Analysis of polymer parts: buried problems

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The analysis of manufactured parts for the source of defects is challenging as these defects are often buried below the surface. An example of this type of problem is a defect that occurs in a molded and multilayered painted part.

The automotive industry continues to increase the amount of plastics used in their vehicles in order to reduce weight and increase fuel efficiencies. The polymers are usually specified based on their mechanical properties as it is these properties that will dictate the effectiveness of the polymer in replacing a metal part. The paintability of the surface is often a secondary consideration.

The polymer alloy of polycarbonate and acrylonitrile/butadiene/styrene is used in some interior and exterior car components. This polymer alloy has a number of mechanical properties that make it attractive for use in automotive parts, however, variations in its domain structure can have an effect on its properties. The process of identifying the root cause of a defect occurring on a painted molded polycarbonate/acrylonitrile/butadiene/styrene part will be examined. Copyright © 2017 John Wiley & Sons, Ltd.

Introduction

Surface analysis labs are uniquely equipped to deal with many types of polymer surface issues but often the issues with painted, molded parts occur at inaccessible interfaces. The process for examining a buried defect in one of these types of parts is presented here.

The automotive industry shifted their focus in the 1970s to increase the amount of plastics used in their vehicles in order to reduce the weight of the automobile and increase fuel efficiencies. In 2015 the average light vehicle contained 370 pounds of plastics and polymer composites and this amount will only increase with the planned vehicle mass reductions.[1,2] Polymers are usually specified based on their mechanical properties as it is these properties that will dictate the effectiveness of the polymer in replacing a metal part. One of the more popular polymers used in applications, such as bumpers, is thermoplastic olefin consisting of a thermoplastic such as polypropylene, an elastomer such as ethylene propylene diene rubber and a filler such as talc.[2] There has been an increased use of the alloy of polycarbonate (PC) and acrylonitrile/butadiene/styrene (ABS), PC/ABS. Bayer introduced its PC/ABS alloy, Bayblend®, at the K Fair in 1972. Significant market success was seen with PC/ABS blend in the mid to late 1970s.[3] The PC/ABS is currently being used in many interior and exterior car components.

ABS is a terpolymer occurring as a two-phase polymer blend with the styrene and acrylonitrile (SAN) comprising one phase and butadiene comprising the other phase. The very fine butadiene rubber particles provide the 'toughness' to the styrene-acrylonitrile polymer. ABS has been widely available since the 1950s and is used in many consumer goods such as toys, telephones and kitchen appliances. It is also commonly used in the automotive and telecommunications industries as it can be processed either by extrusion or injection molding.[4] On blending PC with ABS, the blend retains the processability of the ABS and gains the mechanical properties and heat resistance of the PC. These properties are impacted by the ratio between the two components,[5,6] the additives used[7–9] and the molecular weight of the PC.[10] The two components are immiscible so the molded part consists of a continuous phase of one component containing domains of the other component.[9,11,12] The continuous phase is generally the component that is present in the higher concentration. The ratio of the polymers has a significant impact on the mechanical properties of the blends.

Although the PC/ABS has been studied thoroughly with respect to its mechanical properties, the same amount of study has not been applied to the effect of various solvents and paint layers on the polymer itself. After molding, the adhesion promoter (adpro) is applied, a basecoat is applied and the part is finished with a clearcoat layer. Defects in the finished part can arise at any point in the molding/painting process. In this paper, the process of analysing finished parts in order to identify the source of a defect will be examined.

Experimental

The samples were examined from the top down and in cross section by optical microscopy using a Zeiss Axioplan Compound Microscope Carl Zeiss, Oberkochen, West Germany and a Zeiss Discovery V8 Stereomicroscope, Carl Zeiss MicroImaging GmbH, Gottingen, Germany respectively. Surface profilometry was carried out on the samples using a KLA Tencor P-10 Surface Profiler KLA-Tencor Corporation, Milpitas, California, United States.

