the material was tested via small-scale ASTM methods. The rate of burn (ASTM D635) was not affected with the additive, but the smoke density rating (ASTM D2843) decreased by nearly half.

Ammonium polyphosphate (APP) was the only other phosphorous containing additive tested. The material was fairly opaque with a yellow tint. APP is a common phosphorous based additive, but based on the visual properties APP was not further experimented with for this application.

After POSS was discovered and tested via ASTM methods, it was determined that a “radical trap” additive would also be required because the material was unable to self-extinguish. Brominated additives were unable to dissolve in monomer; therefore, were not tested further. The carbonated additive, 2,3-Dimethyl-2,3-diphenylbutane (CUROX CC-DC), initially seemed capable. After a few flame-retardant tests, it was determined that the lesser amount of CUROX CC-DC that was added, the slower the rate of burn. Because of this, the additive was removed from the formulation (Table 3).

Table 3. Flame retardant results for Methacryl POSS with varying loadings of CUROX CC-DC additive.

<table>
<thead>
<tr>
<th>Method</th>
<th>POSS only</th>
<th>POSS/CUROX (1/2%)</th>
<th>POSS/CUROX (1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D635</td>
<td>0.35</td>
<td>0.35</td>
<td>0.37</td>
</tr>
</tbody>
</table>

As reported above, the test results with DOPO as the synergist was successful. The downfall to having DOPO as the “radical trap” additive is that it tends to yellow the transparent acrylic. It appears that the yellowing tends to concentrate on the surface of the acrylic; therefore, with minimal machining the yellow concentrate is significantly decreased.

Future Work

As mentioned above, the POSS/DOPO acrylic passed flame-retardant test requirements for fenestration applications. In order to certify the material for wall cladding applications, a different set of large-scale tests are required by IBC regulations. Specifically, the material needs to pass ASTM E84 and NFPA 286 tests. The ASTM E84 method tests surface burning characteristics for building materials [9]. The NFPA 286 method tests the contribution of wall and ceiling interior finish to room fire growth [10]. In the future, both large scale flame-retardant tests will be evaluated.

The large-scale test results will help determine the optimal formulation for flame retardancy. Thus far, the 1.5% loading of POSS has met the goal of transparency, mechanical properties and flame retardancy. POSS is known to increase mechanical properties due to crosslinking and thermal stability [2]. If anything were changed, it would most likely be the DOPO loading. Due to the yellowing properties of the synergist, it would be ideal if lower loadings had the same flame retardancy performance. Lowering levels of DOPO could possibly have a positive effect on mechanical properties, as well.

The ASTM D1929 test results were not as predicted for the Methacryl/POSS combination. It has been suggested that there is possible interaction between the Methacryl POSS and DOPO which lowers the SIT, but further testing is essential. To get a better idea of this, an additional test will be run to determine if the results are the same or different. Depending on the results, further steps will be taken to ensure an increase in SIT rather than a decrease.

It is required that the material passes the flame retardant tests for each thickness of interest. Research is necessary to determine the relationship between flame retardant loadings with regard to thickness of the acrylic panels. Most applications will use ¼” -1” thick material; therefore, these thicknesses need to be tested.

After the transparent acrylic is fully certified, opaque acrylic will be experimented with. Zinc borate seemed promising as it dissolved into the polymer mixture and came out the least opaque of all additives tested. The rate of burn did not vary from standard acrylic; therefore, either increased loading or a possible synergist will be needed.

Conclusions

POSS, developed by Hybrid Plastics, provides excellent flame retardancy for transparent acrylic
materials when synergized with DOPO. The ceramic and organic hybrid provides a unique mechanism for flame retardancy that reduces the rate of burn while the synergist helps decrease radical spread in the gas phase. The nature of the additives allows the PMMA to maintain typical optical properties. The mechanical properties were slightly lower, but acceptable for flame-retardant materials. This technology allows for glass replacement in a wide variety of applications.

Acknowledgments

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References

5. TCI America. “9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (CAS Number: 35948-25-5 Product Number: D1874).” TCI America Moving Your Chemistry Forward.