

Microstructural studies of interfacial deformation in painted thermoplastic polyolefins (TPOs)

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The interfacial structure and deformation between chlorinated polyolefin (CPO) adhesion promoter and automotive TPO substrates have been characterized with optical, scanning electron, and transmission electron microscopy techniques. The diffusion of rubber phase into the CPO layer was observed and an interphase thickness around 200 nm was obtained from TEM imaging. In some cases, a coherent failure of the adhesion promoter during the paint delamination was observed, which could be explained by the strong interphase formed due to the interfacial diffusion. It was found that baking at 120°C could significantly enhance the swelling of the rubber phase underneath the polypropylene-rich skin layer and the diffusion of the rubber phase into this layer. With decreasing molecular weight of PP homopolymer, the apparent interfacial strength measured by tensile cracking test increased, which was ascribed to the enhanced interfacial diffusion at low molecular weight. The deformation of materials near the interface during the paint delamination process was found to be more extensive in samples with higher interfacial adhesion.

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1. Introduction

The interfacial adhesion between paints and substrates is one of the most important factors determining the performance of automotive parts made from painted thermoplastic polyolefins (TPOs). Due to their low surface energy, lack of reactive groups, low porosity, and weak surfaces, TPOs inherently have poor adhesion with paints. One of the most often practiced methods to improve the adhesion between paint and TPO substrates is to apply a layer of adhesion promoter, which is mainly composed of chlorinated polyolefin or CPO [1].

It is generally believed that the mechanism of the adhesion promoter is the interfacial diffusion of CPO molecules into the substrate, and the entanglement between CPO chains with the rubber phase providing the adhesion between the paint and the substrate [2–4]. The interaction between the CPO in adhesion promoter and the rubber phase in the substrate has been pointed out to be the key factor controlling the adhesion at the interface [5, 6]. However, the detailed nature of the interfacial structure has been unclear. Time-of-flight secondary-ion-mass-spectroscopy (TOF-SIMS) measurements reported by several groups have shown an interphase between the CPO and TPO substrate with a thickness of several microns [5, 7]. Unlike the TOF-SIMS results, Mirabella *et al.* [8] reported an interface thickness of only several hundred nanometers based on measurements with scanning transmission X-ray mi-

croscopy (XSTM). It is generally acknowledged that the processing conditions have a strong influence on the structure of the interface, including baking temperature and time, molecular weight and distribution of CPO, and the type of solvent used [3, 9].

Since the processing conditions are expected to have a strong effect on the interfacial structure and hence the interfacial adhesion, it is very important to develop methods to measure the paint adhesion of the painted TPO samples as processed. For a multi-layer paint system as in most of the TPO materials, it is equally important to know the location of the failure, i.e., the weakest interface in the whole system.

In a previous paper [10], we discussed the application of a tensile cracking test in measuring the adhesion between multi-layer paint and TPO substrate. Delamination of the paint from the substrate at the end of the cracking processes was observed. This paper will further discuss the interfacial structure between multi-layer paints and TPO substrates, and its correlation with the deformation at the interface during tensile cracking tests.

2. Experimental procedures

Painted TPO plaques were provided by Du Pont Automotive and Visteon respectively and used without any further treatment. The tensile cracking tests were conducted according to the procedures described in

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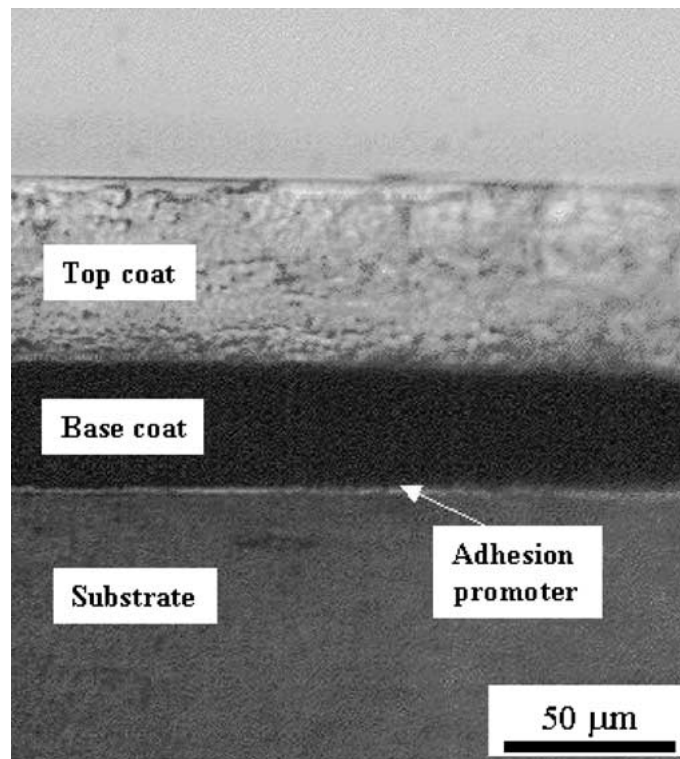


Figure 1 Three layer paint structure.

reference [10]. Local deformation was monitored by a video camera. Reference marks on the sample surface were used to monitor the local strain. To control the possible influence of the non-uniformity in molecular orientation, dog bone samples were cut away from the gate area and the samples were pulled in the injection flow direction. The samples generally have a three-layer paint structure: a top coat, a base coat and an adhesion promoter layer (Fig. 1).

