Ceramifying Polymers for Advanced Fire Protection Coatings

K.W. Thomson\(^1\), P.D.D. Rodrigo\(^2\), C. M. Preston\(^3\) & G.J. Griffin\(^3\)

\(^1\)Ceram Polymerik Pty Ltd, P.O. Box 1024, Waverley Gardens, Vic 3070, Australia
\(^2\)Department of Materials Engineering, Monash University, Vic 3800, Australia
\(^3\)CSIRO Manufacturing & Materials Technology, Graham Rd, Highett, Vic 3190, Australia

Abstract

Ceramifying polymer materials have been developed by incorporating ceramic forming precursors into thermoplastics. These compounds can be processed on conventional plastic extrusion equipment to form sheets, profiles or coatings. In a fire situation, the polymer component is quickly pyrolized. However, a porous, coherent ceramic begins to form at sufficiently low temperatures to maintain the structural integrity of the material through to temperatures of over 1000\(^{\circ}\)C. The ceramic forming systems can be adjusted to minimize dimensional changes, or to provide a degree of intumescence through entrapment of volatile gases from the polymer. This can produce a cellular structure with increased thermal resistance. Ceramifying polymer technology has already been commercialized for fire resistant cable coatings and shows promise for many other fire protection coating applications.

1 Introduction

Traditional passive fire protection materials rely on hydrated inorganic intumecents such as sodium silicates and expandable graphites, which form a thermally insulating char. High expansion factors of over 30 can be achieved, providing excellent thermal resistance. However, these chars have some limitations in fires where they must also have sufficient mechanical strength to resist falling away from the protected substrate in the presence of turbulent airflows and mechanical stresses. One approach to improving fire protective coatings is through the use of ceramifying polymers. These materials contain inorganic filler systems which form a coherent ceramic at high temperatures.

Ceramifying polymers generally consist of a polymer matrix with refractory silicate minerals which form the ceramic framework in combination with a flux system. This can allow a coherent ceramic structure to form at a relatively low temperature. Other functional additives may be added including stabilizers and flame retardants.

Although the total ceramifying additive level must be quite high, the materials can still be processed like conventional plastics. A wide range of ceramifying polymers can be produced, including thermoplastics and emulsions suitable for coatings.

Ceramification can be combined with intumescence through a mechanism which traps volatiles from the polymer decomposition as the ceramic structure is formed. This can produce a strong, cellular coating layer with good thermal resistance for fire protection applications.
Ceramifying polymers are not inherently flame retardant. However, they can be modified with organic or inorganic flame retardant systems to achieve low flammability ratings. Ceramification can also assist fire performance by producing a stable surface layer which insulates the underlying layers and may inhibit volatile emissions. This can delay ignition and reduce heat release rates (1).

In this paper, results are presented for two thermoplastic ceramifying polymers; a poly-(vinylchloride) (PVC) based material and a non-halogen ethylene-propylene diene rubber (EPDM) based material.

2 Ceramifying Polymers

Most polymers begin to decompose through oxidative reactions at temperatures of around 200°C. Higher performance polymers such as silicones persist to over 300°C. But typical fire tests require exposure to a temperature profile (Fig 1) based on the combustion of a cellulose fuel load in a representative room (eg BS476 Part 23, AS1530 Part 4, ISO 834, ASTM E119). This reaches 700°C in about 10 minutes at which all polymers, including silicones, rapidly decompose. The temperature continues to increase to 1000°C after 1 hour. Hence, conventional polymers are generally unable to provide a barrier to fire, or thermal insulation, in systems which require a rating of 60 minutes or longer in these tests. These fire ratings are usually achieved by using intumescent materials, which produce an inorganic char with limited cohesive strength, or thick protective structures made from gypsum board or similar materials.

![Standard Cellulostic Heating Curve](image)

A key characteristic of ceramifying polymers is their ability to form a self-supporting structure throughout the temperature range from ambient service temperature to over 1000°C. Reactions in
the inorganic ceramic forming systems can commence from temperatures as low as 350 °C and continue to 800 °C or higher. This is achieved with fluxes which produce a controlled, low level of liquid phase at these temperatures. Ceramification in these materials is not simply the bonding or fusing of the silicate particles by a viscous liquid phase, such as with relatively high levels of low melting point glasses (2). Such materials tend to collapse at high temperatures and are not self-supporting. Ceramification involves reaction sintering assisted by the controlled level of liquid phase.