Fourier transform infrared spectroscopy (FTIR) was carried out using a Bruker Equinox 55 spectrometer equipped with an IRScope II microscope attachment Bruker Corporation, Billerica, MA, United States. The spectra were collected from 4000–600 cm^{-1} using both transmitted light in conjunction with a diamond compression cell

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for thin sections and using a micro attenuated total reflection (ATR) objective equipped with a germanium crystal. The contributions from water and CO_2 were removed from the spectra, and they were baseline corrected for presentation.

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy was carried out using a Hitachi S-4500 field emission SEM with a Quartz PCI XOne SSD X-ray analyzer Hitachi High-Technologies Corporation, Tokyo, Japan.

X-ray photoelectron spectroscopy analysis (XPS) was carried out using a Kratos AXIS Ultra Spectrometer Kratos Analytical, Manchester, UK using a monochromatic Al K^{α} X-ray source and a spot size of approximately 700 by 160 μm. A flood gun was used to control charging at the sample, and a pass energy of 160 eV was used for the survey scans.

For the analysis of the adpro, the suspension was distilled prior to analysis by gas chromatography coupled with mass spectrometry (GC/MS). Because the adpro contains a significant amount of solids, including carbon black, it was not a suitable sample for direct GC/MS analysis. The solvent component of the adpro was removed by distillation of all components which boiled below 185°C. Based on the material safety data sheet, all of the solvent components should have been removed by 168°C. A black gummy material remained in the bottom of the flask after distillation. The distillate was analysed by GC/MS using a 30 metre DB-5ms column. The injection temperature was 250°C, and the temperature program was 32°C for 5 min, 3°C/min to 100°C then 25°C/min to 325°C with a hold temperature of 1 min at 325°C.

Differential scanning calorimetry (DSC) analysis was performed on the polymer sample to determine if any differences were detectable.

Results and discussion

The defect parts were received in the lab exhibiting an apparent drip-like defect in the silver paint. The defects had an apparent size of approximately 4 cm long by approximately 2 to 3 mm wide. The edges of the defect were not well defined, masking the true size. The parts had a basecoat of silver paint containing aluminum flakes covered by a clearcoat layer. The defect occurred in a similar location on all of the defective parts.

Examination by optical microscopy using a stereomicroscope showed that the defect was not at the outermost surface of the part as the surface of the clearcoat was smooth and shiny in the defect area. Examination of the positions of metal flakes through the clear outer layer was carried out using a higher magnification compound microscope. In some instances, the flakes can agglomerate and tilt,

causing apparent colour changes as more of the underlying layer is seen and reflecting the light differently from the surrounding area. Optical microscopy showed that there was no apparent agglomeration of the flakes. The tilt of the flakes cannot easily be determined by optical microscopy from the top down.

As it has now been determined, by optical microscopy, that the defect does not arise from a surface phenomenon, the samples need to be mounted and polished in cross section both in defect areas and in reference good areas for comparison. It is important that the cross sections of the defect and reference areas come from the same parts, if possible, to eliminate any sample-to-sample variation that might be encountered. Often layer thicknesses can vary from sample-to-sample, and it is very important to be able to determine the significance of these variations.

After mounting and polishing, the defect and reference samples were examined in cross section by both optical microscopy and SEM. The images of the cross sections are presented in Fig. 1. Evident in the cross section are a number of layers; the substrate, the adpro, the basecoat layer containing the aluminum flake and the clearcoat layer.

The substrate in the defect area shows an undulating surface that is replicated in the adpro layer and the basecoat layer. The substrate in the reference area shows the surface as being fairly smooth.

The cause of the undulation on the surface of the substrate in the defect area is unknown at this point. As the defect always occurs in the same area of the part, the most likely explanation is a series of scratches or perturbations on the mold surface that are being replicated on the surface of the molded part and, subsequently, in the adpro and basecoat layers.

