Metal-Exchanged Clay and Zeolite Additives as Smoke Suppressants and Fire Retardants for Poly(vinyl chloride)

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Cone calorimetry studies showed that various metal-exchanged clays and zeolites containing only 3–4% of Cu(II), Cu(I), Zn(II), or Al(III) were effective smoke suppressants and fire retardants for plasticized poly(vinyl chloride). Copper(II)-Zn(II) and Cu(II)-Al(III) synergism for smoke and heat reduction was observed with binary blends of the clays, and the effectiveness of the additives was usually improved considerably by heating plasticizer-additive mixtures under very high shear before combining them with the polymer. Possible mechanisms of action of the additives are described.


INTRODUCTION

The smoke suppression and fire retardance of polymers are favored by crosslinking of the macromolecules. This strategy is effective because it increases the number of chemical bonds that must be broken to create the volatile pyrolysis products that burn in the vapor phase. The additives that cause crosslinking act within the polymer matrix, and in the case of poly(vinyl chloride) (PVC), many of them are known to function there as actual or incipient Lewis-acid catalysts, in keeping with a mechanism first suggested some 30 years ago [1]. This mechanism involves several reactions that generate crosslinks [1–3], one of which is the Friedel-Crafts alkylation of alkene linkages that result from PVC thermolysis (Eq. 1). However, strong Lewis acids suffer from a major disadvantage at the very high temperatures reached in large fires, which is their tendency to promote the cationic cracking of the crosslinked char into volatile aliphatic fragments [2] that are superlative fuels [2, 4].

\[
\begin{align*}
\text{Cl} & \quad \text{CH} = \text{CHCH} \cdots + \text{CH} = \text{CH} \\
\xrightarrow{z} & \quad \text{CH} = \text{CHCH} \cdots \text{CH} \cdots + \text{HCl} \\
\text{z} & = \text{Lewis acid}
\end{align*}
\]

(1)

In an attempt to solve the problem of char cracking, less acidic additives that act as reductive crosslinking agents were developed at the College of William and Mary. During PVC combustion, these additives serve as sources of zero- or low-valent metal species (M\textsuperscript{0}) that promote the coupling reaction shown in Eq. 2 [5]. The metal may actually act as a true catalyst for this process, because the condensed phase of the burning polymer system is a reducing environment that can convert the higher-valent form of the metal back into the active M\textsuperscript{0} state [6, 7].

\[
\begin{align*}
\text{Cl} & \quad \text{2CH} = \text{CHCH} \cdots + \text{M}^0 \\
\longrightarrow & \quad \text{2CH} = \text{CHCHCHCH} \cdots \text{CH} \cdots + \text{M}^{0+2} \text{Cl}_2
\end{align*}
\]

(2)

Much of our research on reductive coupling promoters has been concerned with compounds of Cu(II) or Cu(I) [5, 8–16]. When such additives are used, the most effective coupling agent is probably Cu(0), whose formation in situ seems likely to be assisted by the facile valence disproportionation shown in Eq. 3 [5].

\[
2\text{Cu(I)} \rightarrow \text{Cu(II)} + \text{Cu(0)}
\]

(3)

We have also studied the smoke suppression and fire retardance of PVC by binary blends of mixed-metal Cu(II) oxides [11–13, 15, 16], which are defined as Cu(II) oxides containing a second metal. The effects of some of these blends are extraordinarily synergistic, especially for smoke suppression.

Most recently, we have started to investigate the effects of complex inorganic substances (initially, clays and zeolites) whose original cations have been replaced by Cu(II),...
Cu(I), or other metallic species that are known to decrease both smoke and flame. In this work, a major objective has been to combine the beneficial properties of the cations with those of their complex hosts. Naturally occurring nanoclays, such as sodium montmorillonite (Na-MMT), are layered aluminosilicates consisting of stacks of negatively charged aluminosilicate sheets with the alkali metal cations in the gallery spaces between them. Intercalation of the polymer into these spaces can eventually lead to disruption of the stacking and thus to an exfoliated nanocomposite morphology in which the sheets are now primarily on the surface of the material. There, according to a prevalent theory [17], they can contribute to the suppression of smoke and flame in two ways. One of these is to serve as a physical barrier to the escape into the vapor of volatile flammable species that are formed in the polymer matrix by pyrolysis. The other way is to act as a thermal barrier to this pyrolysis by shielding the matrix from the heat of the vapor-phase combustion. The exchange of metal cations into complex hosts can have other useful effects, as well. It can mask the color of the cation, a desideratum for Cu(II), and it may help to protect the cation from air oxidation, a potential problem with Cu(I).

This article reports the preliminary results we have obtained with metal-exchanged clays and zeolites in plasticized PVC. We also describe an alternative approach to nanocomposite formation that involves the prior heating of mixtures of a plasticizer and a metal-exchanged additive under very high shear. Smoke and flame parameters were measured by cone calorimetry.

**EXPERIMENTAL**

**Materials**

A commercial PVC powder containing no additives was used without purification. Plasticizer di(n-heptyl, n-nonyl) phthalate (“7,9-phthalate”, Palatinol 79P) was supplied by BASF Canada. The Na-MMT (Cloisite® Na+) was provided by Southern Clay Products, and the zeolites were obtained from various commercial sources. All of the other chemicals were commercial products of very high purity and were used as received.

