

# Compatibilization of poly(vinyl chloride) and polyolefin elastomer blends with multiblock/blocky chlorinated polyethylenes

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## Abstract

Asymmetric double cantilever beam and peel test experiments were completed to evaluate the ability of chlorinated polyethylenes to compatibilize poly(vinyl chloride) (PVC) and polyolefin elastomer (POE) blends. A series of chlorinated polyethylenes that are blocky in nature (bCPEs) with varying composition (% chlorine) and molecular weight (melt index) were compared to one chlorinated polyethylene, where the chlorine is randomly distributed throughout the chain (rCPE). Results indicate that improvement in the interfacial adhesion between the PVC and the POE is dramatically more pronounced with the bCPEs than with the rCPE. In addition, the optimum bCPE composition was determined to be 20% chlorine and the interfacial adhesion force was found to increase with increasing molecular weight. Finally, the POE/CPE interaction was found to govern the ability of the chlorinated polyethylene to compatibilize PVC and POE. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polymer blends; Compatibilization; Interfacial modification

## 1. Introduction

In order to achieve properties that cannot be obtained by individual polymers, different polymers may be blended to obtain a more cost-effective material that combines the physical characteristics of both polymers [1–3]. Unfortunately, due to relatively low entropy of mixing, most polymer pairs are immiscible, resulting in the formation of a sharp interface between the two polymer phases, coarse phase morphology, and poor mechanical properties [2–5]. Copolymers are often used as interfacial modifiers in immiscible polymer blends to improve the mechanical properties of the blend creating a compatibilized blend. Compatibilized blends are not necessarily miscible blends, but blends that satisfy certain industrial criteria for usefulness, such as satisfactory mechanical properties. Copolymers composed of monomers or segments that are miscible with both phases work as effective compatibilizers, as their presence at the interface may lead to increased interfacial adhesion between the phases and stable phase morphology. Copolymer molecules cross the interface forming ‘stitches’ which couple the two phases together

compatibilizing the blend. This compatibilization results in improved overall mechanical properties [1–5].

Poly(vinyl chloride) (PVC) is a material with very good physical properties and low cost, however, PVC has low impact resistance (brittle) and is difficult to process. In order to overcome these drawbacks, PVC has been blended with polyolefin elastomers (POEs) [6–10]. These polymers are immiscible, and thus the resultant materials do not attain optimal properties. The polar nature of the PVC and nonpolar character of the polyolefins require that blends of this type be compatibilized in order to obtain a useful material that combines the strength of PVC with the impact resistance of POE [10]. Chlorinated polyethylenes (CPEs) have been used as a third component additive to compatibilize blends of PVC with many polyolefins such as ethylene/propylene/diene terpolymer [6], high density polyethylene [7], low density polyethylene [7], and linear low density polyethylene [8,9]. The presence of chlorinated polyethylene in these blends resulted in improved impact resistance and finer phase morphology relative to the uncompatibilized blends [6–9]. Each of the chlorinated polyethylenes used in these studies was synthesized by randomly chlorinating the polyethylene backbone, resulting in a random copolymer.

However, other types of copolymer structures, such as

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block, multiblock, or graft copolymers, may be more useful in the compatibilization of PVC and polyolefins. Theoretical data suggest that blocky or multiblock copolymers are efficient compatibilizers of polymer blends. Noolandi theorized that multiblock copolymers with blocks long enough to entangle with homopolymers would be effective polymeric surfactants during compatibilization [11]. Balazs used Monte Carlo techniques to demonstrate that the number of effective crossings or stitches at the interface of a copolymer determines the capability of that copolymer to improve interfacial adhesion [12]. Multiblock copolymers have more interface crossings than other types of copolymers and greater number of blocks form more stitches [12–15]. Also, Dadmun discovered that blocky type copolymers expanded at the interface into the homopolymer phases better than copolymers with a random architecture according to Monte Carlo computer simulations [16].

In addition to theoretical results, experimental data also appears in the literature supporting multiblock copolymers as effective interfacial modifiers. Kramer and coworkers published results indicating that multiblock copolymers were proficient at compatibilizing polystyrene and poly(2-vinyl pyridine) [13,17]. In a similar manner, we have experimental results indicating that multiblock copolymers composed of styrene and methyl methacrylate are optimal strengtheners of the interface between polystyrene and poly(methyl methacrylate) [18]. We discovered that optimum strengthening was observed when the copolymer consists of blocks that are longer than an effective entanglement molecular weight of the block. Copolymers with the most of these blocks were most effective at strengthening the interface. Polystyrene and polypropylene blends have also been compatibilized by multiblock copolymers composed of styrene and butadiene monomers [19,20]. Upon addition of styrene and butadiene multiblock copolymers, polystyrene/polypropylene blends demonstrated improved impact strength and tensile properties.

Multiblock copolymers of polyethylene and chlorinated polyethylene (bCPE) can be prepared by the suspension chlorination of polyethylene below the melt temperature by a procedure in the literature [10,21,22]. Suspension chlorination gives copolymers that are highly blocky substituted, while, on the other hand, solution chlorination techniques of polyethylene result in randomly chlorinated polyethylene (rCPE). Suspension chlorination retains unchlorinated polyethylene segments that are still able to crystallize. Thus, suspension chlorination yields multiblock copolymers composed of blocks of amorphous chlorinated polyethylene, which presumably can interact with PVC, and crystalline polyethylene blocks, which may interact with POE. When these bCPEs are added to blends of PVC and POE, the resulting compatibilized blends demonstrate improved impact resistance relative to that of POE/PVC blends that are compatibilized with random chlorinated polyethylenes [23]. However, the mechanism for this improved compatibilization process is still unclear.

Therefore, this study presents experiments that were completed to further understand the mechanism by which the added multiblock copolymer (bCPE) strengthens the PVC/POE interface. The ability of multiblock or blocky distributed chlorinated polyethylenes (bCPEs) to strengthen the PVC/POE interface will be determined and compared to that of randomly distributed chlorinated polyethylene (rCPE) using asymmetric double cantilever beam (ADCB) and peel test experiments. Additionally, the dependence of molecular weight and chlorine content of the bCPE (composition) will be evaluated to ascertain the influence of these parameters on the compatibilization process. The individual PVC/CPE and POE/CPE interfaces are also evaluated to provide further evidence regarding the importance of these individual interfaces on the behavior of the compatibilized PVC/POE blend. Finally, differential scanning calorimetry (DSC) and X-ray diffraction are used to document the influence of cocrystallization of the POE and bCPEs on the interfacial strengthening process.