The X-ray diffraction spectra in Figure 2 show the behavior of a particular silicate-flux ceramifying system. The flux is essentially amorphous at temperatures around 300 - 400°C as indicated by a broad low intensity X-ray diffraction hump at low angles. This amorphous phase has a relatively high viscosity which helps to bind and hold the refractory filler particles together at the early stages of ceramification. It also facilitates sintering between the refractory particles. As the temperature increases to about 600°C, the constituents of the flux system take part in forming new complex crystalline phases. Figure 2 shows the emergence of characteristic peaks for the new crystalline phases as the temperature is increased.

![Figure 2](image)

**Figure 2.** Wide angle X-ray diffraction patterns showing the progressive evolution of a flux system from an amorphous liquid to a mixture of crystalline phases with the increase in temperature. Spectra have been offset on the vertical scale for clarity.

Differential shrinkage between the substrate and a ceramifying coating can result in interfacial cracking and debonding of the protective layer. With appropriate formulations it is possible to produce ceramifying coatings that undergo minimal dimensional changes to avoid these problems.
A consequence of the self-supporting and low shrinkage characteristics is that the resulting ceramic product has a cellular structure. While ceramifying polymers are not inherently good thermal insulators, due to the relatively high thermal conductivity of the inorganic components, the cellular structure improves thermal resistance. The presence of liquid phases within the temperature range at which the polymer is degrading and the evolving gases produced by pyrolysis, also allows intumescence by trapping the gases to cause expansion of the cellular structure. This can greatly increase the thermal resistance (Fig 3).

![Cellular structure after ceramification shown by scanning electron microscopy](image)

### 3 Ceramifying PVC

PVC is widely used in electrical and construction applications. It has some inherent flame retardancy, due to the high halogen content, and offers good mechanical properties with low cost (3). Effective ceramifying materials have been developed with good intumescence and strong ceramic products. They are suitable for conventional thermoplastic extrusion processing. Extruded strips and sheets have been successfully produced and extrusion coating onto substrate materials should also be possible. Expansion factors of more than 7 can be reliably achieved, although the expansion occurs at a relatively high temperature compared to conventional
intumescents. The expansion occurs towards the heat source and can result in quite good resistance to heat transfer.

Several methods exist for measuring the fire resistance of intumescent coatings, which are typically applied as protection to large steel members (ISO 834, ASTM E119). The principle of these tests has been adopted and apparatus constructed (4) to determine the thermal resistance of some ceramifying polymers.

The thermal resistance of the ceramifying materials was measured using a custom refractory enclosure, constructed from 18.7 mm thick calcium silicate board, which was placed within a cone calorimeter. Compression moulded plaques of the sample material were adhered to steel plates using a contact adhesive and placed within the enclosure, which had an internal depth of 55 mm. A thermocouple (1.5 mm diameter, type K, sheathed with stainless steel) was fitted into a 1.5 mm diameter channel drilled into the rear face of the plate (lower), and another thermocouple was placed in contact with the surface (upper) of the material being tested. The upper and lower temperatures were recorded by a data logger at two second intervals during exposure of the sample to a radiant heat flux of 50 kW m$^{-2}$. Experiments were performed in triplicate, and for durations of at least 20 minutes. Excellent repeatability was demonstrated with both surface and substrate temperatures matching closely between subsequent experiments.

![Graph showing temperature over time](image)

*Fig 4. Surface and substrate temperatures of a 4.6 mm thick ceramifying PVC extruded sheet adhered to steel.*

The exposed surface and substrate temperature of a 4.6 mm thick sheet of extruded ceramifying PVC are shown in Fig 4.
The thermal resistance, $R$, was defined as follows,

$$R = \frac{(T_{\text{surf}} - T_{\text{sub}}) \Delta t}{m_{\text{sub}} C_p \Delta T_{\text{sub}} d} \quad - (1)$$

where $C_p$ is the specific heat capacity of the substrate, $m_{\text{sub}}$ is the mass of the substrate, $\Delta t$ is the time increment over which the thermal resistance is measured, $T_{\text{sub}}$ is the temperature of the substrate over period $\Delta t$, $T_{\text{surf}}$ is the average temperature of the exposed surface over $\Delta t$, $T_{\text{sub}}$ is the change in substrate temperature over $\Delta t$, and $d$ is the initial thickness of the specimen.

