Eastman Spectar™ copolyester

Solvent methods for improving the surface appearance of scratched sheet

Copolyesters are often used in expensive articles like decorative "EILT" (Encapsulated Image Layer Technology) laminates or in Visual Merchandising where they replace glass, acrylic, and other competitive materials. Copolyesters are often chosen over these competitive materials because of a combination of several favorable characteristics such as toughness, low flammability, and chemical resistance to everyday cleaners. However, one drawback to sheet of Eastman Spectar™ copolyester is that it has relatively poor scratch resistance properties versus some competitive materials. Procedures have been developed to repair scratches on Spectar sheet using heat from either a hot air gun or a butane microtorch, but these methods can result in warped articles because of Spectar copolyester's relatively low heat distortion temperature for inexperienced fabricators. The work described in this report will detail a solvent-based method of repairing scratches on the surface of extruded or laminated Spectar copolyester sheet.

Experimental

Materials

Solvent scratch repair techniques were evaluated on 0.118-inch-thick Spectar copolyester sheet that had been extruded with polished chrome cooling rolls on both sides of the sheet.

One series of solvent repair solutions used pure acetone and acetone diluted with water at 25%, 50%, and 75% concentrations by volume prior to mixing. It should be noted that mixing acetone and water is an exothermic process so proper precautions should be taken when large volumes are utilized.

A second series of solvent repair solutions used pure MEK (methyl ethyl ketone) and 25% MEK diluted with 75% water by volume prior to mixing. Higher water dilutions were not attempted due to the limited miscibility of MEK in water, being 27 wt%.[1]

Sample preparation

To generate a uniform haze, 3M™ General Trim Adhesive was applied to the reverse side of a 6-inch-square piece of 2000 grit sandpaper and mounted to a 20-inch-square board. A 2.1-kg weight was placed on a 4 x 12 inch strip of Spectar sheet and was pulled across the sandpaper 15 times to generate a uniform level of haze. This procedure was repeated multiple times to generate several samples for a scratch repair evaluation.

To repair the surface, the test strips were dipped in the repair solutions to about 4-inches deep for the specified amount of time. The sample was removed from the solvent repair solution, rinsed with water, and dried with compressed air.

Analytical tests

The haze percentage before and after solvent repair was measured in accordance with ASTM D1003 Method A, Illuminant C using a BYK Gardner Haze-Gard Plus.

[1] *Lange, N. A.;* Lange's Handbook of Chemistry, *11th ed., McGraw-Hill, Inc., 1973, pp. 7–277, ISBN 0-07-016190-9.*

Results and discussion

The idea of repairing a scratched surface derived from the well-established solvent bonding techniques used to join the edges of two sheets of Eastman Spectar™ copolyester. In solvent bonding, a syringe is used to apply a small dose of a liquid that will plasticize the localized area of the two edges being joined. The glass transition temperature of the localized area will be temporarily depressed below room temperature, allowing polymer chain mobility and therefore chain entanglement at the sheet interface. The solvent then either evaporates and/or diffuses farther into the sheet, causing the solvent concentration at the sheet interface to diminish over time, thereby resulting in a bonded edge. If the polymer chains are allowed to remain mobile for too long because of excessive solvent application or improper solvent selection (too aggressive), they can arrange into crystallized spherulites—a polymer morphology that has a detrimental effect on the sheet's optical and physical properties.

Scratch repair using a solvent-based method follows a similar mechanism. When a scratch is formed on the surface of a sheet, it is presumed that a stress gradient is formed in the scratch through mechanical action. If the localized region is brought above the material's glass transition temperature (through solvent plasticization in this case), then polymer chains will mobilize and seek a lower energy state to relieve these stresses. The resultant surface mobility is theorized to directionally level the surface, causing less light diffraction and therefore a lower level of haze.