## 2. Experimental

### 2.1. Materials

PVC resin with an inherent viscosity of 0.92 (ASTM D1243) was provided by BF Goodrich Performance Materials. A methyltin stabilizer [Mark 1900 stabilizer, methyl(thioglycolact) tin(IV), Witco chemical] was used with the PVC resin to prevent thermal degradation during melt processing. The POE, flexomer DFDB 1088, utilized in this study was obtained from Union Carbide. This elastomer is a poly(ethylene-*co*-butene) copolymer, composed of 85 wt% ethylene. Tyrin 3615P was obtained from Dow Chemical, and used as the randomly chlorinated polyethylene compatibilizer (r0.3-36). BF Goodrich also provided all of the blocky chlorinated polyethylenes. These bCPEs were prepared by a suspension chlorination process of high-density polyethylene given in the literature [10]. NMR [21, 23] and DSC [22] characterized the bCPE blockiness. The composition of the bCPEs was varied from 15% chlorine to 48% chlorine. The % chlorine for each CPE was determined by <sup>13</sup>C NMR peak integration and represents the weight percentage of chlorine in the chlorinated polyethylene. The molecular weight of the PVC was determined by gel permeation chromatography (GPC) using tetrahydrofuran as the mobile phase at 40 °C with polystyrene standards. GPC of the other materials were completed by using a 90/10 trichlorobenzene/benzene alcohol solution as the mobile phase at 150 °C with polystyrene standards. Molecular weight information and other molecular details concerning the materials are presented in Table 1. In the symbols column, the initial lower case letter designates ‘b’ for blocky or ‘r’ for random. In this symbol, the first set of numbers indicates the melt index for each polymer and the second set of numbers indicates the % chlorine in the

Table 1  
Molecular characteristics of polymers used in this study

| Symbol  | $M_w$   | $M_n$  | $M_w/M_n$ | Melt index (g/10 min) | % Cl | Young's modulus (MPa) |
|---------|---------|--------|-----------|-----------------------|------|-----------------------|
| PVC     | 133,000 | 79,800 | 1.7       | –                     | –    | 1808                  |
| POE     | 392,000 | 57,000 | 6.9       | 0.1                   | 0%   | 31                    |
| r0.3-36 | 280,000 | 38,000 | 7.4       | 0.3                   | 36%  | 3                     |
| b0.3-30 | 207,000 | 32,900 | 6.3       | 0.3                   | 30%  | 569                   |
| b8.5-30 | 135,000 | 28,000 | 4.8       | 8.5                   | 30%  | –                     |
| b18-30  | 128,000 | 16,000 | 8.0       | 18                    | 30%  | –                     |
| b30-30  | 92,000  | 22,000 | 4.1       | 30                    | 30%  | –                     |
| b0.3-15 | 207,000 | 32,900 | 6.3       | 0.3                   | 15%  | 258                   |
| b0.3-20 | 207,000 | 32,900 | 6.3       | 0.3                   | 20%  | 408                   |
| b0.3-36 | 207,000 | 32,900 | 6.3       | 0.3                   | 36%  | 684                   |
| b0.3-48 | 207,000 | 32,900 | 6.3       | 0.3                   | 48%  | 886                   |

polymer. The same designation is given in Table 2, which is a list of the nine chlorinated polyethylenes used in this study. To determine molecular weight effects on the interfacial modification process, the composition of the copolymer is fixed at 30% chlorine and molecular weight (melt index) is varied. Similarly, to determine composition effects, the melt index is fixed at 0.3 g/10 min and the chlorine content is varied.

## 2.2. Determination of interfacial adhesion/strength

To quantify the ability of the CPEs to compatibilize the PVC/POE interface, two techniques were used, ADCB test and ASTM peel tests. ADCB measures the interfacial fracture toughness ( $G_c$ ) of a crack propagating at the interface. This test determines the amount of energy released as a crack grows at an interface and provides a value for the interfacial strength [24–26]. ADCB is primarily used when the materials studied are glassy [24]. Due to the rubbery nature of POE, peel tests may be more appropriate in determining interfacial strength between our two polymers as peel tests are used to determine interfacial adhesion between two materials when one or both of the materials are flexible [24,27–29].

### 2.2.1. Asymmetric double cantilever beam test

**ADCB trilayer sample preparation.** Stabilized PVC was melt pressed at 200 °C into films. A thin layer (~50 nm thick) of each chlorinated polyethylene compatibilizer (CPE) was then spun coat onto the PVC surface from a 1.4 wt% CPE solution in xylene at 2500 rpm for 30 s. The

PVC/CPE samples were cut into strips with dimensions of 1 cm × 6.5 cm × 0.23 cm. POE was melt pressed at 150 °C into slabs which were cut into strips measuring 1 cm × 6.5 cm × 0.46 cm. A POE strip was placed on top of the CPE layer and the trilayer samples (PVC/CPE/POE) were joined at an annealing temperature of 200 °C for 15 min under approximately 10 lbs. of pressure. Fifteen minutes of pressing time was chosen due to observable yellowing of the PVC with longer annealing times. Due to this limitation, we cannot ensure an equilibrium structure at the interface in this time scale. However, as this limitation exists for all samples, a comparison of the reported interfacial strengths is possible and the conclusions reported below are not impacted.

**ADCB PVC/CPE bilayer sample preparation.** The chlorinated polyethylenes were compression molded at 150 °C and cut into strips with dimensions of 1 cm × 6.5 cm × 0.25 cm. The CPE strips were placed onto PVC strips and the bilayer samples (PVC/CPE) were joined at the same annealing parameters used for the other ADCB samples.

**Fracture toughness measurement.** Interfacial fracture toughness was measured by the ADCB test. Details concerning this type of analysis can be found in the literature and a picture of a sample being tested can be seen in Fig. 1 [13,14,25,26,30–41]. A razor blade was inserted at

Table 2  
Matrix depicting molecular weight and composition of compatibilizers

| Melt index | % Chlorine |         |         |         |                 |
|------------|------------|---------|---------|---------|-----------------|
|            | 15%        | 20%     | 30%     | 36%     | 48%             |
| 30         |            |         | b30-30  |         |                 |
| 18         |            |         | b18-30  |         |                 |
| 8.5        |            |         | b8.5-30 |         |                 |
| 0.3        | b0.3-15    | b0.3-20 | b0.3-30 | b0.3-36 | r0.3-36 b0.3-48 |

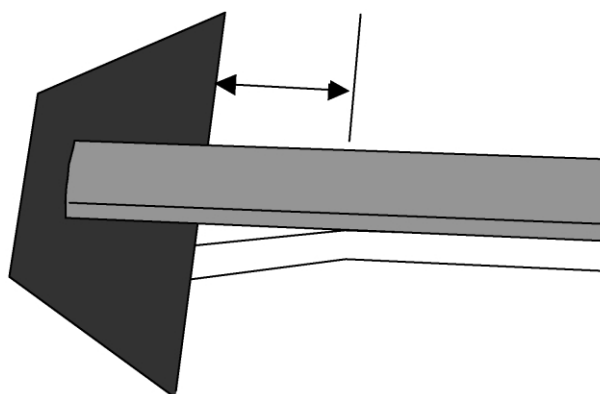


Fig. 1. Illustration of the ADCB test.

