Homogenization in Mechanical Mixing Involving Polyvinyl Chloride. II. Effect of Different Types of Polymers on Breakdown of PVC Particulate Structure and Mixing Mechanism

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ABSTRACT

The process of mixing PVC with other polymers, including an examination of how these polymers contribute to the breakdown of the particulate structure of PVC, is described. The polymers were an immiscible nitrile rubber containing 22% acrylonitrile (NBR-22) and two miscible polymers, poly-ε-caprolactone (PCL) and copolyester thermoplastic elastomer (trademark Hytrel). The mixing of PVC and NBR-30, as investigated in the previous paper (Part I), was also considered as a reference. The overall progress of mixing for the three systems (i.e., PVC/NBR-22, PVC/PCL,

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and PVC/Hytrel) was similar to that for PVC/NBR-30; the removal of skins was followed by breakdown of PVC particles. However, the rate of breakdown differed widely from system to system, depending on the inherent thermodynamic and viscoelastic nature of the individual polymers which served as the medium for stress transfer to the PVC particles. Molecular mixing, which provides a strong interfacial adhesion between PVC and the component polymer, was important in the breakdown process; the immiscible pair, PVC/NBR-22, gave the slowest mixing. The magnitude of the storage modulus, \( G' \) at the onset of mixing and at the mixing temperatures was also important. Among the three miscible polymers, the breakdown rate decreased with decreasing modulus, in the order Hytrel, NBR-30, and PCL. The higher temperatures in PVC/Hytrel mixing contributed to a faster rate of PVC breakdown, due to the more serious weakening of the interparticle bonds and more melting of PVC microcrystallites.

**INTRODUCTION**

In the preceding paper [1], the progress of mixing of PVC with a miscible polymer, nitrile rubber with 30% acrylonitrile content (NBR-20), was examined. Microscopically, the skins of PVC grains (100 ~ 150 \( \mu \text{m} \)) were first peeled off, and then the agglomerates of the primary particles were broken down to the primary particles. The latter were further broken down to domains and the even smaller size, less than ~0.1 \( \mu \text{m} \). Molecular mixing was limited to the interface between the two polymers but it resulted in a strong adhesion, effectively transferring the stress to the PVC particles.

This paper explores how other polymers contribute to the mechanism of mixing with PVC. One sample was a nitrile rubber containing 22% acrylonitrile (NBR-22) and immiscible with PVC [2], in contrast to the miscible NBR-30 in our previous study. Two other samples were poly-\( \varepsilon \)-caprolactone (PCL) and copolyester thermoplastic elastomer (trademark Hytrel), which are miscible with PVC in their amorphous molten state [3–6]. The major difference between the two polymers is that the PCL is a thermoplastic and is in the melt flow state throughout the mixing process, while the Hytrel is a thermoplastic elastomer and transforms from the rubbery to the melt state with progression of the mixing.

As in the case of the previous paper [1], a series of ongoing events through the mixing process were monitored with a scanning electron microscope (SEM) and interpretation of the results was assisted by the temperature-dependent viscoelastic data of the individual polymers.
EXPERIMENTAL

The PVC resin was the same as the one used in the previous study [1], Geon 103 EP F-76 (the Geon Co.). The nitrile rubber was HYCAR 1094-80 (Zeon Chemicals), which contains 22% acrylonitrile; its glass transition temperature is $-40^\circ\text{C}$. The poly-$\varepsilon$-caprolactone (PCL) was PCL-700 (Union Carbide Corp.), with a melting point of $60^\circ\text{C}$ and glass transition temperature of $-60^\circ\text{C}$ [2, 7]. It has been reported that the number average molecular weight is 13,000 and the weight average molecular weight is 41,000 [8]. The copolyester thermoplastic elastomer was Hytrex grade 4056 (E. I. du Pont de Nemours). It is a random block copolymer of crystallizable tetramethylene terephthalate, which forms the hard segments, and poly(tetramethylene ether) glycol terephthalate, the soft segments [9]. The soft segments have a glass transition temperature of $-50^\circ\text{C}$ and the hard segments melt at about $150^\circ\text{C}$ [10]. The number average molecular weight is about 30,000.

Overall the mixing procedures were similar to those reported in the previous paper [1]; 50/50 weight ratios of PVC and component polymer were used and a batch, Banbury-type internal mixer (1.57 L) was employed with a rotor speed of 80 rpm.