The interfacial structure and deformation was studied by optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Optical microscope imaging was performed on a Nikon Optiphot-POL optical microscope equipped with a Sony DXC-101 video camera. Semi-thin slices of 2–4 μm thickness for OM observation were cut with a Reichert-Jung ultra-microtome. After the semi-thin slices were cut off, the surface left was very smooth and ideal for SEM observation. SEM observation was performed on a Philips XFL-30 scanning electron microscope operated at an accelerating voltage of 5 kV for secondary electron imaging and at 15 kV for elemental mapping.

For TEM observation, samples of interest were first stained by ruthenium tetroxide following standard methods [11]. Ultra-thin slices of nominal thickness 70 nm were cut with a Reichert-Jung Ultracut-E[®] microtome with a Diatome[®] 45° diamond knife and a clearance angle of 6° at room temperature. The TEM observations were performed on a JEOL 4000 EX microscope operated at 400 kV.

3. Results and discussions

3.1. Interfacial structure and adhesion mechanism

Past studies have shown that the interaction between the rubber phase and the CPO is essential for the adhesion

between the substrate and the adhesion promoter. The thickness of the interphase was measured to be several microns with TOF-SIMS [5, 7], while the XSTM data suggested a much thinner interphase of about 300 nm. Shown in Fig. 2 is the interfacial structure between TPO substrate and multilayer paint system. It is interesting to see that at some spots, the rubber particles seem to diffuse into the CPO layer. It can also be noticed that there are a lot of voids in the CPO layer, which might be caused by the evaporation of the solvent. Near the surface of the substrate, there is a layer of about 200 nm without any sign of voids. The width of this void-free layer is also approximately the distance that rubber particles diffuse into the adhesion promoter. It is also noticed that the thickness of the interphase is close to the value of 350 nm reported by Mirabella *et al.* [8]. However, discretion should be applied when any comparison is drawn between the thickness measured by TEM imaging and the value obtained through chemical imaging.

Many authors have observed that, in injection-molded TPO samples, there is a PP rich layer at the surface, which was also observed in our samples (Fig. 3). The thickness of this PP rich layer near the surface evidently depends on the processing conditions and can be varied from several hundred nanometers to several microns. It was proposed that the solvent permeated through this pure PP layer and allowed the diffusion of CPO at the interface [9, 12]. There were several factors influencing the diffusion at the interface, including the type of solvent used, the paint baking temperature and the baking time.

Shown in Fig. 4 is the influence of the baking process on the interfacial structure between a TPO substrate and a single layer of CPO adhesion promoter. It is clearly shown in the image (b) that baking at 120°C (250°F) for 45 minutes causes a significant amount of swelling