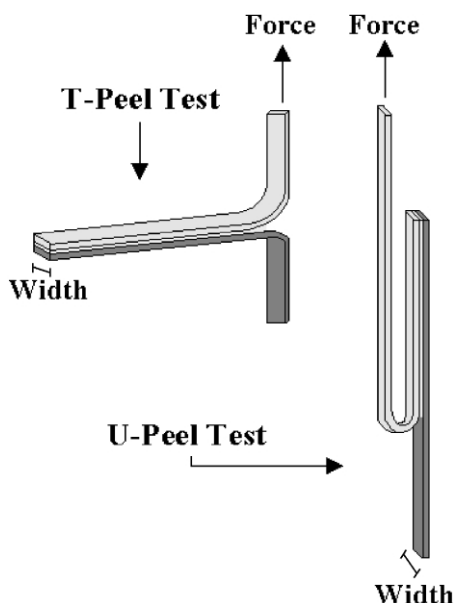


Fig. 2. Illustration of peel tests used to determine interfacial adhesion of layers.

the interface and driven in at a speed of 0.20 mm/min. Pictures were taken every minute using a video camera directly over the sample, and crack lengths were measured from the razor blade to the crack tips. As the blade was being inserted and the crack was propagating, approximately 15–25 measurements of the crack length were made for each sample. The value found for the crack length was then inserted into Eq. (1) and the fracture toughness ( $G_c$ ) was calculated.

$$G_c = \frac{3\Delta^2 E_1 h_1^3 E_2 h_2^3}{8a^4} \frac{E_1 h_1^3 C_2^2 + E_2 h_2^3 C_1^2}{[E_1 h_1^3 C_2^3 + E_2 h_2^3 C_1^3]^2} \quad (1)$$

where  $C_1 = 1 + 0.64h_1/a$  and  $C_2 = 1 + 0.64h_2/a$ .

In Eq. (1),  $a$  is the crack length,  $\Delta$  is the thickness of the razor blade, and  $h_1$  and  $h_2$  are the thickness of the homopolymer layers. Young's moduli of the homopolymers,  $E_1$  and  $E_2$ , were found by tensile testing (ASTM D1708) and given in Table 1. For each ADCB data point for each copolymer sample, 7–12 samples were tested.

In the ADCB test, the loading geometry (sample thickness) can have a significant impact on the crack propagation, and thus on the measured interfacial fracture toughness,  $G_c$ . Xiao et al. [36], Bernard et al. [37], and Sikka et al. [40] have demonstrated the importance of loading geometry on the ADCB test by varying the thickness ratios of each homopolymer beam. Briefly, if both layers are of the same thickness, the crack will swerve into the more compliant material, causing the formation of crazes, which inflates the measured fracture toughness. A minimum  $G_c$  for a given polymer pair is found when the crack remains at the interface and does not deviate into either homopolymer. A similar analysis was attempted for the PVC/POE system, as the fracture toughness was determined as a

function of thickness ratios ( $h_{\text{POE}}/h_{\text{PVC}} = 1.0, 1.5, \text{ and } 2.0$ ) for samples compatibilized with r0.3-36. Increasing thickness ratios resulted in decreasing fracture toughness. However, without modification of the ADCB sample holder, larger thickness ratios could not be obtained. Therefore, the ADCB test that are reported in this paper were completed using a thickness ratio ( $h_{\text{POE}}/h_{\text{PVC}}$ ) of 2.0. While this may not be the optimal geometry to provide the absolute minimum fracture toughness, it was the accessible geometry that provided the minimum  $G_c$ . However, this does not influence the comparisons and correlations presented below.

### 2.2.2. Peel test

*Peel test sample preparation.* Trilayer peel test samples were prepared similarly to the ADCB samples. Again, a thin layer ( $\sim 50$  nm thick) of each compatibilizer (CPE) was spun coat onto the PVC strip surface. Spin coated samples were cut into strips of the same dimensions as the ADCB PVC/CPE sample. The POE was then melt pressed into strips measuring  $1 \text{ cm} \times 6.5 \text{ cm} \times 0.25 \text{ cm}$  and trilayer samples (PVC/CPE/POE) were prepared and annealed at the same temperature and pressure used for the ADCB sample preparation. Bilayer samples were prepared in a similar manner. For POE/CPE bilayers, the CPE had dimensions of  $1 \text{ cm} \times 6.5 \text{ cm} \times 0.23 \text{ cm}$  and dimensions of  $1 \text{ cm} \times 6.5 \text{ cm} \times 0.25 \text{ cm}$  were used for the POE layer. PVC/bCPE bilayers were not tested by peel testing due to the stiffness of the bCPEs, but the PVC/rCPE bilayer was examined by peel testing.

*Peel test.* Samples were peeled with an Instron Model 1122 automated materials tester and evaluated using Instron series IX version 7.27.00 software. The crosshead speed was set at a rate of 10 mm/min. This analysis was based on ASTMs D1876-95 (T-peel) and D903-93 (U-peel), with exception to sample size. An illustration of this type of test can be seen in Fig. 2. Each sample was T-peeled back approximately 1/2 of the sample length then the remaining sample underwent the U-peel test. Within error, there was no observable difference in the amount of force required to peel the samples either by the T-peel or U-peel method. Peel forces were measured via a 200 lb. load cell and 10–12 samples were analyzed for each compatibilized blend. The interfacial adhesion,  $G_a$ , is the work required to separate adhered layers by peeling them apart. It is calculated by dividing the force required to peel the sample by the width of the sample as given in Eq. (2) [28]

$$G_a = \text{Force/width.} \quad (2)$$

### 2.3. Cocrystallization

In order to study possible cocrystallization that may occur in the compatibilized blends, blends of each type of bCPE and POE were prepared and examined by DSC and X-ray diffraction. Equal weight amounts of bCPE and POE were dissolved in toluene followed by subsequent

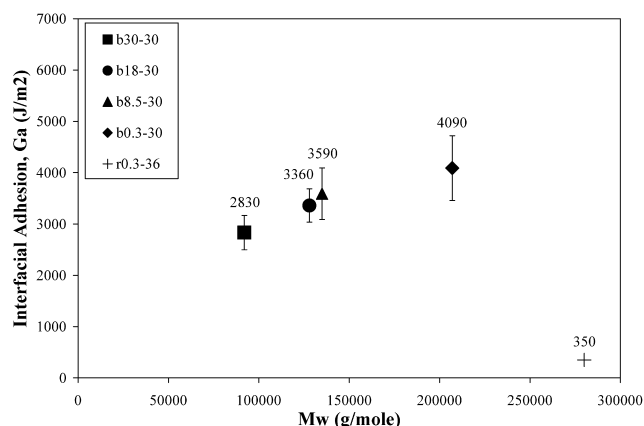


Fig. 3. Plot of the interfacial adhesion of CPE trilayers as a function of molecular weight.

precipitation into methanol. These 50:50 solution cast blends were then dried in a vacuum oven at 75 °C overnight.