Fig 5. Calculated thermal resistance of ceramifying PVC (solid line) and degree of expansion of the same material (dashed line).

The calculated thermal resistance of the ceramifying PVC (Fig 5) increased rapidly from the time of exposure, due to the intumescent activity, but then returned to a steady-state resistance for durations up to 15 minutes. The degree of expansion ($E$), was calculated from equation 2,

$$E = \frac{(d_i - d_0)}{d_0} \quad - (2)$$
where \(d_0\) and \(d_t\) are the initial thickness and thickness at time \(t\), respectively. \(E\) is also plotted in Fig 5. The cessation of expansion corresponds to the plateau of thermal resistance, indicating that the insulation ability of the expanded, ceramified, polymer is related strongly to its intumescent activity.

4 Ceramifying EPDM

EPDM is a flexible, non-halogen, thermoplastic material which may be crosslinked to improve properties, if required. In this work, the EPDM was used as a thermoplastic and was not crosslinked. The flexibility of the EPDM offers the possibility of a durable extrusion coating material which could be enhanced by subsequent crosslinking.

EPDM is inherently quite flammable with poor flame spread characteristics. Therefore, it is necessary to incorporate a flame retardant system for most fire protection applications. A halogen based flame retardant system could be used. However, a fully non-halogen system offers environmental advantages (5) and this approach was selected.

The non-halogen flame retardant system is based on metal hydrates and borate synergists which provide a large endothermic effect when the water is liberated. This suppresses ignition and dampens flame spread. Unfortunately, quite high loadings are required and the flame retardant system must be compatible with the ceramic forming components. The total filler content is therefore quite high. Vertical burn flammability tests on 2 mm thick compression moulded samples have achieved UL94 V0 performance.

Intumescence is also more difficult to achieve than with PVC. This is believed to be due to differences in the decomposition temperatures and products. Expansion factors of 3 have been achieved with specific formulations, although some compromise in the strength of the ceramic product was found to be necessary.

5 Comparative Fire Test Performance

A measure of a material’s fire resistance can be obtained by observing its response to a known incident heat flux. A standardized method involves the use of a cone calorimeter, in which the Rate of Heat Release (RHR) by combustion of the material is measured (6). The RHR is determined via oxygen consumption, and is defined as the “calorific energy released per unit time by a material during combustion under specified test conditions” (7). This is a fundamental property which significantly affects the development of fire. Additionally, the amounts of CO and \(\text{CO}_2\) and particulates (smoke) released, and mass loss rate, are typically measured simultaneously.

Cone calorimetry was performed according to the Australian Standard method, which is drawn directly from the ISO method (4). The specimens consisted of compression moulded plaques, with dimensions of 100 x 100 x 6 mm. The plaques were mounted in standard stainless-steel enclosures, resting on an aluminium foil baffle, and retained by a steel grid, to negate the influence of expansion on surface position. An incident heat-flux of 35 kW m\(^{-2}\) was applied by the calibrated, cone-shaped heating element. The rate of heat release, rate of mass loss, time to
piloted ignition, smoke density, carbon monoxide and carbon dioxide concentrations were measured throughout the radiant exposure.

Typical RHR curves for ceramifying PVC and EPDM are compared with control materials in Fig 6 and 7. A flexible grade of PVC that closely matches the formulation of the ceramifying PVC, but containing no ceramifying additives, was used as the PVC control. An unmodified EPDM was used for comparison to the ceramifying EPDM. The peak of the RHR curve for EPDM went off scale and this data is probably not representative of a larger bulk sample. The measured piloted ignition time, however, is considered to be a valid comparison to the ceramifying EPDM specimen.

Fig 6. Rate of heat release, measured by cone calorimetry, of ceramifying PVC and standard flexible PVC control material.
These experiments showed that the ceramifying EPDM specimen continued to smoulder for in excess of 30 minutes, whereas both PVC materials self-extinguished due to exhaustion of combustibles. When the rate of mass loss of ceramifying EPDM declined to below 0.15 kg min⁻¹, after approximately 1800 s, the experiment was considered completed even though combustion was still occurring.

Table 1. Fire performance parameters measured by cone calorimetry.