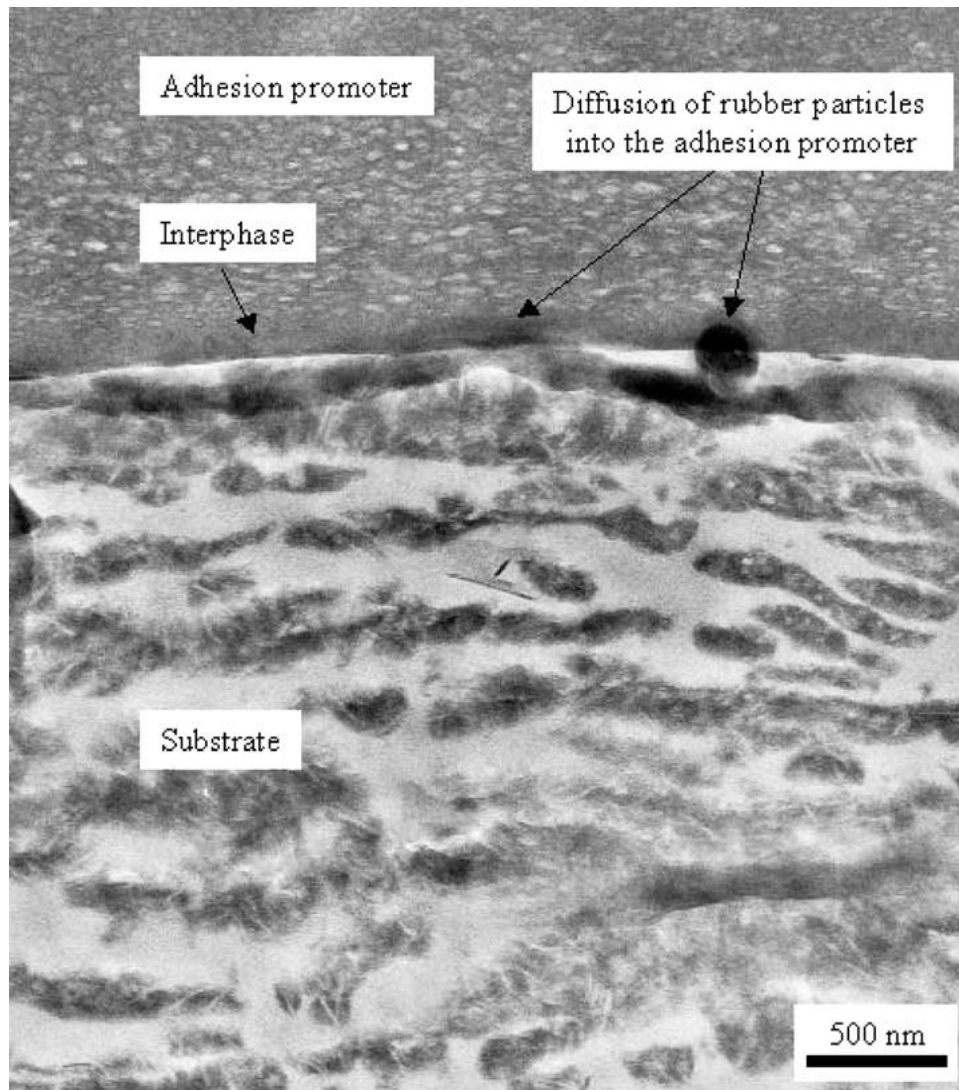


Figure 2 Structure of interface between the adhesion promoter and the TPO substrate.

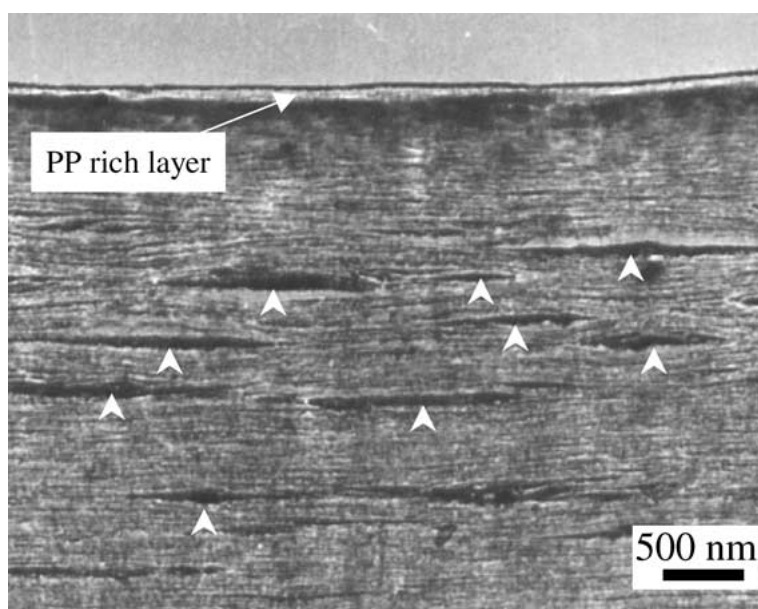
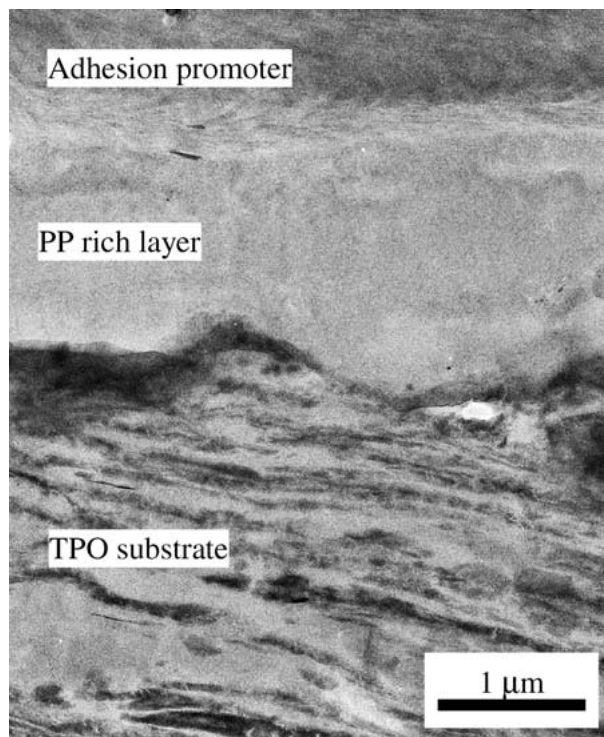
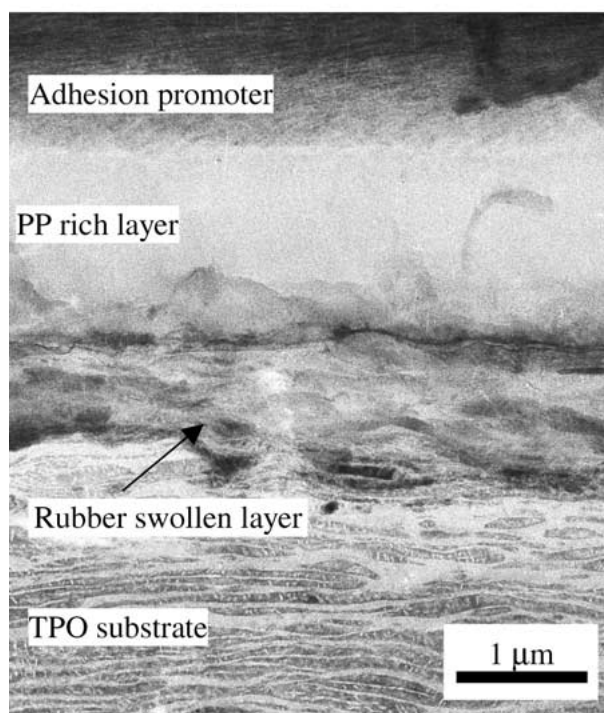


Figure 3 TEM image shows a pp-rich layer at the surface. The surface was coated with a thin gold film. The rubber particles are stained with RuO4 and appear gray in the TEM image, showing a well-elongated fibrous morphology. The talc particles appear black in the image and are marked with arrows.