### 2.3.1. Differential scanning calorimetry

The thermal behavior of blends that are composed of bCPE which is physically separated from POE were also determined for comparison to the thermal behavior of the solution cast blends. To prepare these physically separated POE/bCPE blends, POE and bCPEs were each wrapped in aluminum foil and then placed into the DSC pan. These separated blends, 50:50 solution cast blends, pure bCPEs, and pure POE were all heated to 200 °C at 10 °C/min. The samples were then cooled to 95 °C and held at this temperature for 16 days. After the 16-day annealing period elapsed, samples were allowed to cool to room temperature. Annealing at 95 °C was required to distinguish between the POE and bCPE melting peaks, due to their proximity. Using a Mettler DSC 821e which was calibrated with indium, each sample was heated from 35 to 200 °C at 10 °C/min to obtain DSC curves.

### 2.3.2. X-ray diffraction

X-ray diffraction patterns of the bCPEs, POE, and

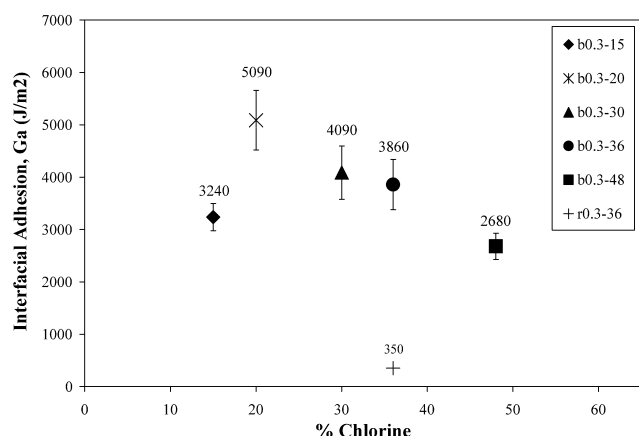


Fig. 4. Plot of interfacial adhesion,  $G_a$ , of CPE trilayers as a function of chlorine composition of the chlorinated polyethylene.

solution cast blends were taken at room temperature using a Philips X'pert MRD X-ray Diffractometer. The 50:50 solution cast blends, bCPEs, and POE were all heated to 200 °C and then cooled to 95 °C for 16 days. Diffraction scans were collected between  $2\theta$  values of 5 and 35° at a scan rate of 1°/min with a 0.02° resolution. X-rays were obtained from Ni-filtered Cu  $K_{\alpha}$  radiation with the wavelength of 1.54 Å. To analyze the diffraction data, the distances between parallel crystallographic planes, called interplanar distances,  $d_{hkl}$ , were determined by the Bragg equation, Eq. (3) [42,43]

$$d_{hkl} = \lambda / 2 \sin \theta \quad (3)$$

In Eq. (3),  $\theta$  is the Bragg angle and  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 1.54$  Å).

## 3. Results

### 3.1. Interfacial strength of the trilayer samples (PVC/CPE/POE)

The bare PVC/POE interface (i.e. samples with no copolymer at the interface) exhibit very weak interfaces. ADCB experiments show that the interfacial fracture toughness of the PVC/POE interface is 1.8 J/m<sup>2</sup>. The addition of chlorinated polyethylenes at the interface, to create a trilayer, gives much stronger interfaces. In fact, the blocky chlorinated polyethylenes produce interfaces that are too strong to be tested by ADCB methods. Resulting crack lengths in the ADCB experiment are less than 1 mm, which is below the resolution of this test. Crack lengths of less than 1 mm long correlate to  $G_c$ s greater than 1000 J/m<sup>2</sup>, thus this value provides a lower limit of the interfacial fracture toughness of the PVC/POE interface that is compatibilized by the blocky CPEs. For the random copolymer, r0.3-36, the interfacial strength is low enough to be determined by ADCB methods and the interface that was compatibilized with the randomly chlorinated polyethylene, r0.3-36, has a  $G_c = 160$  J/m<sup>2</sup> as determined by ADCB. Unfortunately, ADCB cannot be used to *quantitatively* compare the ability of bCPEs and rCPE as interfacial modifiers; however, the data qualitatively demonstrates that the blocky chlorinated polyethylenes produced much stronger interfaces than random chlorinated polyethylene.

In order to quantitatively evaluate the ability of bCPEs to strengthen the PVC/POE interface, peel test methods are used. The peel test is, therefore, used to determine the effects of molecular weight and copolymer composition on the compatibilization ability of bCPEs. These results are shown in Figs. 3 and 4. The effect of molecular weight on the ability of the blocky chlorinated polyethylene to strengthen the PVC/POE interface is shown in Fig. 3, while Fig. 4 shows the dependence of the interfacial strength of the compatibilized PVC/POE interface on the composition of the bCPE.

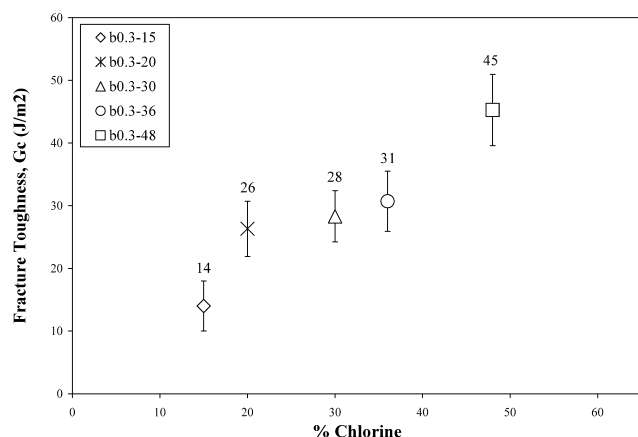


Fig. 5. The fracture toughness,  $G_c$ , of the interface of the PVC/bCPE bilayers plotted as a function of chlorine composition of the bCPE.

Fig. 3 shows that an increase in the interfacial adhesion of the interface is observed with increasing molecular weight for the bCPEs. It is worth emphasizing that the random copolymer, r0.3-36, which has the highest molecular weight studied, gives the lowest interfacial adhesion, with a value of 350 J/m<sup>2</sup>. Fig. 4 shows a plot of interfacial adhesion,  $G_a$ , as a function of copolymer composition. Similar to the data shown in Fig. 3, Fig. 4 shows that the interfacial adhesion of the interfaces modified by any bCPE is an order of magnitude stronger than that of the interface modified by the rCPE.