In pursuing this line of reasoning with the manufacturer, it was found that the same mold produced both good and defective parts, depending on the polymer used in the mold. A request was made of the manufacturer for samples of the raw parts made from the defect-producing polymer, using the mold in question, prior to the application of coatings. These raw parts would be examined in the defect area to determine if any scratches could be detected.

On receipt of the raw molded parts, they were examined using surface profilometry for the possible presence of scratches or roughness that would result in the formation of the defect of interest. No roughness or scratches were noted on the raw parts in the defect area as shown in the images presented in Fig. 2. The undulating surface is not the result of a defect in the mold.

If the undulating surface is not part of the surface of the raw part, it must be induced on the application of one or more of the coating layers. Raw parts with only the adpro layer applied were requested from the manufacturer. These parts were supplied, and

A - Clearcoat, B - Basecoat, C - Adpro, D - PC/ABS substrate
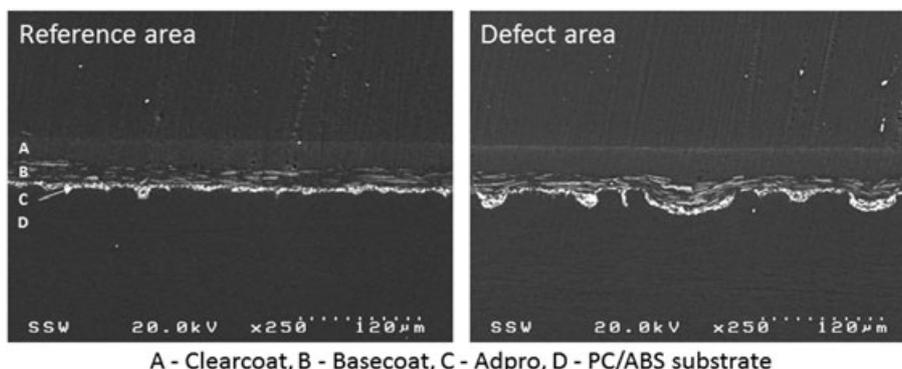
Figure 1. Scanning electron microscopy images of mounted cross sections of the fully painted part in the reference and defect areas showing the undulating layers under the surface in the defect area. The various layers are labelled.
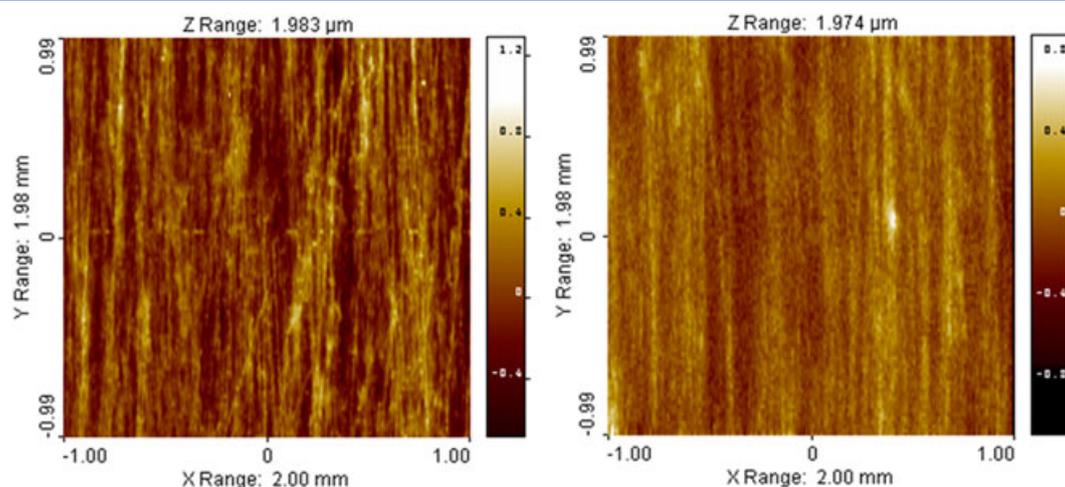
Figure 2. Surface profiles of the raw parts in the affected areas showing similar ranges in the Z-direction.

examination by optical microscopy showed the appearance of an apparent scratch on the surface in the defect area as shown in Fig. 3. The large scratch was surrounded by smaller 'scratches'. The surface of the part was analysed by surface profilometry in an area with 'scratches' and an area away from the 'scratches'. The scratch was approximately 200 microns wide and 35 microns deep. No features of this type had been seen on the raw parts. Based on this information, the application of the adpro is causing significant changes on the surface of the molded raw part.