(a)



(b)

Figure 4 The influence of baking on the interfacial structure between CPO and TPO substrate (a) unbaked and (b) baked at 120°C (250°F) for 45 min.

of the rubber phase in the near-interface area. It is also interesting to see that there is a diffusion of the rubber phase into the PP rich layer, which means that in addition to the diffusion of CPO to the substrate, the diffusion of rubber phase at the interface also has an influence on the interfacial structure. The distance over which the rubber phase diffuses into the PP rich layer is about 500 nm. The average diffusivity during the 45 min baking process is estimated to be $\sim 1 \times 10^{-10}$ cm²/sec,

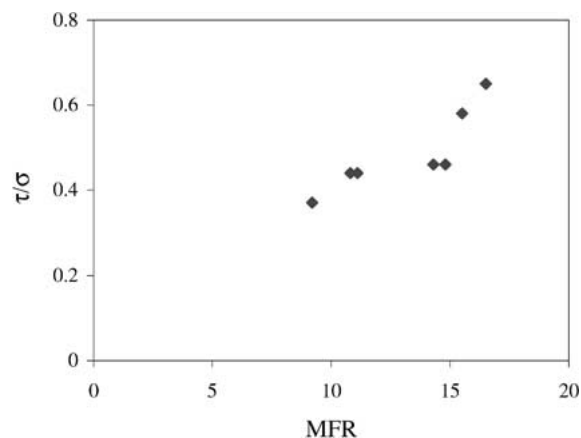


Figure 5 Influence of melt flow rate (MFR) of PP homopolymer on the normalized apparent interfacial shear strength between paint and TPO substrate, which is defined as the ratio between the apparent interfacial shear strength (τ) and the tensile strength of paint (σ).

which is about one order of magnitude larger than the diffusivity of PP in the melt state [13]. Evidently the swelling of the substrate by the solvent plays an important role in the increase of diffusion, as supported by the fact that solvent type has strong influence on the interfacial adhesion [9].

Shown in Fig. 5 is the influence of the melt flow rate (MFR) of the polypropylene homopolymer on the apparent interfacial shear strengths of the same paint system on different TPO substrates as measured by tensile cracking test. The MFR is a function of the molecular weight, i.e., the lower the molecular weight, the higher the melt flow rate. It can be clearly seen that a decrease in the molecular weight of the PP homopolymer (increase in MFR) increases the apparent interfacial shear strength. Considering the diffusion of rubber phase observed at the interface (Fig. 4), the increase in the interfacial shear strength with the decreasing homopolymer molecular weight can be explained with the increase in diffusion at the interface with the decreasing molecular weight of PP homopolymer, which makes it easier for the solvent in CPO and paint to permeate through the pure PP skin layer.

The flexural modulus of the substrate can be controlled by changing the amount of polyethylene component in the rubber phase, and thus the crystallinity of the rubber phase. Fig. 6 shows the influence of the

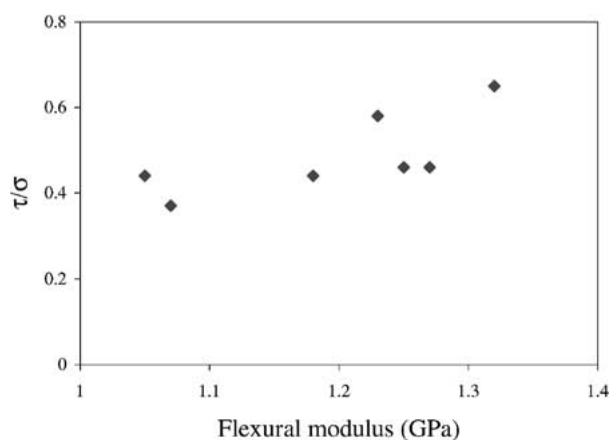


Figure 6 Influence of the flexural modulus on the normalized apparent interfacial shear strength between paints and TPO substrates.

flexural modulus on the interfacial shear strength. No obvious trend can be drawn from the data shown. The increase in the polyethylene component and the crystallinity in the rubber phase can increase the strength of the rubber phase and thus the strength of the entanglement at the interface. However, the increase in crystallinity might also hinder the diffusion of rubber phase at the interface. These two factors evidently counteract each other and thus no obvious influence of the rubber phase strength on the apparent interfacial shear strength was observed.