Further analysis of Fig. 4 shows that the blocky copolymer with the highest chlorine content, b0.3-48, gave the lowest  $G_a$  of the bCPEs, while decreasing the % chlorine yields an increase in  $G_a$  until reaching a maximum value for the 20% chlorine material, b0.3-20. When the chlorination levels decrease further to 15% chlorine, the interfacial adhesion again drops. It is conjectured that the bCPE with the highest chlorine content (b0.3-48) has too much chlorine present to interact well with the POE, therefore this results in poor adhesion and interaction between the bCPE and the POE. While b0.3-48 has too much chlorine to interact well with POE, it is surmised that the bCPE with the lowest chlorine content (b0.3-15) does not have enough chlorine to interact well and adhere with PVC. It appears that the chlorine composition of b0.3-20 balances the interactions of the bCPE with PVC and POE most effectively to obtain the strongest interfacial adhesion of 5090 J/m<sup>2</sup>.

Investigation of the POE surface of the trilayer samples (PVC/CPE/POE) indicates two types of failure that take place, adhesive and cohesive. Cohesive failure arises when failure occurs within one of the materials being adhered [1]. In this case, it occurs within POE and is indicated by obvious, significant roughening of the POE surface upon peeling. Cohesive failure occurs when the interfacial adhesion is very high due to strengthening of the interface by the presence of the chlorinated polyethylene. For example, b0.3-20, b0.3-30, and b0.3-36 all exhibit cohesive

failure. Adhesive failure occurs when failure occurs at the interface rather than within one of the materials [1]. CPEs with lower  $G_a$ s such as b0.3-15, b0.3-48, r0.3-36 indicate failure by adhesive failure.

From the trilayer peel test data, it is clearly evident that multiblock or blocky chlorinated polyethylenes promote adhesion between PVC and POE much more effectively than random chlorinated polyethylene. These results are in agreement with theory [11,12,16] which predicts that multiblock copolymers should be the most effective compatibilizers and that the copolymer structure will have a profound effect on the copolymer alignment at the interface, which will impact the interfacial strengthening and modification by the copolymer. For instance, diblock copolymers, with blocks longer than the critical molecular weight for entanglements, align perpendicular to the interface and entangles with each homopolymer phase [30,34,35]. Diblock copolymer chains are able to stretch deep into the homopolymer phases and anchor effectively; however, each diblock chain crosses the interface only once. Other type of structures such as random copolymers are believed to have multiple interface crossings (although the exact number is not known), but random copolymer chains do not anchor as strongly as diblock copolymer chains. Multiblock copolymers such as bCPEs may provide the right balance of multiple interface crossings and anchoring in the homopolymer phases to be effective compatibilizers. The multiblock or blocky chlorinated polyethylenes, bCPEs, have amorphous blocks of chlorinated segments that are believed to entangle with PVC and crystalline polyethylene blocks that can entangle and/or cocrystallize with the POE resulting in bCPEs chains weaving back and forth into the PVC and POE phases. The phases are 'stitched' together giving multiple interface crossings by the bCPE chains, which may strengthen the interfacial adhesion between PVC and POE. The absence of long blocks in the rCPE and ineffective anchoring into PVC and POE may account for the observed differences in interfacial adhesion.

### 3.2. Bilayer samples (PVC/CPE and POE/CPE)

Interactions of the chlorinated polyethylenes with both PVC and POE individually will provide insight into the affinity of the copolymers to the homopolymers and may provide further insight into the mechanism by which bCPEs strengthen PVC/POE interfaces; therefore, the interfacial adhesions of the PVC/CPE and POE/CPE bilayers were also investigated. ADCB is primarily used to evaluate the PVC/CPE bilayers and the interfacial fracture toughness,  $G_c$ , for these bilayers are plotted as a function of CPE percent chlorination for the blocky copolymers in Fig. 5. The PVC/bCPE interfaces gets stronger with increasing chlorination with maximum fracture toughness observed with maximum chlorination, 48%. The greater chlorination produces chlorinated polyethylenes that are more similar to PVC and thus adhere more strongly to the PVC. The

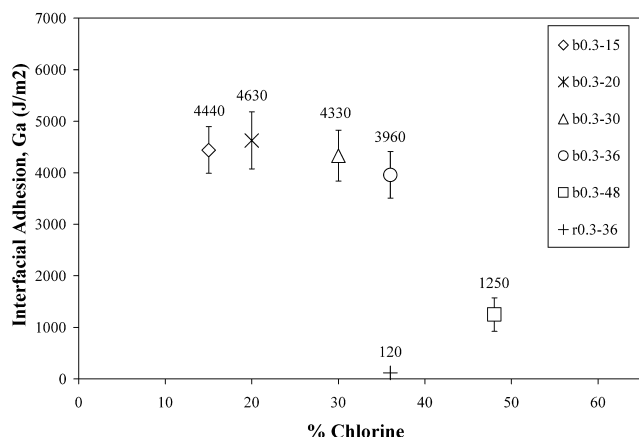


Fig. 6. The interfacial adhesion,  $G_a$ , of the interface of the POE/CPE bilayers plotted as a function of chlorine composition of the CPE.

strength of the PVC/rCPE interface is also evaluated by ADCB, and was found to be significantly stronger than the PVC/bCPE interfaces with a  $G_c$  of 550 J/m<sup>2</sup>. The random CPE is less crystalline than the bCPEs and thus is much more flexible. Because of this flexibility, PVC/rCPE bilayer can also be tested by peel test methods. Peel testing of PVC/rCPE yields an interfacial adhesion,  $G_a$ , of 1024 J/m<sup>2</sup>.

Discussion and comparison of the results obtained by the peel test and the ADCB experiment is in order. For a given sample, peel tests and ADCB experiments do not provide identical measures of the interfacial strength, and this must be clarified. For example, the r0.3-36 (rCPE) trilayer analyzed by ADCB produced a  $G_c$  of 160 J/m<sup>2</sup>, while the peel testing resulted in a  $G_a$  equal to 350 J/m<sup>2</sup>. Similarly, the PVC/rCPE bilayer gave a  $G_c$  equal to 550 J/m<sup>2</sup> from the ADCB test and a  $G_a$  equal to 1024 J/m<sup>2</sup> from the peel test. The peel test appears to measure interfacial adhesion values,  $G_{a,s}$ , that are approximately twice the fracture toughness,  $G_{c,s}$ , values found by ADCB. It is important to remember that these two experiments are measuring different parameters that are related to interfacial strength. The ADCB ideally measures the interfacial fracture toughness ( $G_c$ ) of a crack propagating at the interface between two homopolymers, while the peel test measures the force needed to pull apart two adhered layers. One obvious contribution to this discrepancy is that some of the force measured in the peel test goes into pulling and stretching the POE rather than separating the layers during the peel test. Hence, observed  $G_a$  values are slightly inflated. Because of this occurrence, it is difficult to obtain an absolute measure of interfacial strength using peel testing. However, peel testing can be used to gain a relative relationship of samples prepared and tested in the same manner and is used as such in this set of experiments. Clearly, the two experiments are measuring different aspects of the interfacial strength and care must be taken when comparing the peel test quantification of the interfacial strength to that of the ADCB experiment. Additionally,