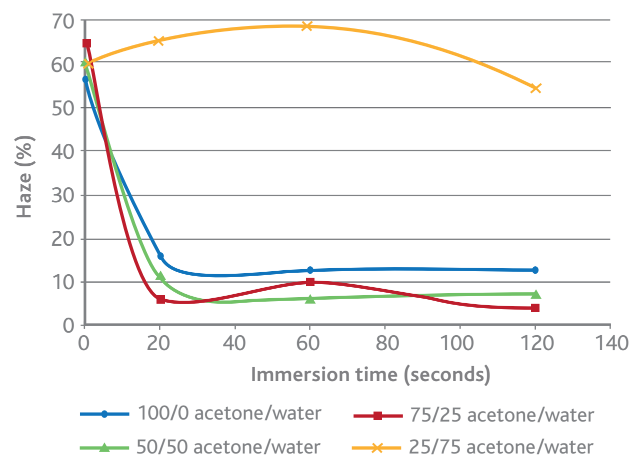
The objective of this study was to demonstrate scratch repair using solvents with relatively low heath risk factors that are commonly available in hardware stores. It was also desirable that these solvents have some miscibility with a second, inexpensive diluent that doesn't significantly plasticize the Spectar sheet surface so that a solution with a tunable solubility parameter could be formed. Acetone and MEK solutions were therefore used with water as the diluent.

Figure 1 shows the effects of acetone and acetone/water solutions on the scratch-induced haze level on Spectar sheet at various immersion times. Immersion in pure acetone (blue line) lowered the haze from surface scratching from about 60% to about 13%. Acetone diluted with 25% water (red line) and 50% water (green line) by volume also helped repair the scratched surface. In these instances, the initial haze value of about 60% was lowered to around 8% on average. The acetone solution diluted with 75% water did not exhibit surface repair.

Figure 1

Solvent scratch repair on extruded Spectar sheet

Haze (%) versus solvent immersion time



While haze measurements showed that certain solutions with acetone partially repaired a scratched surface, a visual inspection was also needed to identify slight surface anomalies. The sheet treated with pure acetone showed some surface hazing from solvent-induced crystallization at all immersion times. Similarly, slight edge crazing was seen on the sample treated with a 75% acetone solution at a 60-second dip time while the 120-second exposure led to nonhazy yet slightly visible crystallization domains. These defects were not apparent from the haze measurements that were taken. The 50% acetone solution showed no detrimental effects at any immersion time. Figures 2 and 3 show several samples that demonstrate the slight crazing or crystallization domains.

Figure 2

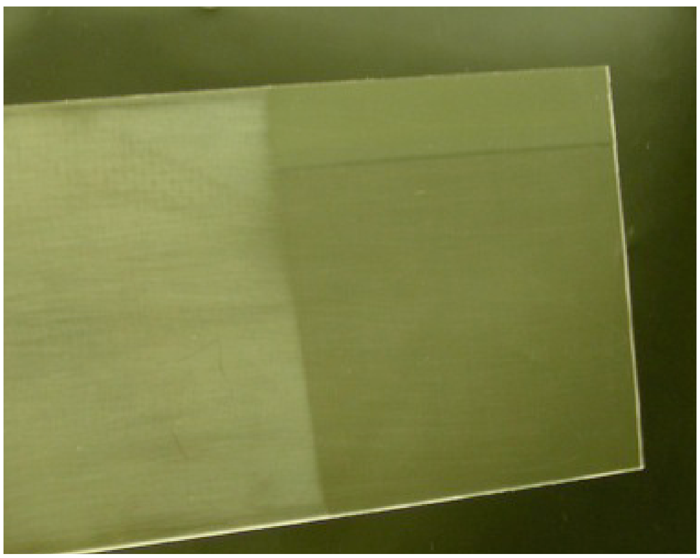


Figure 2 shows a sample of extruded Spectar sheet that has been scratched and then dipped in a 75/25 acetone/water solution for 120 seconds (X30484-084-5). The haze from surface scratching can be seen on the left side of the sample whereas the right side exhibits much less haze after being dipped in the surface repair solution.

Figure 3 is the same plaque shown in Figure 2. Note the small domain of surface crystallization that can be seen when the sample has been rotated. This effect may explain why haze measurements did not detect the crystallization domains seen in some samples in this experiment—haze was measured with samples oriented normal to the incident light from the instrument whereas slight surface crystallization can only be seen when the sample has been rotated.