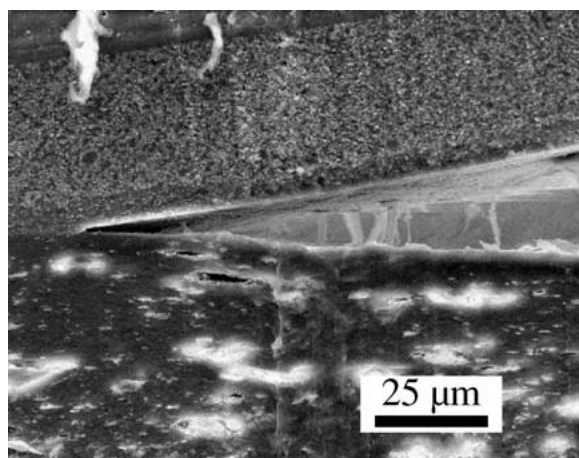
3.2. Interfacial deformation and delamination

At the end of the tensile cracking test, paints tend to delaminate from the substrate at the edges of cracks. The adhesion promoter layer generally contains a certain amount of pigment to modify its electrostatic properties. The titanium in the pigment as well as the chlorine in the adhesion promoter can be used in the elemental mapping to show the crack propagation trace as shown in Fig. 7. It is of interest that the delamination propagates through the cohesive failure of the adhesion promoter layer in the specific case shown in Fig. 7. A strong interphase formed by the diffusion and interaction of CPO and the rubber phase at the interface might be the reason for the cohesive failure of the adhesion promoter. It needs to be pointed out that the interfacial crack propagates through either the cohesive failure of the adhesion promoter or the adhesive failure at the interface between the adhesion promoter and the substrate. The local variation of the interphase structure might be the dominant factor in controlling the precise path of the delamination.

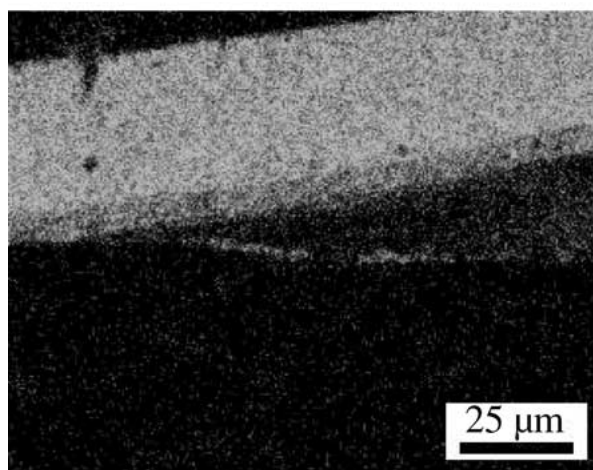
Polarized light OM imaging revealed very intense birefringence in the substrate near the interface at the initial stage of cracking (Fig. 8), which reflects that the near-interface substrate material undergoes a significant amount of plastic deformation. It is also worth pointing out that in the paint layer, there is no obvious birefringence observed, which shows that the paint layer mainly undergoes elastic deformation.

Tomasetti *et al.* [4] reported that the adhesion of CPO to blends of PP and ethylene-polypropylene-rubber (EPR) was much better than the adhesion to pure PP. Force modulation microscopy study showed that there was considerable plastic deformation in the rubber particles. They observed a “nodule” structure at the surface due to the plastic deformation of the EPR particles. It was postulated that the energy dissipated by the plastic deformation of the rubber phase could account for the better adhesion between CPO and PP/EPR blend than the adhesion between CPO and pure PP. In our experiments, we observed that the birefringent zone extended about $20\ \mu\text{m}$ into the substrate, and therefore the plastic deformation in the PP matrix should also contribute significantly to energy dissipation during the paint delamination.

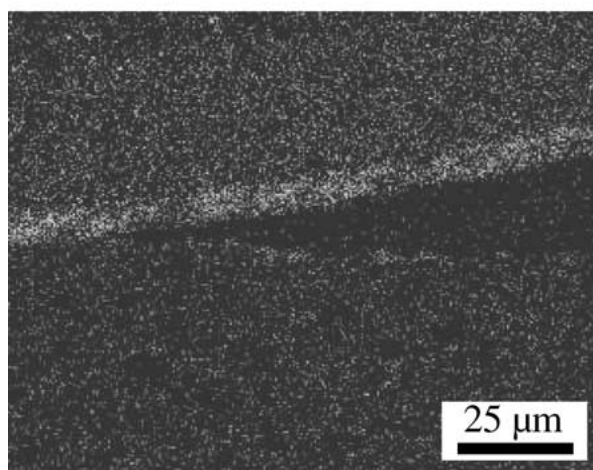
The delamination of the paint layer is through buckling from the edges of cracks as shown in Fig. 9 [14]. The SEM image shown in the figure reveals rippling surface roughness on the TPO after the delamination of



(a)



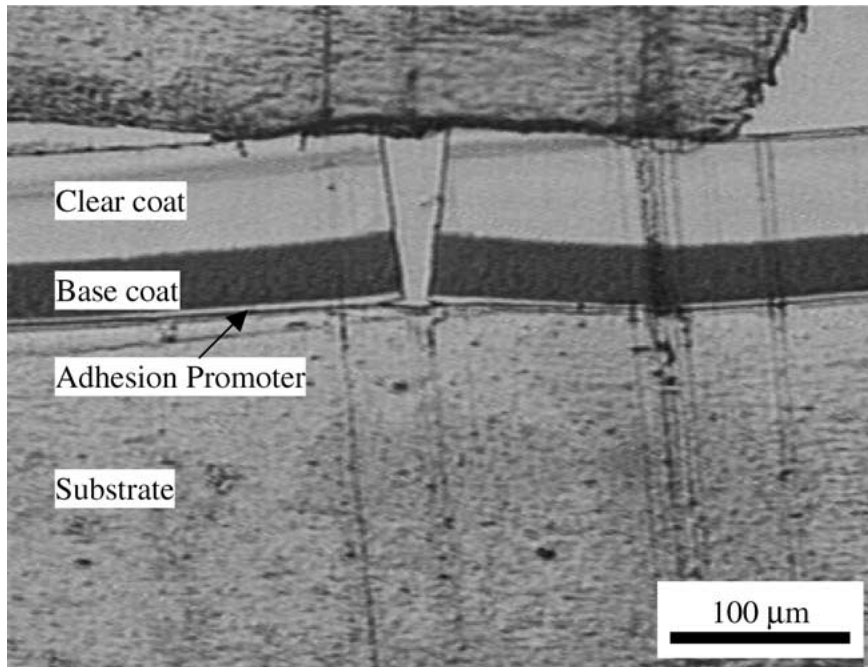
(b)