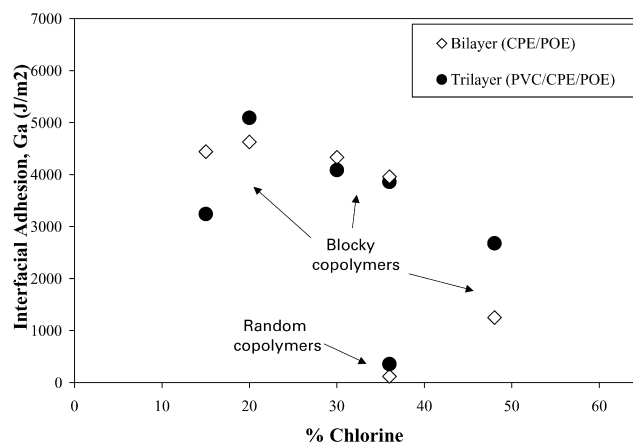


Fig. 7. Comparison of interfacial adhesion of the PVC/CPE/POE trilayer and that of the POE/CPE bilayer. Each diamond and circle pair represents the strength of the bilayer or trilayer (respectively) that contains the indicated chlorinated polyethylene. Note that the similarity of the strength of each bilayer and trilayer.

the ADCB test has been designed and optimized for glassy polymer systems. The elasticity of either polymer has not been accounted for in the development of Eq. (1) and thus the absolute values reported in this study do not quantitatively depict the amount of energy released as the crack grows. Undoubtedly, there is systematic error in these numbers that is related to the deformation of the elastic POE layer. However, as the same POE layer is used in all samples, the existence of this systematic error does not impact the discussion and conclusions detailed below.

The peel test is also used to determine the interfacial adhesion of the POE/CPE bilayers. Fig. 6 presents the interfacial adhesion of the POE/CPE samples for both bCPEs and the rCPE. The POE/bCPE interfaces are much stronger than that found for the POE/rCPE interface. Similar to the trilayer peel data, all of the bCPEs are an order of magnitude stronger than that containing the rCPE. For bCPEs, interfacial adhesion initially increases dramatically as the composition of the CPE decreases from 48 to 36% chlorine and then plateaus at 30% chlorine to give an interfacial adhesion around 4500 J/m<sup>2</sup>. A comparison of PVC/CPE/POE trilayer and POE/CPE bilayer data is shown in Fig. 7. Surprisingly, the POE/bCPE interfaces are essentially as strong as the compatibilized PVC/POE interfaces. This plot is created by combining the data of Figs. 4 and 6 and exemplifies the similarity between the POE/CPE interfaces and that of the compatibilized POE/PVC interface. This phenomenon implies that the strength of the compatibilized PVC/POE interfaces is governed by the POE/CPE interaction. This is surprising for the bCPEs as this is the stronger interface and one would expect that the weakest interface would govern the fracture behavior.

Fig. 8 presents the interfacial adhesion of the trilayer and bilayer samples containing the rCPE as measured by peel

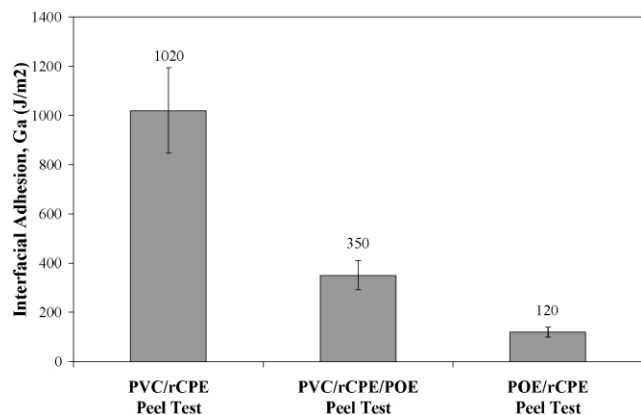


Fig. 8. Peel test results for the PVC/rCPE/POE trilayer, the PVC/rCPE bilayer, and the POE/rCPE bilayer samples.

tests. These results indicate that the random chlorinated polyethylene, r0.3-36, produces a very strong interface with PVC (1020 J/m<sup>2</sup>), but a fairly weak interface with POE (120 J/m<sup>2</sup>). The compatibilized PVC/rCPE/POE interface, which is a combination of the PVC/rCPE and POE/rCPE interfaces, is mid-way between the two, exhibiting an interfacial adhesion,  $G_a$ , equal to 350 J/m<sup>2</sup>. Therefore, contrary to the bCPE interfaces, the weaker interface (POE/rCPE) significantly influences the strength of the PVC/POE interface that is compatibilized with the rCPE.

Viewed another way, however, it can be stated that for either copolymer structure, the POE/CPE interaction appears to govern the ability of the chlorinated polyethylenes to compatibilize PVC and POE. One possible explanation for this phenomenon is that the interaction between the POE and CPEs is stronger and differs from the interaction between PVC and the CPE. One physical explanation that correlates to this possibility is that, as the bCPEs are similar in structure to the POE, it may be that the POE and bCPEs cocrystallize to form stronger interfaces and this cocrystallization governs the overall behavior of the final compatibilized POE/PVC interface. To examine this

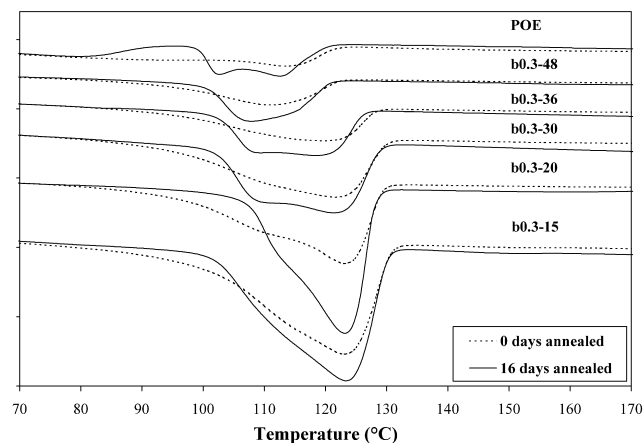


Fig. 9. DSC melting curves of the bCPEs that have been annealed for 16 days (solid curves) and unannealed (dotted curves).

