COLORING OF POLYESTERS

Richard L. Abrams. PhD
Ferro Corporation, Independence, OH

Abstract

The paper describes various advantages of means of coloring polyester plastics. The three methods examined are: Liquid Color, a proprietary no-dry carrier, and conventional polyester as a carrier. There are investigations on the effect of each system on color uniformity, lubricity, and other characteristics.

Paper

Polyester resins are condensation polymers, formed by the reaction of an organic diol and a dicarboxylic acid. The most common is Poly (ethylene terephthalate) (PET), a reaction product of terephthalic acid and ethylene glycol (Figure I). A hydrogen from the carboxylic acid combines with the OH from the alcohol to produce a water molecule, and an ester linkage forms.

PET is a very popular resin, because of its versatility. The most familiar PET product is the common plastic bottle, the kind used for carbonated beverages, some alcoholic beverages, and toiletries. The recycling symbol is 2; it and HDPE are the most commonly recycled resins. PET is also very common as a fiber - in tire cord, carpets, upholstery, and draperies. PET is the usual polyester fiber used in clothing. It is mixed with cotton fiber in underwear, provides the luster in some neckties. Yes, it was also the fabric of the notorious leisure suit of the sixties.

PET is a very stable polymer and can be in contact with water for long periods without ill effect - therefore its use in water and soda bottles. At processing temperatures, however, the reverse of the reaction that formed the polymer takes place. Water reacts with the ester linkage to split the bond, leaving an acid and an alcohol group - and two much shorter polymer chains. PET exists in amorphous and crystalline phases. Crystals form more readily in lower molecular weight resin, and crystals produce a hazy, sometimes even pearlescent effect. Short polymer chains from water degradation compromise clarity. They also reduce product strength properties. Tensile strength, burst resistance

PET readily absorbs small amounts of water, although its water permeability is low. Very small amounts of water have some drastic effects on the molecular weight of the polymer in processing. The resin has an equilibrium percentage of 0.3 to 0.35% water if stored at 50% relative humidity, compared to the desired 0.005%. With 0.15% water, a resin with an initial IV of 1.00 can drop to about .35 IV, not really a practical working resin.

Consequently, the resin must be very carefully dried before it is extruded or molded. The low water permeability also means that the drying process can be long and time-consuming. An eight-hour drying cycle is not unusual. The drying requires desiccated air (-40^{o} dew point) and high temperatures (300^{o} F, 150^{o} C). The goal is to have less than 0.005% water present. Any more can affect clarity and physical properties.

Low molecular weight esters can also degrade polyester films, through the process of transesterification. The polymer molecule is split into two molecules, one reacted with the acid group of the smaller ester, and one molecule reacted with the alcohol group.

Key temperatures in the processing of PET are its melt temperature of 260^{o} C and its glass transition temperature of 73^{o} C. The usual way of expressing the molecular weight is "intrinsinsic viscosity" or IV. This is a type of solution viscosity measurement, which increases with increasing molecular weight. Most commercial grades of PET have IV's between about 0.7 to about 1.05. The 0.7 IV is mostly considered a bottle grade, while the higher IV is used for film and fiber extrusion. Most PET grades are approved for food contact; 21 CFR 177.1630 is the applicable regulation for the resin. If the application is to be for food contact, all components of the final product must meet food contact regulations, or be proven to be nonmigratory.

Coloring of polyesters is a delicate process, since pigments may carry significant amounts of water. PET manufacturers often color bottle resins in the reactor as it is made, avoiding the water problem. Because of the limited availability of colors in PET resins and the variable pricing of colored PET, it is often necessary to color PET using raw pigment or color concentrates.

Raw pigment typically has a large surface area and considerable adsorbed water. Inorganic pigments may also have water of hydration in their crystal structures, so raw pigments must be dried very carefully before use. There is also a danger with raw pigment of poor dispersion and uneven coloration. Cleanliness is a further consideration, since pigment may become airborne and spread contamination. The cleanup between colors is very difficult; pigment lodges in very small spaces and can show up even late into the next run.