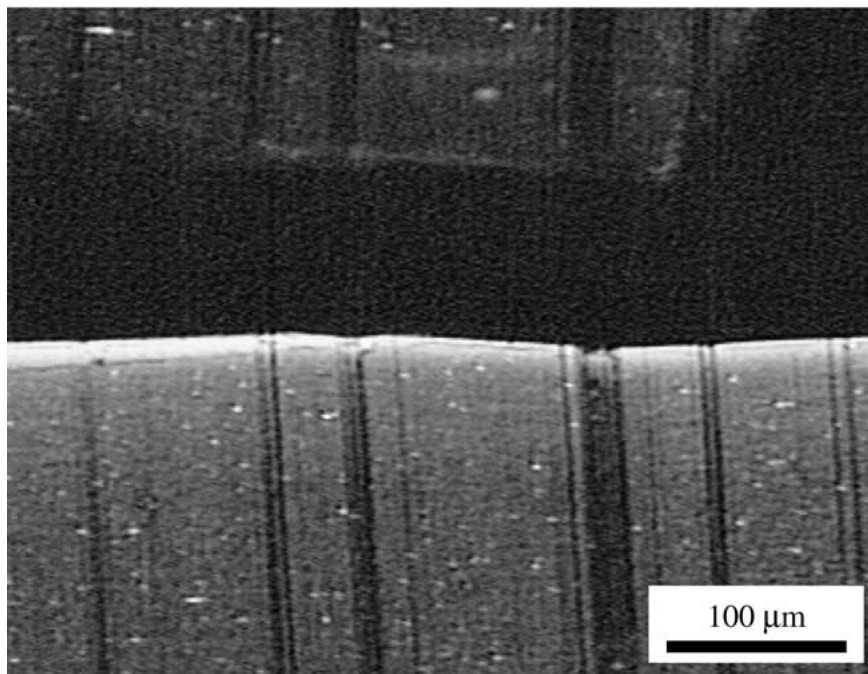
(c)

Figure 7 Delamination occurs near the adhesion promoter and substrate interface, propagating either inside the adhesion promoter or at the interface: (a) Secondary electron image; elemental mapping of (b) titanium and (c) chlorine.

the paint layer. This kind of rippling roughness on TPO substrate after the paint delamination is universal for all the samples we studied. A defective-adhesion area was observed on one of the samples (Fig. 10). The defective zone of adhesion was a linear strip that showed evidence for poor adhesion and easy paint delamination, perhaps due to some sort of surface contamination that was deposited during manufacturing. The rippling roughness



(a)



(b)

Figure 8 There is intensive plastic deformation in the near-surface substrate (a) non-polarized light OM image and (b) polarized light OM image.

on the surface is much less intense inside this area than outside the area. This observation implies that the rippling roughness is due to the material tearing during the delamination as seen in Fig. 7a.

Zhang-Newby *et al.* [15] reported that a large interfacial shear strength prevented the slippage of viscoelastic adhesive at the interface and favored material tearing, which could further increase the energy dissipation during the delamination. Shown in Fig.11 are images of interfacial delamination of two interfaces with different apparent interfacial shear stress measured by tensile cracking tests. The interface with the higher apparent interfacial shear stress ($\tau/\sigma = 0.65$) (Fig. 11a) under-

goes significant material tearing during the paint delamination, as shown by the filaments with width up to $5 \mu\text{m}$ and length up to $10 \mu\text{m}$ running across the interfacial crack. On the other hand, the interface with the lower interfacial shear stress ($\tau/\sigma = 0.44$) (Fig. 11b) undergoes much less material tearing, as shown by the fact that very few material filaments were seen running across the crack. In peel strength tests, it was also observed that a higher peel strength was always correlated with a much rougher peel strength vs. peeling distance curve, which might be due to the force fluctuation caused by the material tearing at the interface when the adhesion is strong [16].