Before the mixing started, the following steps were taken:

1. With PVC/NBR-22, the rubber was first masticated at room temperature for 30 sec and then the rotor was stopped. At this stage, the temperature was 65°C, as monitored with a built-in thermocouple.
2. With PVC/PCL, the temperature of the mixer was first set at 65°C and PCL was charged. Then the rotor was rotated slowly for about 20 sec to melt the PLC completely.
3. With PVC/Hytrel, the Hytrex was masticated until the temperature reached 135°C.

Following each of the above steps PVC was introduced into the mixer, the ram was lowered, and the rotor was restarted. From this moment, the mixing time was measured.

The SEM examination was performed with an ISI model SX-40. Samples for the SEM were prepared in the same way as reported in the previous paper [1], i.e., by freeze-facturing in liquid nitrogen.

RESULTS AND DISCUSSION

Figures 1 and 2 present the storage modulus, $G'$ and the loss modulus, $G''$, respectively, of NBR-22, PCL, and Hytrex. Both $G'$ and $G''$ were
measured as a function of temperature at 1.6 Hz over the temperature range of mixing. In both figures, the significant differences among the polymers are clearly demonstrated. Table 1 summarizes the temperatures monitored with a built-in thermometer at various mixing times and the viscoelastic data of the individual polymers at the corresponding temperatures.

With NBR-22, the ratio of $G'$ to $G''$ is about 2:1 over the range of the temperature; the trend is very similar to that of NBR-30 [1]. The $G'$ and $G''$ values of the former are slightly lower than those of the latter because of the lower acrylonitrile content [11, 12]. The magnitudes of $G'$ and $G''$ of PCL are much lower than those of NBR-22 or Hytrel, and $G''$ is higher than $G'$ through the entire range of temperature because the polymer is in the molten state. The melting of the crystalline hard segments of Hytrel starts at a temperature somewhere around 150°C and continues past 160°C. There is a corresponding sharp drop of the modulus between 150° and 170°C. Among the three polymers, Hytrel has the highest moduli, particularly $G'$, at the onset of the mixing.
FIG. 2. Loss modulus, $G''$ of NBR-22, PCL, and Hytrel as a function of temperature. The frequency of oscillation is 1.6 Hz.

Figures 3 through 7 are SEM micrographs of the morphological changes of the PVC particulate structure in the process of mixing with NBR-22. At a mixing time of 30 sec, Fig. 3(a), the PVC grains are shown to be intact. At 50 and 70 sec, Figs. 3(b) and 4(a), skins of some PVC grains are stripped off and the skinless particles become incorporated into the rubber matrix. Also shown is an early sign of destruction of the skinless particles. In the samples taken at the mixing time of 90 sec, Fig. 4(b), skins of all the grains are removed and somewhat more particles are broken.

As shown in Fig. 5(a), the sample mixed for 110 sec still contains a considerable amount of agglomerates, indicating that the mixing is much slower compared to that of PVC with NBR-30 [see Fig. 8(a), Ref. 1]. Recognizing that the mixing conditions such as the rate of deformation (i.e., rotor speed) and initial mixing temperature are exactly same for both PVC/NBR-22 and PVC/NBR-30, and that viscoelastic moduli of both NBRs are only slightly different from each other, the reason for the large difference in the rate of breakdown must be in the difference in interaction
<table>
<thead>
<tr>
<th>Mixing time (sec)</th>
<th>Temperature (°C)</th>
<th>PVC/NBR-22</th>
<th>PVC/PCL</th>
<th>PVC/Hytrel</th>
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<tr>
<td></td>
<td></td>
<td>G' (Pa)</td>
<td>G'' (Pa)</td>
<td>G' (Pa)</td>
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<td>3.6 × 10^4</td>
<td>2.0 × 10^4</td>
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</tr>
</tbody>
</table>

^aHighest temperature reached during the mixing.
FIG. 3. Scanning electron micrographs of PVC/NBR-22 mixture at mixing times of 30 sec (a) and 50 sec (b). The white scale bar at the lower right of each micrograph represents the stated scale.
FIG. 4. Scanning electron micrographs of PVC/NBR-22 mixture at mixing times of 70 sec (a) and 90 sec (b).
FIG. 5. Scanning electron micrographs of PVC/NBR-22 mixture at a mixing time of 110 sec (a) and the boundary between PVC and NBR-22 (b).
FIG. 6. Scanning electron micrographs of PVC/NBR-22 mixture at mixing times of 130 sec (a) and 170 sec (b).
FIG. 7. Scanning electron micrographs of PVC/NBR-22 mixture at mixing times of 250 sec (a) and 450 sec (b).
FIG. 8. Scanning electron micrographs of PVC/PCL mixture at mixing times of 30 sec (a) and 50 sec (b).
at the interface. A sharp boundary exists between PVC particles and NBR-22 matrix, as shown in Fig. 5(b), which is in contrast to the diffused interface due to mixing of PVC and NBR-30. The PVC particles in the absence of an interfacial mixing may lack sufficient adhesion and slip when forces are applied from the rubber to the PVC particles.