Color concentrates are used to solve the problems of raw pigment. Color concentrates are dispersions of color in a compatible carrier. They are designed so that, when added to a natural resin in a set proportion, they color the resin evenly to match the desired color. The color may consist of mixtures of pigments, which are particles of insoluble colored material, in the resin. For PET, there are also several polymer-soluble dyes that are suitable - alone or in combination with pigments.

Choice of carrier resin is important in the design of a color concentrate. The carrier must be chemically compatible with the PET, and able to wet out the pigment or dye crystals. It must be able to distribute easily throughout the product, and not break down at processing temperatures. Just as important - it must not contribute to chemical breakdown of the resin. It must not contain significant amounts of water, or lower molecular weight esters.

Conventional PET can be used as a carrier. Solid concentrates are usually extruded in cylindrical strands and cut into 1/8" sections. These can be blended into natural resin at a given letdown ratio for coloring the product. Letdown ratios of 25:1 (about 4%) or more are necessary to achieve even coloration. The color concentrate must be blended beforehand with the natural resin and dried with it. As you can see from Figure II, it is a real problem for a single pellet to mix evenly after melting to color all the other pellets, even if distribution of the color pellets in the natural is perfect. At 200:1, the problem is evenmore difficult. PET concentrate absorbs water on storage, and can degrade performance of the colored resin if the drying is not done.

Alternatively, other carriers can be used, as long as they are compatible with PET resins. These carriers can be hydrophobic, that is, have little affinity for water. If the carrier does not pick up water on storage, there is no need for pre-drying These concentrates can be metered in at the throat of the molder or extruder during the run. There is no need to pre-blend the color, so large blenders are unnecessary. Color changes can be quicker, and resin is not committed to a given color before the actual processing.   There is no danger of blending more color than is necessary, or needing to make a small batch to finish a run.

Two carriers which are available are a liquid color, where the carrier is a liquid at room temperature, and a low-melting waxy “no-dry” carrier. Since both carriers are liquids in the mixing section of an extrusion screw, and melt readily in an injection molder, the concentrates made from these carriers spread evenly over the natural pellet surfaces before the melting of the natural. This gives mixing a “head start,” allowing better mixing at low letdown ratios. The liquid and no-dry carriers, and conventional PET will be compared in a molding study, without drying,, at various letdown ratios. We will use a polymer-soluble dye, Solvent Red 135, as the colorant. Performance will be measured by color consistency and strength, and IV of the finished product. Back pressure and shot weight will be used to measure lubricating properties of the various carriers. The experimental trials have not been run at the time of this writing, but will be reported at the presentation of this paper.

Expectations are that the liquid and no-dry carrier will perform better at 100:1 and 200:1 letdowns (1% and 0.5%) - giving good color consistency. At 12.5:1 (8%), these carriers are expected to give some problems because of their lubricity.

The writer wishes to thank Robert Opalko and Dr. Stephen Jolly for their assistance. Some data were derived from Shell Chemical Company product literature.