**Metal-Exchanged Clays and Zeolites**

Exchange reactions with Na-MMT were carried out by heating and stirring a suspension of the clay overnight in a dilute aqueous solution containing an appropriate metal salt. In a typical experiment, 40 g of clay was heated and stirred magnetically at 90–95°C in 200 mL of deionized water containing 5 g of cupric sulfate pentahydrate. The clay was recovered by suction filtration, washed thoroughly with water and methanol in succession, and then dried to constant weight at 40–50°C. Samples prepared in this way retained the grayish color of the starting clay and were shown to contain 2.72–2.88% of copper (theoretical value for complete exchange, 2.92%) by atomic absorption spectroscopy (Perkin-Elmer instrument, Model 1100B). Similar exchanges were carried out with the Cu(I)-thiourea [Cu(I)-Htu] and Cu(I)-ethylenethiourea [Cu(I)-Etu] complexes [Cu2(Htu)5]SO4•2H2O and [Cu2(Etu)6]SO4, prepared as described elsewhere [14], as well as with sources of Zn(II) and Al(III), which were ZnSO4•H2O and Al2(SO4)3•18H2O, respectively. Exchange reactions with zeolites were performed in an analogous way, and when CuSO4•5H2O was used, the zeolite copper contents ranged from 3.11 to 3.77%.

**Preparation of Plaques for Cone Calorimetry**

Procedure A: Plaques (100 × 100 × 3 mm³) containing about 34 g of PVC, 30 phr of plasticizer (parts by weight per hundred parts of resin), and the desired amount of clay or zeolite additive were prepared by grinding the ingredients together with a mortar and pestle and molding the resultant mixture in a Carver laboratory press (Model C) at 1.4 × 10² MPa (20,000 psi) and 65–150°C (see Ref. 11 for more details). Procedure B: This method was used when preliminary heating and shearing were desired. In general, a suspension of the additive in the plasticizer was heated under air at 80–85°C for the chosen length of time while being subjected to shearing at 10,000 rpm with the BioSpec BioMixer® apparatus shown in Fig. 1. The polymer then was added, and molding was accomplished according to Procedure A.

**FIG. 1.** BioMixer® with blade. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
Cone Calorimetry

A Fire Testing Technology cone calorimeter was used to burn polymer plaques in the flaming mode with spark ignition, according to the standard ASTM E 1354 procedure. The heat flux was 50 kW/m², and a horizontal receptacle was used that allowed samples to be immobilized with a stainless steel grid. Parameters of particular interest were TSR (total smoke released), HRRav (average heat release rate), HRRpk (peak heat release rate), THR (total heat released), and CY (char yield).

RESULTS AND DISCUSSION

Figure 2 presents a rationale for the prior heating and shearing of a mixture of plasticizer and clay. Replacement of the natural cations of the clay by a coordinating cation such as Cu(II) will make the gallery space of the clay more receptive to the incorporation of a typical ester plasticizer. This incorporation should be facilitated by the energy input from heating and shearing. The plasticizer and the coordinating cations in the gallery space will cause it to be highly receptive to the introduction of PVC, which perhaps can now be intercalated into this space without the use of very high shear. Exfoliation of the modified clay during (or prior to) burning should then lead to smoke suppression and/or fire retardance, for the reasons discussed in the Introduction. Most of the plasticizer needed in the final formulation can be added along with the PVC; thus, the preliminary heating and shearing can be done on a relatively small scale.

Table 1 presents the cone calorimetry data for PVC plaques containing various Cu(II)- or Cu(I)-exchanged clays derived from Na-MMT. The tabulated data for TSR and HRRav are also shown in Fig. 3 as bar graphs. Duplicate plaques are designated by the terminal numbers 1 and 2 in the additive column.

Despite the rather unsatisfactory reproducibility found with Na-MMT, this additive clearly had only a minimal effect on total smoke and actually caused a significant increase in the rate of heat release. On the other hand, the

Table 1. Cone calorimetry results for plasticized PVC containing montmorillonite additives.