A sample of the adpro was supplied to us and applied to the surfaces of eight raw parts to see if the line defects in the parts could be replicated. Of the eight samples to which it was applied, three were found to have the line defects at the surface after the application of the adpro. The severity of the defects varied from sample-to-sample even though care was taken to apply the adpro the same way to each sample.

Representative samples of the affected and unaffected samples were mounted and polished in cross section to show the effect of the adpro on the surface. The difference was striking and illustrated the fact that the undulations at the surface of the severely affected sample were not present on the part outside of the area where the adhesion promotor was applied. It was the application of the adpro that was causing the defects in some of the parts.
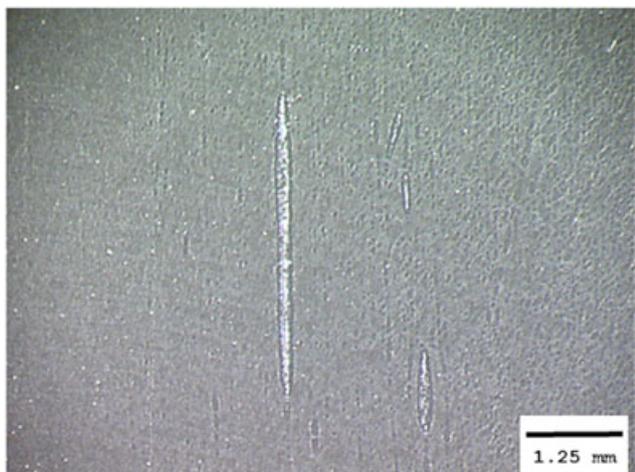
Figure 3. Optical image of a part in the defect area with only adpro applied. Note the appearance of the 'scratch-like' features.

The adpro, in this instance, is black, being a mixture of a chlorinated polymer, carbon black, barium sulphate and a mixture of solvents. It is unlikely that the chlorinated polymer, the carbon black or the barium sulphate is causing the perturbation at the surface of the raw PC-ABS part. It is far more likely that the solvent, used to disperse the components, is causing the perturbation.

As the perturbation at the surface is only occurring in a particular location, using a particular grade of polymer, one theorizes that there is a variation in the polymer composition in that location on the molded part. PC/ABS is referred to as a polymer alloy. Its constituent parts are PC, acrylonitrile, butadiene and styrene. The styrene and acrylonitrile polymers are miscible and are referred to as the SAN component. The butadiene is not miscible with the SAN component and forms very small domains in the SAN to form ABS. The ABS is blended with the PC, but the two polymers are not miscible. The polymer is usually composed of domains of one of the components within a continuous phase of the other. The polymer forming the domains is usually present at a lower concentration.

It would not be unexpected to find that the surface concentration of one of the components is higher than the concentration in the bulk. Analysis of a polymer surface can be done using a number of techniques. Time of flight secondary ion mass spectrometry is a very surface sensitive technique, but it is not quantitative. It may not probe deeply enough to reveal the polymer, especially if there is a contamination layer at the surface. FTIR, using the micro ATR objective on the microscope, probes the surface on the order of microns and would be sensitive to the styrene, acrylonitrile and PC components.