Figure 3

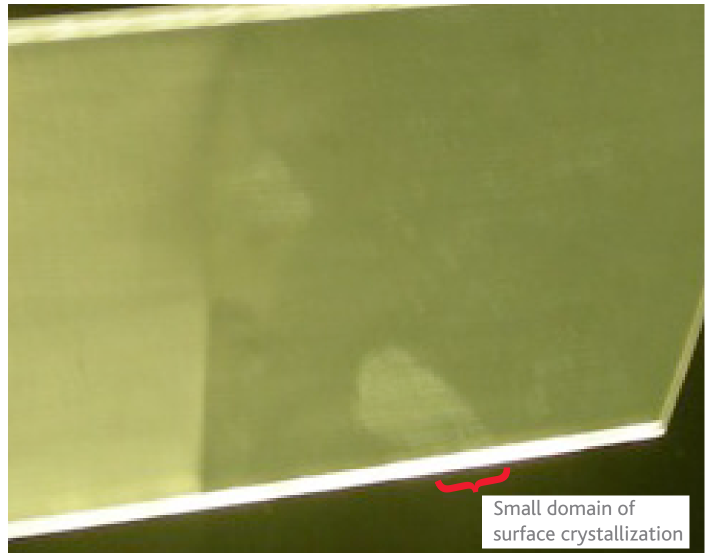


Figure 4

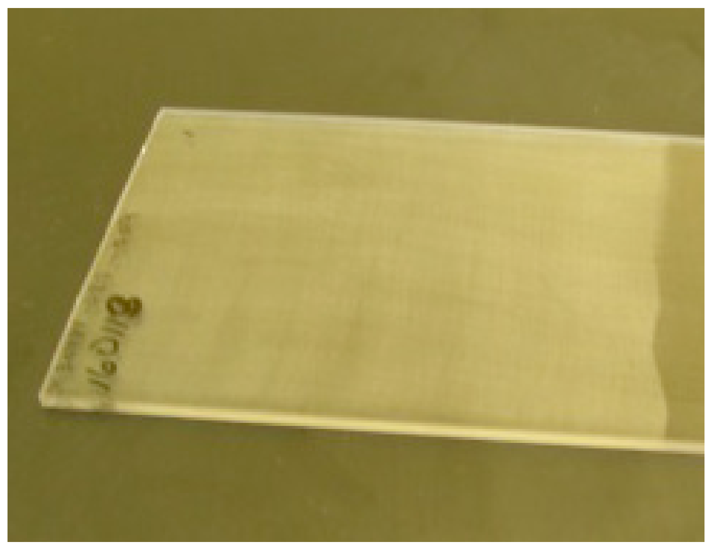


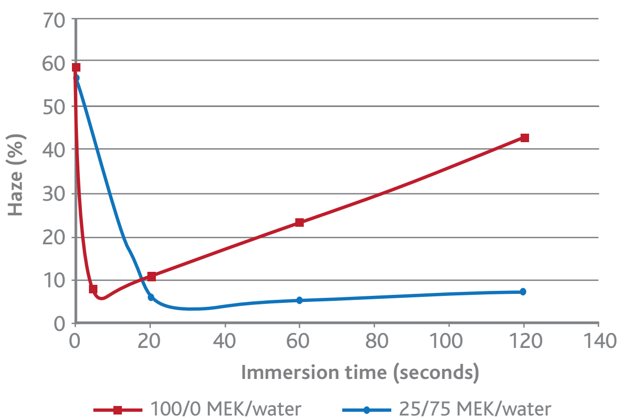
Figure 4 represents a sample of extruded Spectar sheet that has been scratched and then dipped in a 50/50 acetone/water solution for 120 seconds (X30484-084-9). Haze was measured at ~60% on the left side of the sample (scratched surface with no repair) whereas haze was measured at ~7% on the right side which had been dipped in the repair solution. No crazing or regions of crystallization were seen on the samples dipped in the 50/50 acetone/water solution.

Figure 5 shows the effects of MEK and a MEK/water solution on the scratch-induced haze level on Spectar sheet at various immersion times. While immersion in pure MEK (red line) lowered the haze from surface scratching from about 60% to about 5% after a 5-second dip time, haze began to develop from polymer crystallization in a linear relationship with longer dip times. The 25% MEK/75% water solution by volume (blue line) also repaired the scratched surface at all immersion times. The sample that experienced a 120-second exposure showed one small nonhazy crystallized domain and a few crazes at the edge.