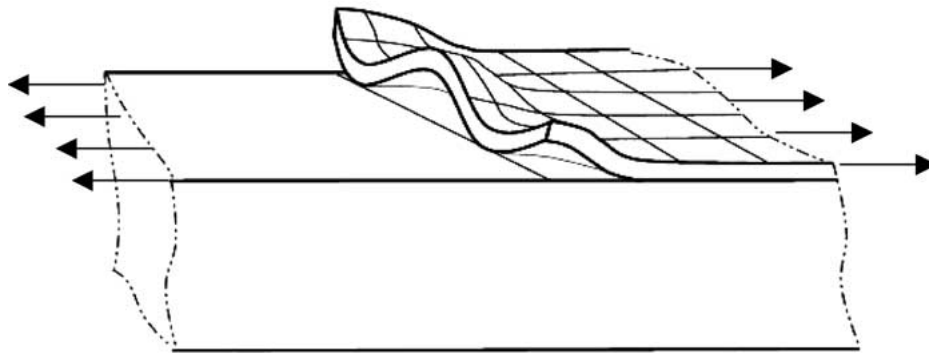
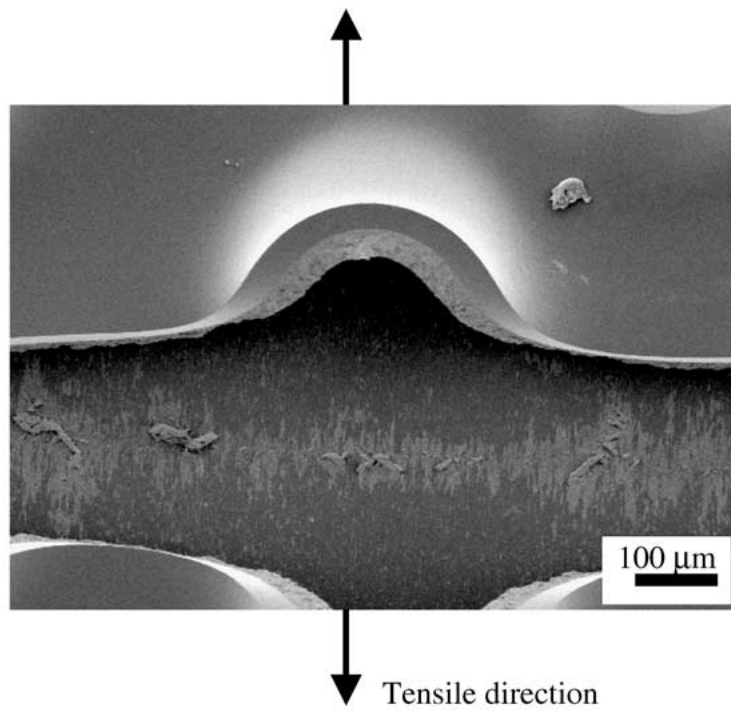


Figure 9 Buckling of paint layer from the edges of cracks.

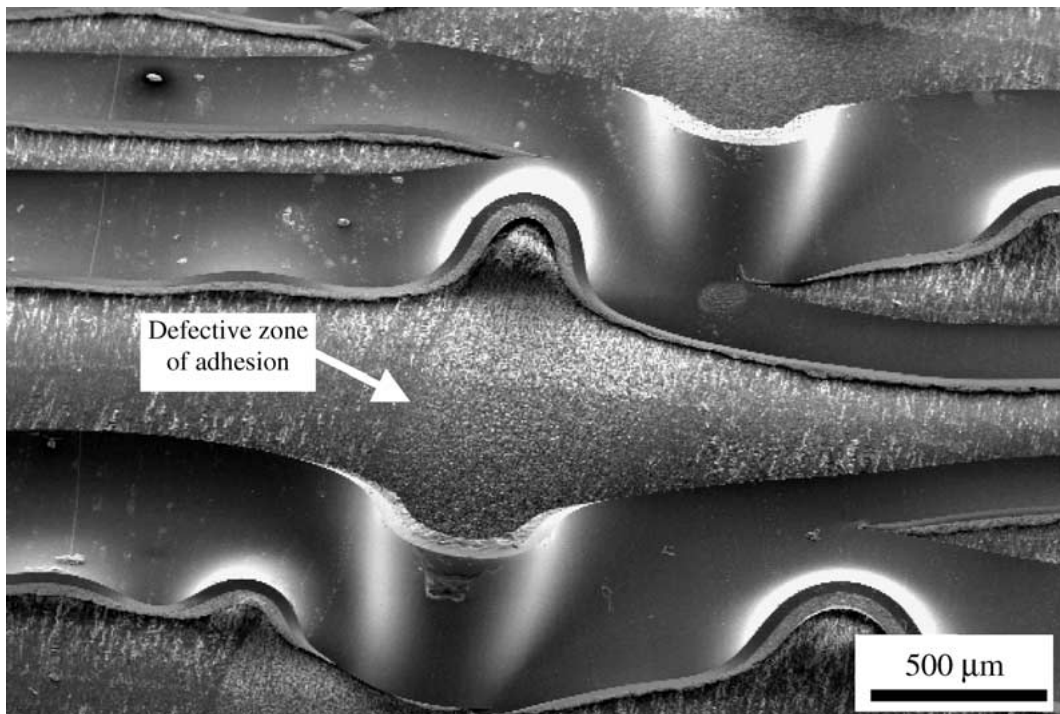
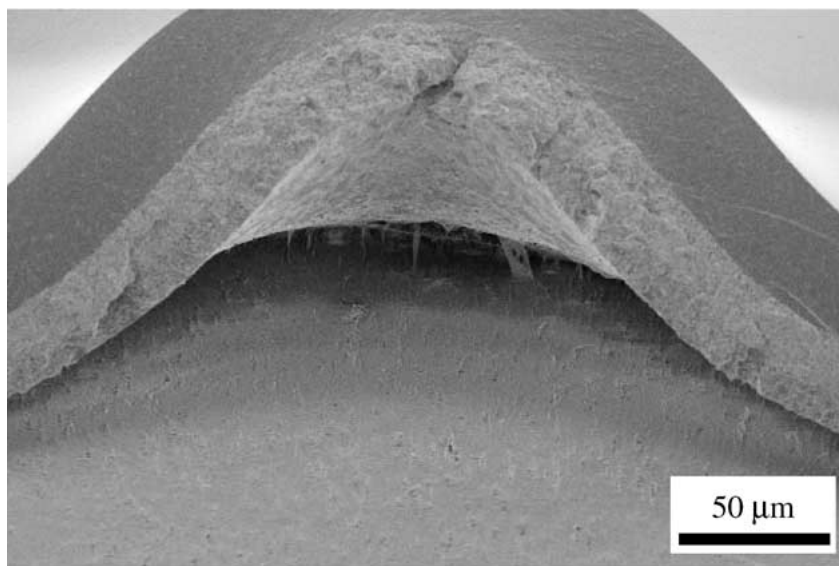
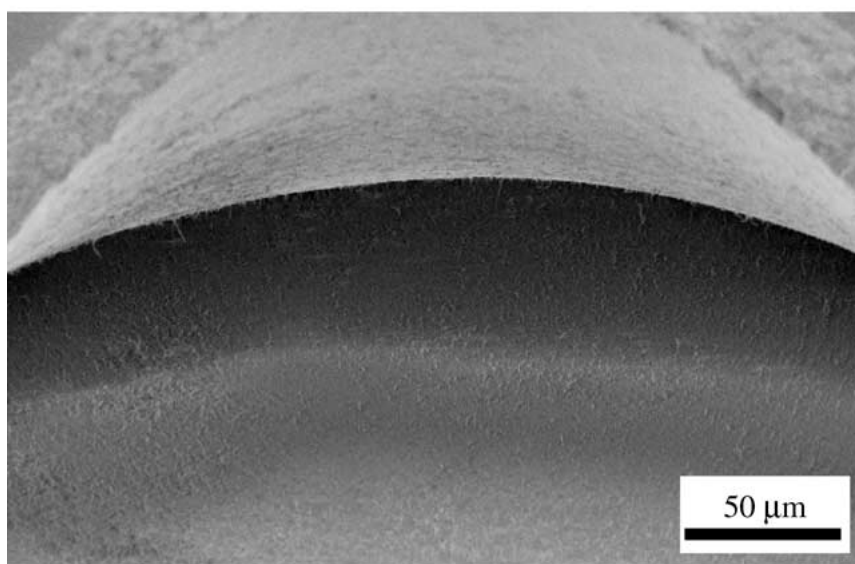


