Peroxide crosslinking of PVC foam formulations

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Abstract

Infrared and thermal analyses were used to evaluate the presence of residual unsaturation of a flexible foam formulation of PVC crosslinked by a peroxide/co-agent system. The crosslinking density of some samples was measured and compared with a sample crosslinked by triazine/MgO system in order to know more about the structure of the crosslinked network. Thermal stability of crosslinked samples was evaluated to compare both the crosslinking systems. Morphology of foamed and crosslinked samples was also investigated. Peroxide/TMPTMA appeared to be a reliable method of producing foamed and crosslinked plasticized PVC formulations; it allows the formation of a highly dense network, due to the trifunctional nature of the co-agent compared with the network formed with the triazine/MgO. The crosslinked samples by the peroxide/TMPTMA system did not show residual unsaturation after the optimum curing time. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PVC; Foam; Crosslinking; Peroxide

1. Introduction

The use of vinyl foams continues to increase, due to their good balance between properties and cost, in applications as diverse as flooring, upholstery in the home and automobile, handbags and many clothing accessory items. The majority of these types of foam are made from liquid plastisols. The foams are generally produced by the technique of chemical blowing; in this case, the chemical blowing agent together with a catalyst (“kicker”), uniformly dispersed in the plastisol, is thermally decomposed, so that enough gas is generated to expand the system [1].

In spite of the great demand and the wide range of applications of these materials, mainly in synthetic leather and upholstery, their mechanical properties and dimensional stability are easily affected, mainly by temperature and mechanical stress, due to their low density. These losses in properties can occur during processing, e.g. when the materials are engraved or thermoformed. Crosslinking is a method of improving the dimensional stability at higher temperatures and increasing resistance to mechanical stresses which produce deformation. Different systems for crosslinking flexible foams have been reported [2–4]. Most of these involve relatively elaborate chemistry; in this work, a simpler peroxide crosslinking system, that has already been shown to work adequately, has been used [5–7].

2. Experimental

2.1. Materials

Formulations were based on an emulsion grade PVC, VinyCel-124 from Cydsa; its characteristics are shown in Table 1. Additives used were azodicarbonamide (ADCM) as blowing agent; di-2-ethylhexyl phthalate (DOP) as plasticizer; octyltin stabilizer T-192,
Barlocher; Ca/Zn stabilizer/catalyst NT-223, Barlocher; Ba/Cd catalyst; crosslinking co-agent trimethylolpropane-trimethacrylate (TMPTMA), Aldrich; 2,5-di-methyl-2,5-bis(t-butyl peroxy)hexane, Akzo Chemical; 6-dibutylamine-1,3,5-triazine-2,4-dithiol (DB); magnesium oxide, Baker.

2.2. Formulations

Initial experiments were carried out using a standard flexible foam formulation (standard, Table 2), in order to establish the optimum processing conditions, plasticizer content and the best stabilizer/kicker system. Crosslinkable foams were prepared from formulations (Table 2) with continuous varying concentrations of peroxide and TMPTMA (1–6). In a previous article [6], the effect of peroxide and TMPTMA content on the gel content, apparent density and tensile strength was analysed. In order to compare some properties of the samples crosslinked by the peroxide/co-agent system, formulations (Table 2) using a triazine/MgO crosslinking system (7, 8) were also prepared.

This article reports a study of the crosslink density, softening temperature, morphology, residual unsaturation and thermal stability of crosslinked samples produced using a peroxide/TMPTMA system and comparing some of these characteristics with samples crosslinked by a triazine/MgO system.

On the other hand, a sample of commercial crosslinked foam was also used only for comparison purposes; although we did not know the used system to crosslink it, neither the formulation nor the curing conditions used to prepare it.

Table 2
Molar mass data of the PVC resin

<table>
<thead>
<tr>
<th></th>
<th>(K) value</th>
<th>(M_n \times 10^{-4})</th>
<th>(M_w \times 10^{-4})</th>
<th>Polydispersity(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC V-124</td>
<td>66</td>
<td>5.13</td>
<td>11.09</td>
<td>2.16</td>
</tr>
</tbody>
</table>

\(^a\) GPC determination.

2.3. Sample preparation

The plastisol formulations were blended in a food mixer at room temperature for approximately 30–35 min, using the following procedure: the liquid additives were dispersed in the plasticizer, then the solid additives were added and mixed for 5 min. Finally, the PVC resin was incorporated and mixing was continued for 20–25 min. The plastisols obtained were spread over a flat surface and were heated in an air oven at 195°C for different duration of time in order to obtain the crosslinked PVC foams.

2.4. Sample testing

2.4.1. Gel content

The samples were Soxhlet extracted for 20 h with tetrahydrofuran (THF), and the final residue was dried for 12 h at 80°C and weighed. The amount of gel was expressed as the percentage of the total amount of material which could form the gel.