<table>
<thead>
<tr>
<th>Additive,b 30 phr</th>
<th>TSR (kW/m²)</th>
<th>HRRav (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>CY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (PVC-1)</td>
<td>4635</td>
<td>53.1</td>
<td>175.6</td>
<td>16.7</td>
</tr>
<tr>
<td>None (PVC-2)</td>
<td>4632</td>
<td>59.1</td>
<td>275.6</td>
<td>21.2</td>
</tr>
<tr>
<td>Na-MMT-1</td>
<td>4766</td>
<td>110.6</td>
<td>267.2</td>
<td>40.8</td>
</tr>
<tr>
<td>Na-MMT-2</td>
<td>4251</td>
<td>74.2</td>
<td>132.5</td>
<td>21.4</td>
</tr>
<tr>
<td>Cu(II)-Clay-1</td>
<td>3906</td>
<td>21.0</td>
<td>31.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu(II)-Clay-2</td>
<td>4074</td>
<td>17.2</td>
<td>29.0</td>
<td>7.2</td>
</tr>
<tr>
<td>Cu(II)-Clay-c</td>
<td>4533</td>
<td>18.3</td>
<td>28.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu(II)-Clay-d</td>
<td>4329</td>
<td>19.4</td>
<td>36.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu(I)-Htu-Clay-1</td>
<td>3661</td>
<td>15.4</td>
<td>20.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Cu(I)-Htu-Clay-2</td>
<td>3723</td>
<td>12.8</td>
<td>19.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Cu(I)-Htu-Clay-d</td>
<td>4460</td>
<td>33.6</td>
<td>87.6</td>
<td>9.2</td>
</tr>
<tr>
<td>Cu(I)-Etu-Clay-1</td>
<td>4212</td>
<td>47.0</td>
<td>67.1</td>
<td>12.0</td>
</tr>
<tr>
<td>Cu(I)-Etu-Clay-2</td>
<td>4712</td>
<td>12.1</td>
<td>24.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

TABLE 1. Cone calorimetry results for plasticized PVC containing montmorillonite additives.

a 30 phr of “7,9-phthalate.”
b For abbreviations, see text. Additives were heated and sheared for 10 min at 80–85°C unless noted otherwise.

Cu(II)-clay reduced both TSR and HRR_{av}, and the average decrease in smoke was noticeably greater when the preliminary heating-shearing time was maximized. The data for the Cu(I)-Htu-clay are even more striking. With this additive, preliminary heating and shearing greatly improved the results for both smoke and heat release. In contrast, the Cu(I)-Etu-clay was a rather ineffective smoke suppressant but quite active for heat reduction. Surprisingly, though, in both respects, its performance was essentially unaffected by heating and shearing.

Table 1 also shows that the various copper-bearing clays generally tended to reduce the values of HRR_{pk} and THR. In addition, they tended to increase the value of CY, as expected. However, the most interesting aspect of the results in Table 1 is that they were obtained for samples containing only tiny amounts of copper. The copper contents of all of the plaques containing Cu(II)-clay were only about 0.3 phr, and the color of this clay was very similar to that of the unexchanged Na-MMT.

The effects of Zn-clay and Al-clay were also studied in the simple formulation of Table 1. Results showed that the TSR decrease due to the Zn-clay was comparable to that caused by the Cu(II)-clay and that the Zn-clay was also responsive to heating and shearing. After shearing and heating for 10 min at 80–85°C, a 1:1 (w/w) mixture (10 phr) of Zn-clay and Cu(II)-clay exhibited a modest

FIG. 3. Graphs of TSR and HRR_{av} data from Table 1. *Additives were heated and sheared for 10 min at 80–85°C unless noted otherwise. A, heated and sheared for 5 min; B, not heated and sheared. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
synergism for smoke suppression and afforded a 34% reduction in TSR versus the additive-free control. In a parallel experiment, a TSR decrease of 34% also was produced by a 1:1 (w/w) mixture of Al-clay and Cu(II)-clay, and the behavior of the Al-clay closely resembled that of the Zn-clay in the other ways that were just described. As the Zn(II) and Al(III) cations are strong Lewis acids, their synergism with the reductive-coupling promoter Cu(II) was to be expected.

Analogous studies were begun with metal-exchanged zeolites and their mixtures. Various Cu(II)-, Zn(II)-, and Al(III)-exchanged zeolites suppressed both heat and smoke, and preliminary heating and shearing improved their performance in some cases. Reductions of TSR were in the range of about 30–45%, whereas those for THR were some 30–85%. However, with the zeolite additives, there was no conclusive evidence for Zn(II)-Cu(II) or Al(III)-Cu(II) synergism in the suppression of either smoke or heat. The most significant finding we have made in the zeolite area thus far has been a 47% reduction of TSR by a heated and sheared Cu(II)-zeolite (10 phr) in the formulation of Table 1.

Unlike the MMT clays, the zeolite additives do not have a laminar structure. Thus, the scenario outlined in Fig. 2 cannot apply to the zeolite systems. In them, the heating and shearing may simply improve the dispersion of the zeolites and (perhaps) reduce their particle size. These factors, rather than (or in addition to) nanocomposite formation, may be at work in the clay systems, as well. For that reason, additional information is needed to verify or disprove the creation of nanocomposites via the scheme in Fig. 2. X-ray diffraction studies of the Cu(II)- and Cu(I)-clay systems, now in progress, are expected to demonstrate whether or not the spacing between the clay lamellae is changed in ways that are indicative of nanocomposite formation.

CONCLUSIONS

Certain metal-exchanged clay and zeolite additives are effective retarders of smoke and flame in plasticized PVC. Their ability to act in this way requires the presence of remarkably small amounts of the metal [0.3–0.4 phr in the case of Cu(II)] and is usually improved significantly by the preliminary heating and shearing of plasticizer-additive mixtures. When used with the clays, this pretreatment procedure may facilitate the formation of polymer-clay nanocomposites. Mixtures of the Cu(II)-clay with the Zn- or Al-clay are synergistic for the suppression of both smoke and heat.

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REFERENCES