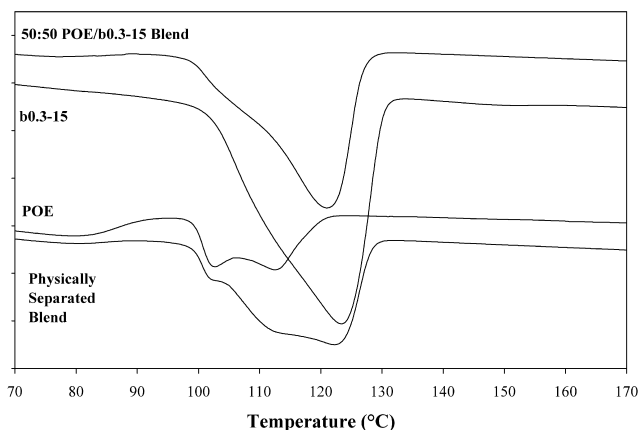


Fig. 10. DSC curves of the b0.3-15 blocky copolymer, the POE, a 50:50 POE/b0.3-15 blend, and the physically separated 50:50 POE/b0.3-15 blend.

possibility, the crystallization behavior of mixtures of POE and the bCPE are examined.

### 3.3. Cocrystallization in POE and blocky chlorinated polyethylene blends

DSC and X-ray diffraction are used to study the cocrystallization behavior of the bCPEs and POE. In DSC, cocrystallization of two polymers is associated with a single melting peak that occurs between the melting peaks of the pure polymers [46,47]. There are a number of difficulties associated with the thermal properties of the components in this system that complicates this evaluation. First, the POE and bCPEs have very similar melting peaks. In order to separate the peaks, samples were melted and then annealed at 95 °C for 16 days. Fig. 9 shows the melting behavior as determined by DSC of the pure POE and the pure bCPEs. The dotted lines in Fig. 9 show the melting behavior of the unannealed samples while the solid lines designate samples that have been annealed for 16 days. As expected, annealing sharpens the peaks and aids in separating the melting peaks of the different samples. Unfortunately, it also results in the definition of multiple peaks for a given sample, presumably due to multiple crystal structures. For example, the POE shows a single melting peak around 114 °C before annealing, but reveals two peaks at 103 and 113 °C after annealing. For the bCPEs, increasing the chlorination levels gives rise to new peaks around 110 °C. At lower chlorination, b0.3-15 and b0.3-20, the melting peak around 123 °C dominates the peak structure with only a slight shoulder around 112 °C. The 30 and 36% chlorine bCPEs reveal two fairly equal peaks at 123 and 110 °C. The highest chlorine bCPE, b0.3-48, has a dominant peak around 108 °C and a shoulder around 117 °C.

The melting behavior of a 50:50 blend is then compared to the DSC curves of the pure components, as shown in Fig. 10 for a blend of POE and b0.3-15. In addition, a DSC curve of a physically separated blend of POE and b0.3-15 is included to provide a reference thermogram for a blend



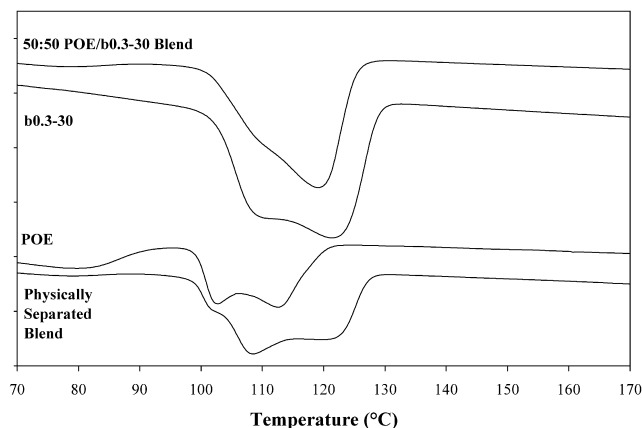


Fig. 11. DSC curves of the b0.3-30, the POE, a 50:50 POE/b0.3-30 blend, and the physically separated 50:50 POE/b0.3-30 blend.

where cocrystallization cannot occur. All samples were annealed for 16 days at 95 °C before these thermograms were obtained. In Fig. 10, the physically separated blend reveals three peaks, peaks at 103 and 113 °C that correspond to the POE, as well as a peak at 124 °C corresponding to the b0.3-15. The 50:50 POE/b0.3-15 blend, however, reveals only a peak at 121 °C and a slight shoulder around 104 °C. The large peak at 121 °C is in between the melting peaks of the pure POE and b0.3-15, suggesting that cocrystallization does occur in the blend of these two materials. Moreover, peaks found in the physically separated blend are absent for the 50:50 POE/b0.3-15 blend. Similar DSC evaluations for blends of the POE with b0.3-20, b0.3-30, b0.3-36, and b0.3-48 demonstrate the same phenomenon, large melting peaks in between the bCPE and POEs melting peaks and slight shoulders as is shown in Fig. 11. This combination of data, therefore, strongly suggests that the POE will cocrystallize with each of the bCPE, providing a possible mechanism for the strengthening of the POE/PVC interface by the blocky copolymers.

X-ray diffraction is also used to verify the presence of cocrystallization as it is a commonly used technique to analyze the crystalline state in polymers [48]. Diffraction patterns can be analyzed to provide, among other things, information regarding the spacing of atoms, layers, and chains in the ordered structure of a polymer [48,49]. Unfortunately, both POE and bCPE have similar structures that crystallize, mainly polyethylene segments, which may result in very similar diffraction patterns. As can be seen in Fig. 12, POE and b0.3-15 both have very similar diffractograms. POE has a large 1st Bragg peak at  $2\theta$  of 21.39°, while b0.3-15 reveals a similar Bragg peak at 21.67° corresponding to the reflections along the (110) crystallographic planes of the orthorhombic crystal lattice of polyethylene [45]. In addition, both have smaller 2nd Bragg peaks at 23.71° for POE and 24.03° for b0.3-15, which is due to reflection along the orthorhombic (200) crystallographic plane. One major difference between the two is that POE has a very large

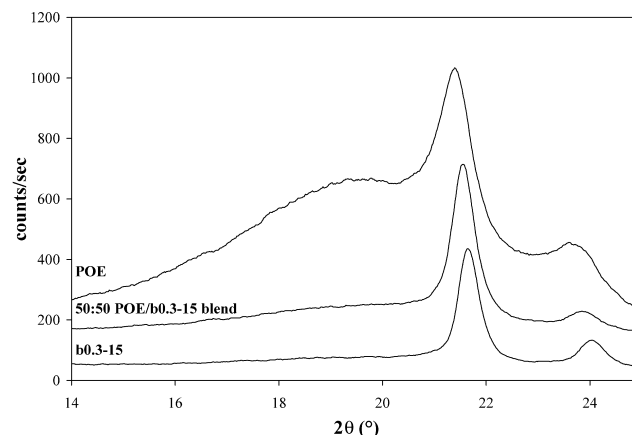


Fig. 12. X-ray diffraction curves of the b0.3-15 copolymer, the POE, and a 50:50 POE/b0.3-15 blend.

amorphous peak at 19.65°, while b0.3-15 has a much smaller amorphous contribution. Even though the POE and b0.3-15 have very similar diffraction patterns, the crystalline structure of the 50:50 blend of POE and b0.3-15 does reveal differences from that of the individual components. In comparing the X-ray patterns of the blend to that of the pure component, only the 1st Bragg peak results will be discussed, as it is much more intense than the (200) reflection. However, it should be noted that analysis of the 2nd Bragg peaks reveal the same trends as those described below.