<table>
<thead>
<tr>
<th></th>
<th>Ignition Time (s)</th>
<th>Peak RHR (kW m⁻²)</th>
<th>Average RHR over 10 min (kW m⁻²)</th>
<th>Average CO₂ (kg kg⁻¹)</th>
<th>Average CO (kg kg⁻¹)</th>
<th>Average Smoke Density (m² kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control PVC</td>
<td>35</td>
<td>361</td>
<td>185</td>
<td>0.59</td>
<td>0.072</td>
<td>1037</td>
</tr>
<tr>
<td>Ceramifying PVC</td>
<td>64</td>
<td>166</td>
<td>84</td>
<td>0.66</td>
<td>0.045</td>
<td>551</td>
</tr>
<tr>
<td>Control EPDM</td>
<td>98</td>
<td>NA</td>
<td>NA</td>
<td>2.08</td>
<td>0.02</td>
<td>479</td>
</tr>
<tr>
<td>Ceramifying EPDM</td>
<td>189</td>
<td>112</td>
<td>92</td>
<td>0.93</td>
<td>&lt; 0.001</td>
<td>20</td>
</tr>
</tbody>
</table>

The onset of the RHR curve coincides with piloted ignition times, as shown in Table 1. In both cases, the time until ignition was delayed significantly in the ceramifying materials compared with their control counterparts.
For the ceramifying PVC, the CO\textsubscript{2} emission was slightly higher, and CO emission was slightly lower than the control. Smoke density was significantly lower.

The peak and average RHR values were unavailable for the unfilled EPDM control material due to the thin specimens used for comparison purposes. Both CO\textsubscript{2} and CO levels were lower for the ceramifying EPDM, consistent with the lower rate of combustion. Smoke emission was significantly reduced.

5. Discussion

The ceramifying PVC material shows significant intumescence with an expansion factor of around 7. The mechanism appears to be through the degradation and dehydrochlorination of the polymer, resulting in gas evolution. This gas can be trapped by the ceramifying structure to form a porous ceramic product. This provides an increase in thermal resistance, limiting the rate of increase in the back face temperature. The ceramic product is quite strong and stable. It has the potential to protect the underlying substrate for a considerable period.

It should be noted that the ceramifying PVC material has been optimized for ceramic formation rather than for fire performance. However, the fire performance results are significantly better than for an unfilled PVC control material. The time to ignition is higher and the heat release rate is much lower. This effect is believed to be a result of the formation of an inert ceramified surface layer that restricts diffusion of degradation volatiles into the combustion zone above the surface.

The higher CO\textsubscript{2} and lower CO levels suggest that the combustion is more complete compared to the control material. This may be due to a less reducing atmosphere resulting from the lower combustion rate.

The RHR curves show that the extinguishment time for the ceramifying PVC corresponds to the point where thermal resistance begins to decrease. This may be caused by a number of factors. As intumescence is an endothermic effect, cessation of the process removes a heat sink from the process, thus heat transfer to the substrate increases. Additionally, the movement of the expanding surface away from the substrate, and evolution of degradation volatiles retards the transport of energy to the underlying substrate. When this process ceases, heat transfer through the degraded material becomes more efficient.

The ceramifying EPDM has excellent flame spread characteristics as shown by the long time to ignition and low heat release rates. However, expansion is lower than for the ceramifying PVC and the ceramic product has lower strength. Fire performance results are much better than for conventional EPDM. The reduction of peak and average RHR is again thought to be due to the formation of a stable ceramified surface layer, aided by the action of the flame retardant additives. The lower CO\textsubscript{2} and CO levels are consistent with the lower rate of combustion.

6. Conclusions

Ceramifying thermoplastic materials offer a new approach to fire protective coatings.
Ceramifying materials based on PVC and EPDM exhibit significantly improved fire performance compared to the respective unmodified (or virgin) polymer materials.

Thermal resistance of the PVC-based ceramifying material reaches a maximum at the early stages of exposure to fire and maintains a fairly high level of thermal resistance even after the ceramification. The initial rapid increase in thermal resistance is consistent with the observed intumescence.

References


Acknowledgements

This work was carried out through the Co-operative Research Centre for Polymers at CSIRO Manufacturing & Materials Technology, Monash University Department of Materials Engineering and RMIT Department of Applied Chemistry. The assistance of Mr Vince Dowling, Professor Yi-Bing Cheng and Professor Robert Shanks is gratefully acknowledged. Antonietta Genovese, Vanja Pasanovic-Vujo and Jefferson Hopewell are also acknowledged for various contributions to this work.