Figure 5

Solvent scratch repair on extruded Spectar sheet

Haze (%) versus solvent immersion time



It should be noted that while the solutions containing either acetone or MEK significantly reduced the haze generated by severe scratching, the deep scratches were not completely removed. This conclusion is both visually perceptible and evident since the repaired surfaces showed a haze level as low as about 5% whereas nonscratched 0.118-inch Spectar sheet typically records a haze level around 1%. Additional scratch repair experimentation using 3-micron paper indicated that complete scratch repair is possible. For situations where deep scratches need to be repaired, it may be necessary to employ a series of buffing/sanding steps with sandpaper of various grit levels.

It should be noted that this study was conducted on flat, extruded, nonstressed Spectar sheet. This testing configuration is applicable for most installations using decorative EILT-type laminates and for some Visual Merchandising displays. However, caution should be taken when attempting to remove scratches from articles that contain sheet stress from thermoforming, cold bending, or similar fabrication operations. Residual stress in the sheet combined with chemical attack during the solvent repair process may exceed the critical strain value for a particular solution which could result in crazing, cracking, and part failure. Additional studies are needed, but it is surmised that the least aggressive solutions should therefore be used to repair surface scratches to avoid part failure from exceeding the critical strain.

Predicting solution repairability characteristics

The solvent dilutions with water discussed previously may lead to the presumption that the solvating ability of a solution may be predicted by averaging the individual component solubility parameters. The Hildebrand solubility parameters are often used and are shown as the following for this experimental work.

Table 1

Hildebrand solubility parameters

Substance	δ ($cal^{1/2}cm^{3/2}$)[a]	δ ($cal^{1/2}cm^{3/2}$)[b]
Acetone	9.77	
MEK	9.27	
Water	23.5	
PET	10.1	11.54
PETG		11.16

[a]*Burke, J.;* Solubility Parameters: Theory and Application; *AIC Book and Paper Group Annual, Volume 3, 1984, pp. 13–58. http://sul-server-2.stanford.edu/byauth/burke/solpar/*

[b]*Hale, W. R.;* Thermodynamics of Polymer Blends—An Overview of Topics and Some New Applications: Tools for Predicting Miscibility; *Eastman technical report #TR-2002-02481*

The solubility parameters from reference 3 in Table 1 were calculated using Coleman's group contribution method and are approximately equivalent to the Hildebrand values.[2] Noting that Table 1 shows acetone has a solubility parameter closer to Spectar than MEK, yet recalling that Figures 1 and 5 show nondiluted MEK attacked Spectar much more aggressively than nondiluted acetone, it is concluded that any predictions for solution surface repairability must involve factors beyond just solubility parameters. This result is not totally unexpected as Hansen explained that " . . . ethanol and nitromethane . . . have similar Hildebrand solubility parameters . . . but their affinities are quite different. Ethanol is soluble in water, while nitromethane is not."[3] The broader topic may involve the diffusivity of the solvent in Spectar since this factor is affected by multiple components such as molecular affinities, hydrodynamic volume, and the like. The mechanisms affecting surface repairability are beyond the scope of this report, but it should be noted that the subject is complex and results will therefore be difficult to predict.

[2]*Hale, W. R.; conference call held on September 17, 2008.*
[3]*Williams, L. L.;* Removal of Polymer Coating with Supercritical Carbon Dioxide*; PhD Dissertation, Department of Mechanical Engineering, Colorado State University, 2001, pp. 4–57.*
http://www.scrub.lanl.gov/2002/scf/pubs/scf_williams.htm

Conclusion

This study demonstrated that scratch-induced haze on the surface of extruded sheet of Eastman Spectar™ copolyester can be significantly reduced when the article is immersed in various solutions. Solutions using pure acetone and acetone diluted with up to 50% water by volume decreased scratch-induced haze from about 60% to about 10% for immersion times of 20 to 120 seconds. However, only the 50% acetone solution left the samples undamaged from slight crazing and crystallization. MEK also repaired the scratched surface at a dip time of 5 seconds, but longer residence times led to unacceptable crystallization-induced haze. MEK diluted with 75% water by volume significantly reduced the level of haze at all immersion times but slight crazing developed at the 120-second exposure. Based on these results, a 50% acetone/50% water solution by volume is preferred for surface scratch repair but 25% MEK in 75% water will also achieve comparable results up to a 60-second exposure.

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