The surfaces of the affected and unaffected raw parts were analysed by FTIR. There were no discernable variations in the relative intensities of the peaks from PC and ABS in the FTIR spectra of the surfaces of the raw parts that were unaffected by the application of the adpro as compared with those that were affected. The samples were analysed using the germanium crystal on the micro ATR objective that allows one to restrict the depth of penetration of the analysis to the top 1–2 microns of the surface. For both samples, an area just slightly away from where the adhesion promotor had been applied was analysed.

X-ray photoelectron spectroscopy analysis examines only the top 5–10 nm of the surface in an area approximately 700 by 160 microns. With PC-ABS blends, the oxygen content should arise only from the PC component while the nitrogen should arise only from the nitrile group in the styrene/acrylonitrile component of the ABS.

The PC-ABS blends exist as domains of one of the components in a matrix of the other. Neither FTIR nor XPS has the spatial resolution to identify the domain structure.

The oxidation state of the carbon in the carbonate group was such that the XPS carbon 1s response from these carbons was shifted significantly higher (~5 eV) than the main carbon 1s peak. The degree of this shift allows one to quantify the carbonate and the nitrogen from the survey scans and calculate a ratio between the two.

The affected and unaffected raw parts were analysed by XPS on the top surface, the surface of the edge where the defect was occurring and in cross section. The data from the analysis is included in Table 1. The amount of nitrogen at the surfaces was very similar to the amount detected in the cross sections. The amount of carbonate at the surface was much less than that seen in the cross sections. The relative amount of carbonate was least on the edge surface of the raw part, the location where the defect forms after being exposed to adpro. The XPS data indicated that there could be a change in the domain structure of the polymer alloy at the surface.

The XPS analysis indicated that there was a polymer segregation taking place in a particular spot on the molded part. As the part is formed by injection molding of the molten polymer, the thermal characteristics of the polymer in this area would be useful to know.

Sections of a raw part where the defect had been seen and sections from a part which had not shown the defect were analysed by DSC. This is a bulk analytical technique that measures the polymer response to heating. As the PC and ABS are immiscible, two different glass transition temperatures would be seen. These glass transition temperatures can be measured and used to determine if the polymers flow at different temperatures. They can also be used to determine if there is a significant difference in the ratio between the two polymers. Differences in the glass transition temperatures can have an impact on how the polymers flow, and flow is critical in injection molded parts. The DSC analysis did not show any significant differences in the relative amounts of PC and ABS in the two samples nor were there differences seen in the glass transition temperatures of the samples. The compositions appear to be the same.

Having the XPS data indicate that there was a variation in the composition at the surfaces of the molded parts led us to further examine the mounted cross sections of the parts exposed to adpro. On this further examination, it became apparent that there was an effect from the adpro on the underlying PC/ABS substrate. As can be seen from the images in Fig. 4, there was a line in the substrate below where the adpro was applied. The line was missing where there was no adpro applied.

The cross section was examined by FTIR to see if the difference between the layers could be determined. The layers of reference substrate (below the line) on both samples, and the material between the lines and the adpro on both samples, were analysed by FTIR. The spectra are compared in Fig. 5. One can see from the comparison that the carbonate peak in the spectra collected from the substrates away from the exposure to adpro is situated near 1776 cm^{-1} for both samples. For the sample with a smooth interface between the substrate and the adpro, the peak has shifted from 1776 to 1774 cm^{-1}. For the sample with the undulating interface, the carbonate peak has shifted to 1771 cm^{-1}. Based on the literature, the shift of this peak to lower wavenumbers is indicative of increased crystallinity of the PC portion of the polymer substrate.[13] Based on this result, the PC appears to have become more crystallized on exposure to the adpro. Although some crystallization was noted in the polymer wherever the adpro was applied, it was the greatest in the areas showing the formation of the undulating interface.