Figure 10 The rippling roughness arising from the materials tearing is much less intense in an inadvertent defective-adhesion area. It can also be seen that this area with poor adhesion also serves as a favorable nucleating site for buckling.



(a)



(b)

Figure 11 Difference in the amount of tearing observed during the paint delamination with different normalized apparent interfacial shear strengths. (a) $\tau/\sigma = 0.65$, and (b) $\tau/\sigma = 0.44$. The normalized apparent interfacial shear strength is defined as the ratio between the apparent interfacial shear strength (τ) and the tensile strength of paint (σ).

In a study on the effect of copolymer formation on the interfacial adhesion between semi-crystalline polyamide (PA) and polypropylene (PP), Boucher *et al.* [17] found that the interfacial toughness varied as the square of the areal density of copolymer at the interface. The authors further pointed out that the areal density was controlled by the diffusion at the interface at a relatively low concentration of reacting groups. Terzis *et al.* [18] recently reported that a relatively low areal density of tie chains (0.1 chain/nm^2) across the interface was needed for the optimal adhesion at PA/PP interface to be achieved. As pointed out by Boucher *et al.* [17], the structure of substrates on both sides of the interface, especially the softer substrate, would play an important role in the interfacial adhesion if plastic deformation was triggered in the substrates. Neither of the studies explored the effects of structure defects on the interfacial adhesion. This might not be a serious issue in a laboratory-generated material system, but is surely

present in industrial materials, as shown in Fig. 10. The detailed influence of interfacial diffusion on the different structural factors is still pending further study.

4. Conclusion

We have studied the interfacial structure between paint and TPO substrates using different microscopy techniques. We observed diffusion of the rubber phase at the interface, which implies that not only the diffusion of the CPO at the interface plays an important role in the interfacial structure and adhesion, but also the diffusion of the rubber phase plays an important role. It is observed that baking at high temperature favors interfacial diffusion. A decrease in the molecular weight of the PP homopolymer increases the permeability of the pure PP skin layer and thus increases the interfacial adhesion, as measured by the tensile cracking test. It was shown that the delamination of the paint propagates

near the interface between the adhesion promoter and the substrate, either through the cohesive failure of the adhesion promoter or through the adhesive failure between the adhesion promoter and the substrate. The microscopy study of the interfacial delamination has revealed that a high interfacial shear strength gave rise to more material tearing during the delamination, which is consistent with an increase in the energy dissipation during the delamination.

Acknowledgements

This project was supported in part by Du Pont Automotives and Visteon Co. We would like to thank Dr. Robert Matheson at Du Pont and Dr. Rose Ryntz at Visteon for supplying samples and many fruitful discussions.

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Received 5 March
and accepted 13 April 2002