2.4.2. Residual unsaturation

The percentage of residual unsaturation as the crosslinking reaction proceeds, in a sample with high content of co-agent, was determined by infra-red spectroscopy (FTIR) in a Nicolet Magna 550 spectrometer. Films prepared from formulation 4 which contains 20 phr of TMPTMA were cured for 1, 1.5, 2.0, 2.5, 3.0, and 4.0 min. The films were analysed by FTIR in order to detect the gradual change in the signal at 1640 cm\(^{-1}\) that corresponds to the unsaturated C=C in TMPTMA. The absorbance at 1640 cm\(^{-1}\) was ratioed to that at 1430 cm\(^{-1}\) which corresponds to the methylene groups (CH\(_2\)) of the PVC, in order to compensate for film thickness. These ratios were used to investigate the decrease in residual unsaturation as the reaction proceeds.

2.4.3. Thermal analysis

Some of the cured samples were also evaluated by DSC in order to detect the disappearance of the exo-
therm for the TMPTMA homopolymerization with cure time, using the technique previously described [5].

Calorimetric measurements on the plastisol and on the cured samples, at different times, of formulation 4 were carried out using a DuPont thermal analyser fitted with a DSC cell. The heating rate was 20°C/min and nitrogen was used as atmosphere.

2.4.4. Thermomechanical analysis
A DuPont thermomechanical analyser (TMA) was used to measure the penetration of a loaded probe as a function of temperature for some of the samples. The heating rate was 20°C/min.

2.4.5. Swelling equilibrium and crosslinking density
The number average molar mass between the crosslinks ($M_c$) was determined using the Flory–Rehner equation [8]. Samples, without blowing agent, of formulations 2, 3, 4 and 8 were swollen in methyl ethyl ketone for seven days at room temperature. The swollen and dry weights were used to calculate the volume fraction of PVC in the network swollen to equilibrium. The value is used in the equation to calculate $M_c$, to provide information about the crosslinked network structure.

2.4.6. Morphology of crosslinked foams
The cell morphology of the crosslinked foams obtained was analysed by optical microscopy in an Olympus BH-2 microscope and AMS Optomax V image analyser. An empirical test to observe liquid absorption was also carried out. The foamed sample was submerged in water for 24 h, then was cut into pieces to verify visually the presence or absence of water.

2.4.7. Thermal stability
Thermal stability was determined according to ASTM-D2115 at 177 ± 1°C. The samples were evaluated for up to 140 min, samples being taken every 20 min. The crosslinked foams evaluated were 1 (1/15) and 6 (3/15). An uncrosslinked foam which was used as a standard and a commercial crosslinked one were also tested.

The thermal stability of a series of samples without the blowing agent was also investigated, to enable peroxide and triazine/MgO systems to be compared. For this purpose, samples used were 1 (1/15), 3 (2/15) and 6 (3/15) which were peroxide based and 7 (5/3) and 8 (5/5) which were crosslinked by triazine/MgO.

3. Results
Table 3, shows the gel content results for the crosslinked formulations. As has been reported before [5,6], the gel content increased with peroxide and TMPTMA content and also with the curing time. The gel content increase was more evident as the co-agent content increased. From this information, 4 min was taken as the optimum cure time.

The presence of residual unsaturation in the sample 4 (2/20), crosslinked at different times, was analysed by infra-red spectroscopy. In samples that have been crosslinked using irradiation, it has been reported [9] that 20% of the double bonds remain unreacted after all the monomer has reacted. On the contrary, for the samples studied here (Fig. 1), unsaturation could not be measured after 4 min curing time. The alkoxy radicals produced by decomposition of the peroxide can diffuse rapidly in the liquid medium, enabling them to react readily with the double bonds present. These results were in accordance with thermal analysis results (Fig. 2) for the same plastisol formulation and the samples crosslinked, at the same temperature, but at different times (1–5 min). It was observed that the exotherm, clearly visible in the first traces (plastisol, 1–3 min), after 3 min crosslinking, decreased noticeably as crosslinking time increased; after 5 min most of the monomer has reacted. These results are also consistent with the reported gel content results (Table 3) which showed a maximum gel content after 4 min, most of the TMPTMA monomer has been reacted, at the temperature used.

When irradiation is used, the macroradicals produced are not able to move readily, particularly as crosslinking proceeds, so not all the unsaturation is able to react [9,10].

Fig. 3 shows the results for the penetration temperature, measured by thermomechanical analysis, for two foamed crosslinked samples (5 and 6) with different levels of TMPTMA and also the standard foam.

### Table 3
Gel content of crosslinked formulations

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
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<tr>
<td>3</td>
<td>15.4</td>
<td>9.7</td>
<td>21.5</td>
<td>24.9</td>
<td>12.6</td>
<td>24.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>22.5</td>
<td>11.1</td>
<td>26.7</td>
<td>34.2</td>
<td>17.7</td>
<td>32.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>20.4</td>
<td>12.8</td>
<td>28.0</td>
<td>31.9</td>
<td>16.1</td>
<td>33.9</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>64</td>
<td>88</td>
</tr>
</tbody>
</table>
Fig. 1. Disappearance of residual unsaturation with respect to the curing time for the crosslinked foam formulation 4.