From the XPS data, there was a variation in the relative concentrations of the PC and ABS at the outer surfaces of some of the parts. Based on the FTIR analysis, the PC portion of the alloy in cross section was crystallizing more in the affected sample than in the unaffected sample. There was a change in the domain structure of the PC-ABS blend at the outermost surface of the affected samples, and the defect was related to the effect of the solvent in the adpro on the PC/ABS. It is nearly impossible to visualize the effect of the solvents in the adpro on the surface of the polymer as the adpro contains carbon black and polymer along with barium sulphate in the mixture. The carbon black and polymer coat the surface and obscure the changes to the surface. The supplier of the adpro would not supply a breakdown of the components so that a test solution could be designed which contained only the solvent components of the adpro. It was decided to distil the solvent portion from the polymer/barium sulfate components in the mixture. Based on the material safety data sheet, all of the hazardous components should be removed by heating to 168°C. The sample temperature rose to 185°C during the distillation. The examination of the distilled liquid by GC/MS showed the presence of a large number of components in the adpro solvent, including: methyl benzene, butyl acetate, ethyl benzene, xylene, dimethyl benzene, 1-methoxy-2-propyl acetate, methyl n-amyl ketone, propyl benzene, 1-ethyl-3-methyl-benzene, trimethyl-benzene and ethyl 3-ethoxypropanoate.

With the solvent mixture from the adpro available, it was possible to examine the effects of the solvent on the surface of the molded part.

The solvent mixture was brushed onto the surfaces of the raw parts that had shown a response to the adpro and those that had not. The solvent evaporated quickly from the surface. The effects of the solvent on the polymer surfaces were dramatic, as shown in the optical image in Fig. 6. The surfaces of the solvent-exposed parts were further examined by SEM. The images are labelled as grey area – least exposure to solvent, white area – where two brush strokes overlapped and white circle – the end of the stroke with the most solvent exposure. One can see from the images in Fig. 7 that the solvent has an effect on both types of raw surfaces but, on the surface that showed little response to the adpro, the effect is that of a fine open structure at the surface. The raw surface that showed a significant response to the adpro showed a significant response to the solvent. A lower magnification image of the surface of the highly affected surface is presented in Fig. 8. These features are very similar to those seen in the painted defect area of the finished manufactured part.

Table 1. Elemental composition in atomic percent by X-ray photoelectron spectroscopy

177 defect raw sample

	C	Cl	N	Na	O	S	Si	Carbonate	N/carbonate
Top surface	81.4	0.1	2.2	0.6	12.7	0.3	1.3	1.4	1.6
Edge surface	79.2	0.1	2.4	1.0	14.9	0.5	1.4	0.4	5.6
Cross section	85.9	0.0	2.0	0.0	7.7	0.0	0.1	4.3	0.5

172 good raw sample

|	C	N	O	S	Si	Carbonate	N/carbonate
Top surface	82.0	1.9	11.4	0.0	3.1	1.6	1.1
Edge surface	85.3	1.7	10.4	0.1	0.7	1.7	1.0
Cross section	85.5	1.5	7.3	0.0	0.0	5.8	0.3

Figure 4. Optical images of the cross sections of raw molded parts with and without adhesion promoter (adpro) applied. Sample 177 showed defects while sample 172 did not. Note the appearance of a line, well below the interface, where the adpro was applied. The areas labelled A, B, C and D were analysed by Fourier transform infrared spectroscopy.

The differing reactions of the surfaces of the raw parts to the solvent indicate that the reaction is related to the morphology of the polymer. An examination of the literature on the structure of PC/ABS polymers reveals that the morphology of the polymer in the molded part changes drastically based on the ratio of the PC to ABS and, sometimes, on the butadiene content in the ABS.[6,9,12,14,15] The polymeric mixture of PC/ABS exists as domains of one of the polymers in a continuous phase of the other polymer. The continuous phase is usually composed of the polymer in the higher concentration although there are references to 'co-continuous' phases of the blend.[11]

Studies have been performed on the effect of molding on the morphology of the polymer. The distance from the gate and the presence or absence of compatibilizing additives can impact the morphology of the polymer, especially at the points furthest from the gate.[14,16,17] The morphology of the system can change from one of smaller, spherical domains of one phase into another one of elongated domains of the polymers. These elongated domains can be seen at the surface of the molded polymer, running parallel to the flow direction of the polymer. The injection speed can have an impact on the formation of these domains, as can the presence or absence of compatibilizers.

