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The Morphology of Suspension Polyvinyl Chloride

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ABSTRACT

A literature survey is presented on the relationship between the plasticizer absorption capacity and "fish-eyes" content of suspension polyvinyl chloride resin and polymerization conditions (suspending agent, agitation, extent of reaction, etc.) and the resulting resin morphology.

Among the properties required of a good polyvinyl chloride (PVC) resin are a good capacity for plasticizer absorption and a low "fish-eyes" content. The patent literature contains many recipes for producing PVC resin of good quality, but very little basic research has been done on suspension polymerization; in particular, on the suspension polymerization of vinyl chloride. The objective of this review is to summarize the present state of knowledge on the morphology of the suspension PVC grain and its relationship to the properties of the resin.

It is well known that the mode of agitation and composition of the suspending agent are critical in determining the properties of the resin, but these topics are proprietary secret "know-how" of PVC producers, and very few details can be found in the scientific literature. Thus it has been reported that, under laboratory conditions, fish-eyes content decreases with increasing rate of agitation of the suspension, other parameters (concentration and composition of monomer, initiator, suspending agent, etc.) being equal [1]. This shows that fish-eyes are caused not only by impurities such as resin of different molecular weight and foreign materials [2], but that fish-eyes are also formed by resins produced under meticulously clean conditions. The influence of the composition of the suspending agent on resin properties was investigated by Benetta and Cinque [3], who studied the effect of the "hydrophylic-liophylic balance" on the suspending agent, which in their case was a mixture of polymeric substances and nonionic soaps. They established a relationship between the ability of a suspending agent to raise the plasticizer absorption capacity of the resulting resin and a decrease in interfacial tension between water and trichloroethylene (used as a model substance for the gaseous vinyl chloride) caused by the suspending agent. Hence the larger the initial degree of dispersion of the monomer in water and the smaller the initial droplets, the larger the porosity and plasticizer absorption capacity of the resulting resin.

A remarkable property of PVC is that it is completely insoluble in its own monomer. Monomer sealed into a Carius tube together with a suitable polymerization initiator turns turbid after a short time due to precipitating polymer. Bort et al. [4] have shown by electron microscopy that the precipitating polymer consists of spherical particles with a diameter of the order of magnitude of 1 μ. The number of particles does not change during the progress of polymerization, only the size of the particles increases. Each particle consists of a number of microglobules. The higher the temperature of reaction or the rate of polymerization, the smaller the number of microglobules, so that reactions at high temperature or high speed produce compact material, while, at lower temperatures and with slow reactions, a material of more open structure is obtained. Bort et al. explain their observations with the considerations applied when explaining the structure of precipitate formed from a supersaturated solution upon fast or slow cooling.

The precipitating polymer forms an opaque solid block, and at high degrees of conversion the block becomes more and more transparent and glassy. Electron microscope studies have shown that the opaque material consists of spheres of about 2 μ diameter, with the individual character being distinctly discernable. But no individual particles can be seen in the transparent material—the resin has become "monolithized." Bort et al. believe that such a formation of glassy material also takes place during polymerization in suspension at high degrees of conversion and causes fish-eyes formation. This is in agreement with the postulate of Fukawa and Daimon [5] who concluded from the dependence of resin porosity on the degree of conversion that at high conversion the pores of the grain are filled up with polymer. Their observations were corroborated by those of Lalet et al. [6].

Tregan and Bonnemayre [7] applied electron microscopy to suspension PVC. They concluded from their studies that at the beginning of polymerization the monomer is dispersed in water as droplets of 100 to 200 μ diameter. All the phenomena observed by Bort et al. occurring in bulk polymerization occur in each of these droplets, so that solid polymer separates in each droplet, and glassy material forms at high conversion. In addition, there are processes particular to the fact that the monomer is suspended in water. The most important one is that during the first stages of polymerization the water-soluble suspending agent is transformed into a spherical rigid layer somewhat beneath the surface of the droplet, and the thickness of the layer is of about 100 Å. This change seems to be caused by grafting of monomer on the suspending agent. Tregan and Bonnemayre could isolate this layer by selective dissolution, and they studied it by electron microscopy. (The assumption that the suspending agent becomes immobilized in the PVC resin is corroborated by the observation [8] that the surface of a PVC resin prepared with poly(vinyl alcohol) as the suspending agent turns blue upon addition of a H_3BO_3-I_2 solution, while the color of the supernatant liquid remains brown. The observation shows that, whereas the polyvinyl alcohol entrapped in the PVC can react with H_3BO_3-I_2, it cannot pass into aqueous solution.)

During the progress of polymerization, depending on the intensity of agitation and nature of the suspending agent, the rigid shell is occasionally broken. The cell contracts after spilling the monomer, and combines with other deflated cells to agglomerates. On the other hand, the spilled monomer is encased by some unconsumed suspending agent from which another rigid sphere is eventually formed. The extent of the processes of shell rupture and of agglomeration decides whether the resulting resin is rather "unicellular," of a compact, nonporous structure with low plasticizer absorption capacity; or "pluricellular," of an open, porous structure with a good plasticizer absorption capacity. In a "unicellular" resin the glassy particles are macroscopic and hence noticable, while in a "pluricellular" resin they are microscopic so that, from the practical point of view, a "pluricellular" resin is free of fish-eyes.

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