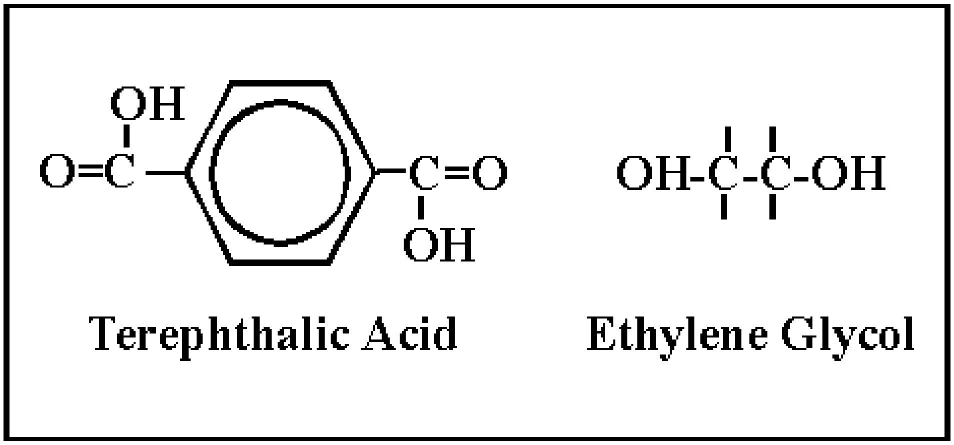

Figure I. Monomers Used in PET

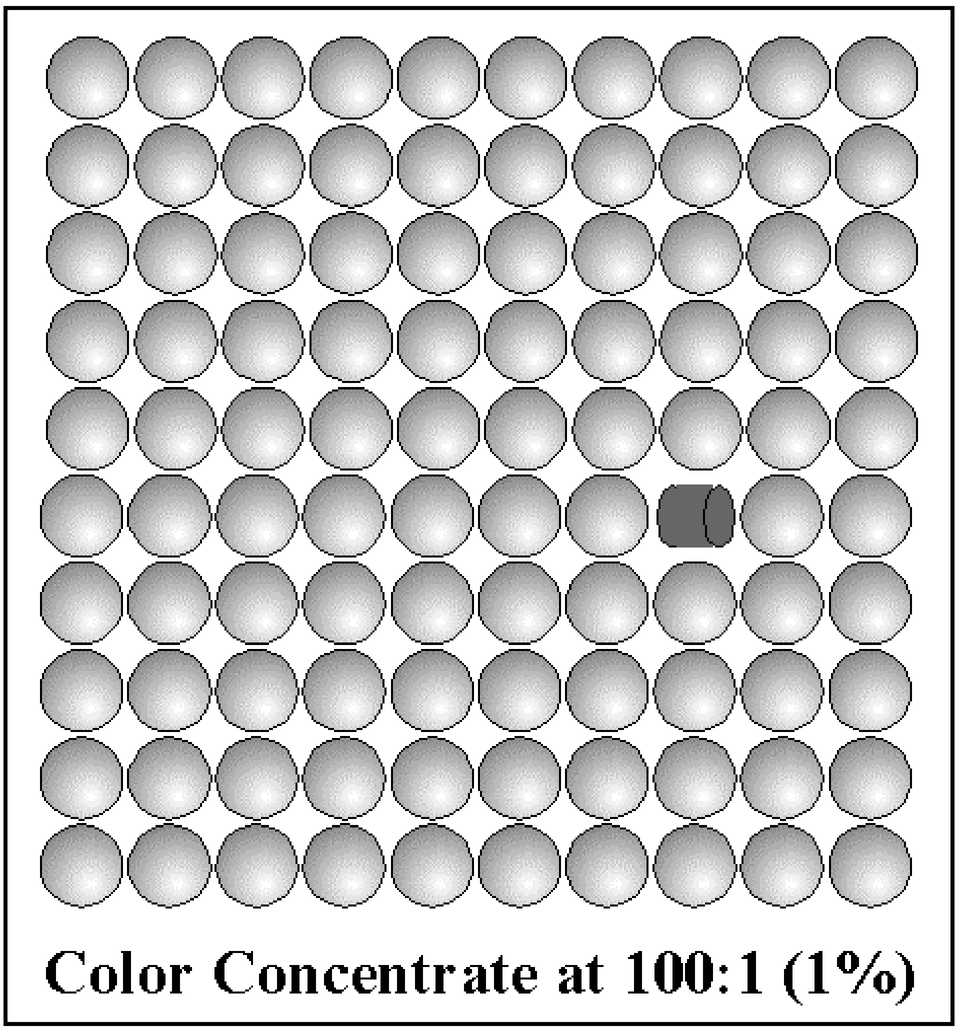

Figure II