There have also been studies on the solvent crystallization behaviour of PC at surfaces.[18–20] These studies have focused on changes to the surface of the PC that affect the wettability of the surfaces. Exposure to solvent changes the morphology of the PC at the surface as it crystallizes. The change in the morphology of
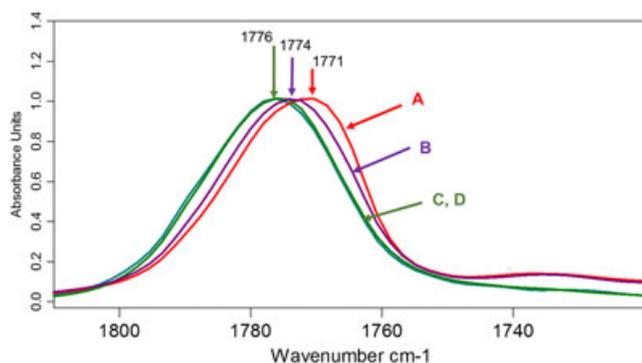
Figure 5. Fourier transform infrared spectroscopy spectra of the carbonyl region of the polycarbonate and acrylonitrile/butadiene/styrene in the four areas indicated in Figure 4. Note the shift to lower wavenumbers, indicating increasing crystallization of the polycarbonate portion of the alloy.
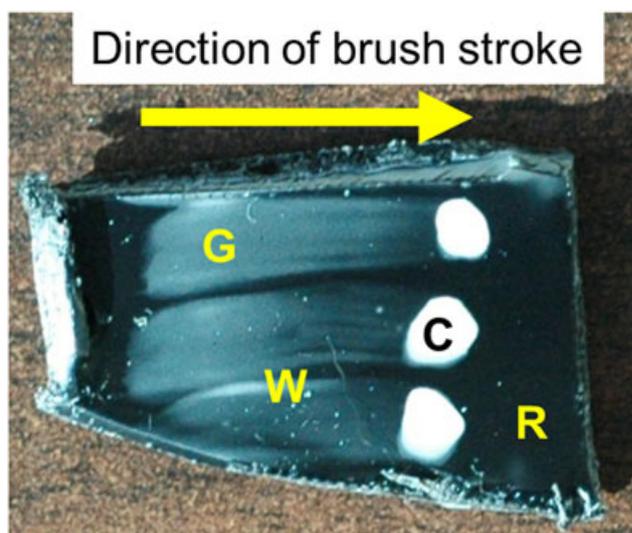
Figure 6. Image of the raw part after the application of the solvent portion of the adpro. The areas analysed by scanning electron microscopy are indicated by the letters G (grey area, single stroke), W (white area, overlapping strokes), C (end of a stroke where a droplet formed) and R (reference area).
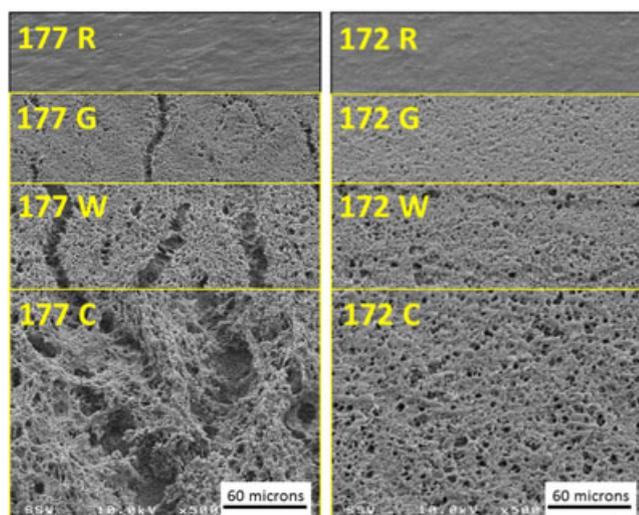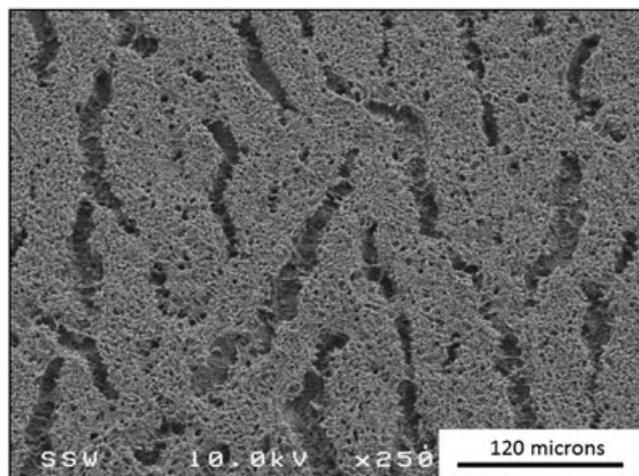
Figure 7. Scanning electron microscopy images of the surfaces of raw part 177 showing defects and raw part 172, a good part. The letter 'R' indicates an area prior to exposure to the solvent. The letters G, W and C indicate the areas shown in Figure 6.