When the mixing passes 130 sec and then reaches 170 sec (Fig. 6), there are still broken pieces of agglomerates and primary particles in contrast to the PVC/NBR-30 where the particles were reduced to a size smaller than domains (≤0.1 μm). With further mixing, for 250 sec [Fig. 7(a)], there are many primary particles and even at 450 sec [Fig. 7(b)], the size of the PVC particulate is between primary particles (∼1 μm) and domains (∼0.1 μm).

In the mixing of PVC and PCL (Figs. 8 and 9), after 30 sec the skins of PVC grains are already gone and the skin-free particles are incorporated in the PCL matrix, Fig. 8(a). The spherical holes are the skins of the PVC grains and on the opposite fracture surface, the skin-removed particles are presumably present. As the mixing continues further, the skin-free particles become disintegrated into smaller particles; at a mixing time of 130 sec [Fig. 9(b)], the demolished pieces of the agglomerates of primary particles and their spherical voids are detectable. The rate of breakdown in PVC/PCL mixing is much slower than that of PVC/NBR-30 and is comparable to that of PVC/NBR-22. This is explained by the much lower storage modulus of PCL than that of NBR-30. The loss of skin at 30 sec may be due to better adhesion of PCL/skin than NBR/skin.

In the mixing of PVC with Hytrel, even at a mixing time of 30 sec (Fig. 10), the skins of the PVC grains no longer existed, the grains were broken to much smaller particles and incorporated into the Hytrel matrix. When the mixing time reaches 50 sec (Fig. 11), the breakdown of the PVC particles is much more progressed compared to that of the other systems and the interfacial mixing is more pronounced. The faster breakdown of PVC/Hytrel at the initial stages is ascribed to two facts: First is the highest storage modulus which results in higher forces than for the other component polymers, and second there is a much higher starting temperature (135°C) which facilitates weakening of the interparticulate bonds and melting of some PVC microcrystallites.

For an additional mixing to 70 sec [Fig. 12(a)], the PVC particles were broken down to the primary particles (∼1 μm) which were further reduced to the domains (∼0.1 μm) at 90 sec [Fig. 12(b)]. For mixing times 50 through 90 sec, the temperature increased from 153° to 168°C, during which there is a big drop in the viscoelastic moduli of Hytrel. Thus, the Hytrel becomes much less effective in exerting force but the disintegration of the primary particles to domains occurred. This may be explained by the melting of the PVC crystallites at these temperatures.
FIG. 9. Scanning electron micrographs of PVC/PCL mixture at mixing times of 90 sec (a) and 130 sec (b).
FIG. 10. Scanning electron micrographs of PVC/Hytrel mixture at a mixing time of 30 sec and at two magnifications.
FIG. 11. Scanning electron micrographs of PVC/Hytrel mixture at a mixing time of 50 sec and at two magnifications.
FIG. 12. Scanning electron micrographs of PVC/Hytrel mixture at mixing times of 70 sec (a) and 90 sec (b).
CONCLUSIONS

1. The progress of mixing of PVC with NBR-22, PCL, and Hytrel followed similar patterns as observed previously with NBR-30 [1]; (i) The skins of PVC grains were removed first. (ii) The companion polymers formed a continuous phase as a medium for stress transfer to the PVC particles. (iii) PVC particles disintegrated stepwise into smaller particles in the structural hierarchy.

2. A major difference among PVC/NBR-22, PVC/PCL, and PVC/Hytrel was the rate of breakdown of the PVC structural hierarchy.

3. The molecular miscibility and hence development of strong adhesion at the interface was one of the crucial factors affecting the breakdown rate; this was demonstrated by comparing NBR-30 and NBR-22, the former giving a strong adhesion and the latter very weak.

4. The magnitude of the storage modulus, $G'$ at the onset of mixing played a significant role in the breakdown rate; this was demonstrated by comparing Hytrel, NBR-30, and PCL in the order of higher to lower modulus and hence a faster to a slower breakdown process.

5. The mixing temperature was also important in that the viscoelastic and physical properties of both the medium and PVC were affected. At the higher temperatures, the PVC particles are more easily breakable because the internal bonds between particulates are weakened and part of the microcrystallites melt.

REFERENCES


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