Fig. 2. Thermograms of plastisol and crosslinked samples of formulation 4, crosslinked at different curing times.
formulation (uncrosslinked) and the commercial one. It could be seen that the penetration temperature was lowest for the standard foam and increased with TMPTMA concentration. Moreover, it could be observed that the produced foam formulation 6 with peroxide/TMPTMA ratio 3/15 had a higher penetration temperature than the commercial foam.

Table 4 shows the $M_c$ values (the number average molar mass between crosslinks) for the sample series 2–4, as the TMPTMA content increases. The $M_c$ values are similar to those reported earlier [5] (It can be noted that an error is present in the 1/2$M_c$ values in Ref. [5, Table 14] in which the multiplier for (1/2)$M_c$ should be 10$^5$). It is seen that $M_c$ decreases when the TMPTMA content increases; i.e. the crosslinking density increases. The trifunctional nature of this monomer produces relatively low values of $M_c$ and the formation of gel with rather a tight network [6]. In the same table, these values are compared with those for a sample crosslinked with the triazine DB/MgO.

Although the peroxide/TMPTMA samples have much lower gel content, the $M_c$ value is lower in all cases than the value for the triazine crosslinked sample; this is an indication of the kind of network structure that is promoted by the presence of the TMPTMA co-agent due to its trifunctional nature, where the three unsaturated groups are available to react. The triazine, according to Mori and Nakamura [11] forms only two points of crosslinking per molecule, by reaction of the SH groups. These results are in accordance with the tensile properties of these samples reported previously [6], when it was observed that samples crosslinked with the peroxide/TMPTMA system showed higher tensile strength than those crosslinked using triazine (DB)/MgO, despite higher gel content of the latter sample.

Fig. 4 shows a photograph of the cell structure generally observed in the crosslinked foams. It is seen to be an open cell structure with interconnections between the cells. Moreover, when the foams were immersed in water it was possible to see diffusion of the liquid through the material, which confirmed the presence of open cells. A closed structure does not allow the passage of liquid through the material because the cells are separated; on the other hand, an open cell structure allows saturation of the material due to the interconnections that exist between the cells.

When the thermal stability of the crosslinked foams was compared with a standard (uncrosslinked) foam and with a commercial crosslinked foam, it was observed (Fig. 5) that the sample crosslinked (1) with peroxide/TMPTMA in the ratio of 1/15, had a similar behaviour to the uncrosslinked foam with darkening being observed after 80 min. Sample (6) crosslinked with peroxide/TMPTMA in the ratio 3/15 showed significant

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Gel content (%)</th>
<th>$M_c \times 10^{-4}$ (g/mol)</th>
<th>$\bar{M}_c \times 10^3$ (mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide/TMPTMA 2/10</td>
<td>11.1</td>
<td>2.523</td>
<td>1.98</td>
</tr>
<tr>
<td>Peroxide/TMPTMA 2/15</td>
<td>26.7</td>
<td>1.273</td>
<td>3.92</td>
</tr>
<tr>
<td>Peroxide/TMPTMA 2/20</td>
<td>34.2</td>
<td>0.298</td>
<td>16.73</td>
</tr>
<tr>
<td>Triazine DB/MgO-5/5</td>
<td>88.0</td>
<td>3.543</td>
<td>1.41</td>
</tr>
</tbody>
</table>
blackening at the half of this time, probably due to the presence of radical residues due to the higher amount of peroxide in the sample. The commercial crosslinked foam showed almost total blackening after 20 min, indicating that the peroxide/TMPTMA system showed better thermal stability.

Fig. 6 compares the thermal stability of peroxide crosslinked samples with those crosslinked using triazine.
DB/MgO. The two samples with triazine (7 and 8) showed similar behaviour irrespective of MgO concentration. Their behaviour was also very similar to that of the samples with peroxide/TMPTMA ratios of 1/15 and 2/15, showing significant blackening after 80 min.

4. Conclusions

The peroxide/TMPTMA system allows the formation of a highly dense network, due to the trifunctional nature of the co-agent, compared with the network formed with the triazine DB/MgO.

The samples crosslinked by the peroxide/TMPTMA system did not show residual unsaturation after the optimum curing time, which was different to the behaviour reported for irradiation crosslinking.

The thermal stability of the foamed samples crosslinked by peroxide/TMPTMA was always better than the commercial foam examined, while the thermal stability of the unfoamed crosslinked samples was similar at lower peroxide/TMPTMA ratios (1/15, 2/15) to the samples crosslinked by triazine DB/MgO.

References