the PC on exposure to solvent is reminiscent of the changes seen on the surface of the molded part on exposure to the adpro.

The studies of the domain shapes and sizes with respect to the distance from the injection molding gate show that elongated domains of PC and ABS can be formed parallel to the flow direction in areas away from the gate. Although the sizes of these domains seen in the literature are much smaller than the effects that are seen on solvent exposure of the molded part in the defect area, the shape of the defects is similar. Exposure to solvent can have a dramatic impact on the surface morphology of the polymer, leading to crystallization of the PC.

Based on the data collected, the FTIR analysis shows that there is a crystallization of the PC component of the blend on exposure to the solvents in the adpro. The optical images of the cross sections show that the effect of the adpro penetrates deeply into the PC/ABS. XPS analysis shows that there is a variation in the

carbonate/nitrile groups across the surface and in cross section. SEM images of the surfaces of the defective and good PC/ABS parts after exposure to the solvent portion of the adpro show that the morphologies of the surfaces of the parts are strikingly different.

As shown in this paper, preliminary examination of the sample from the top down and in cross section can allow one to identify the location of the defect and theorize on possible causes. A variety of analytical techniques is required to eliminate some of the possible causes (gross changes in the polymer, contamination, etc.) and allow one to narrow the investigation. The availability of the raw materials and the coatings involved were greatly beneficial to this analysis. They allowed us to thoroughly pursue the cause of the problem. The most difficult question to answer in this analysis was not 'what is causing the problem', it was 'why'. Why only on some parts, why only in one area? The answer to the 'why only in one area' was answered based on the mold design and the distance from the gate. The 'why only on some parts' is more challenging as it is likely related to slight variations in the composition of the raw polymer and the presence or absence of compatibilizing agents.

Conclusions

The defect occurring in the painted molded part is arising from an interaction between the PC/ABS surface and the solvent mixture used in the adpro. The defect only occurs when there has been a presumed change in the domain structure of the PC/ABS alloy in a particular area on the molded part at a particular distance from the injection gate. The application of the adpro to the molded part is inducing crystallization of the PC at the surface. In the defect areas, the crystallization is causing wide channels to form at the surface of the part that mimic the domain structure. The appearance of the defect in the finished part is related to the wide shape of the defect formed at the surface and the tilt induced in the aluminum flakes in the basecoat layer. The tilt of the aluminum flakes results in light being reflected at an off-normal angle from the surface. The tilt of the flakes makes the defect appear as a drip.

Figure 8. Scanning electron microscopy image of the surface of raw part 177 after exposure to solvent. Parts of this type showed the presence of defects on painting.

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