Comparison of the properties of the crystalline structure of the blends and the pure components is, therefore, utilized to indicate the presence of cocrystallization. Qualitatively, Fig. 12 shows that the (110) and (200) peaks of the blend are not broader than those of the neat polymers, suggesting cocrystallization. More quantitatively, all blends display Bragg peaks in between that of the pure bCPE and POE, suggesting the formation of new cocrystallites [50]. For example, in the 50:50 blend, the 1st Bragg peak is at 21.55°, which is in between the 21.39° of POE and 21.67° of b0.3-15. Blends with other bCPEs exhibit similar phenomenon as documented in Table 3. Similarly, interplanar distances indicate that cocrystallization occurs between b0.3-15 and POE. More specifically, the interplanar distance for the pure b0.3-15,  $d_{110}$ , is equal to 4.096 Å, while upon blending with POE, the interplanar distance increases to 4.119 Å. Blends with other bCPEs reveal similar evidence of cocrystallization by demonstrating increased interplanar distances. Therefore, each analysis of the crystalline structure of the POE/bCPE blends strongly indicates that cocrystallization occurs between the bCPE and POE [44].

There also exists other evidence that cocrystallization occurs in these blends. For instance, the chlorine content of the bCPE has a significant effect on the cocrystallization with POE. This is to be expected as bCPEs with lower chlorination levels retain more crystalline polyethylene blocks, which can interact with POE to a much greater

Table 3  
Result of analysis of X-ray data

| Polymer                 | 1st Bragg peak<br>( $2\theta$ , °) | Interplanar distance,<br>$d_{hkl}$ (Å) |
|-------------------------|------------------------------------|--|
| POE                     | 21.39                              | 4.15                                   |
| 50:50 POE/b0.3-15 blend | 21.55                              | 4.12                                   |
| b0.3-15                 | 21.67                              | 4.10                                   |
| POE                     | 21.39                              | 4.15                                   |
| 50:50 POE/b0.3-20 blend | 21.57                              | 4.11                                   |
| b0.3-20                 | 21.67                              | 4.10                                   |
| POE                     | 21.39                              | 4.15                                   |
| 50:50 POE/b0.3-30 blend | 21.59                              | 4.11                                   |
| b0.3-30                 | 21.65                              | 4.10                                   |
| POE                     | 21.39                              | 4.15                                   |
| b0.3-36                 | 21.65                              | 4.10                                   |
| POE                     | 21.39                              | 4.15                                   |
| 50:50 POE/b0.3-48 blend | 21.61                              | 4.11                                   |
| b0.3-48                 | 21.65                              | 4.10                                   |

extent. The new cocrystallite peaks of the blends give greater shifts of the 1st Bragg peak of the bCPE ( $21.67^\circ$ ) with bCPEs of lower chlorination levels. For example,  $21.55$ ,  $21.57$ ,  $21.59$ , and  $21.61^\circ$  are the  $2\theta$  positions of POE/b0.3-15, POE/b0.3-20, POE/b0.3-30, and POE/b0.3-48 blends, respectively. All of these trends indicate greater interaction and cocrystallization between POE and bCPEs with lower chlorine composition.

Therefore, the results reported in this paper demonstrate that the blocky chlorinated polyethylenes provide a compatibilized interface between PVC and a POE that is an order of magnitude stronger than the interface that is compatibilized by a random chlorinated polyethylene. DSC and X-ray diffraction indicate that the blocky chlorinated polyethylene can cocrystallize with the polyethylene, suggesting that this mechanism contributes to the strengthening process of the compatibilized interface. It must be emphasized, however, that this study does not preclude other mechanisms that may also contribute to the improvement in compatibilizing efficiency of the blocky copolymers. For instance, the miscibility of the blocky copolymer with the homopolymers may differ from that of a random CPE with the same composition. This could result in the blocky copolymer expanding into the homopolymer more readily than the random copolymer and produce a stronger interface. Thus, there exist a number of possible experiments that could be completed to provide further insight into these systems including miscibility measurements of the copolymers with the two homopolymers, the effect of pressing time on the interfacial adhesion, thermodynamic analysis of the interfaces, and a more complete cocrystallization study of the copolymers blended with polyethylene.

#### 4. Conclusion

Both ADCB and peel test experiments revealed that blocky chlorinated polyethylenes (bCPEs) improve the interfacial strength between PVC and POE much more than a random chlorinated polyethylene (rCPE) is able to. More specifically, addition of any bCPE to the PVC/POE interface improved the measured interfacial adhesion by an order of magnitude *more* than that of an interface modified by the rCPE. In the bCPE structures, it is believed that the amorphous blocks of chlorinated segments entangle with the PVC, while the crystalline polyethylene blocks are able to entangle and cocrystallize with the POE. These interactions, which are absent in rCPE, yield very strong adhesion between PVC and POE indicating that the bCPE is a very good compatibilizer for PVC and POE. Increasing molecular weight of the bCPEs results in increasing interfacial adhesion. The optimum composition in the bCPEs was found to be around 20% chlorine present in the bCPE.

Investigation of the bilayers offered some insight into the affinity of the chlorinated polyethylenes to PVC and POE. Blocky CPEs had very weak affinities for PVC, and a very strong affinity for POE. The POE/bCPE interface was essentially as strong as the PVC/POE interface compatibilized by bCPEs. This implied that the bCPE interaction with POE governs the compatibilization of the PVC/POE interface. The POE/rCPE interaction demonstrated similar controlling aspects over compatibilization when using rCPE as the compatibilizer. In rCPE bilayers, the PVC/rCPE interface was very strong and the POE/rCPE interface was relatively weak. Random CPE molecules entangled with PVC very well, but due to the lack of crystallinity, it was not able to cocrystallize with POE effectively.

Due to the presence of similar polyethylene segments in both POE and bCPEs, it was difficult to prove that cocrystallization is occurring. However, both DSC and X-ray diffraction experiments provide evidence of cocrystallization between POE and bCPEs. DSC analysis of 50:50 POE/bCPE blends revealed melting peaks that were in between melting peaks of the individual polymers, and melting peaks found for the physically separated blends were noticeably absent from the 50:50 blends. X-ray diffraction provides further evidence of cocrystallization. 50:50 blend samples revealed new Bragg peaks in between the  $2\theta$  positions of the individual polymers indicating new atom spacings or cocrystallites present.

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