Detection of Polymerization Adjuncts by Diphenylamine

The object of the present investigation is to find a method for detecting small amounts of methyl cellulose in poly(vinyl chloride) resins, such as those present as residual suspending agent. The Dische method[1] has been adapted for the colorimetric determination of methylcellulose[2] at concentrations of 10 ppm. It should thus be a very sensitive color[2] test.

Vinyl chloride was suspension polymerized in our laboratory, using methyl cellulose (Methocel produced by Dow) as suspension agent. Dried polymer, 100 g, was boiled with 200 g water for 1 hr; then the slurry was filtered and the filtrate dried at 80°C. The residue (about 1 mg) was treated with 10 cc reagent (3.75 g diphenylamine, 150 cc glacial acetic acid, and 90 cc concentrated HCl), and refluxed for 30 min. A light-blue color developed. When, however, 1 g of *dry* polymer resin was treated directly with 5 cc reagent and the mixture heated, a much more intense dark-blue color developed in a much shorter time. Hence the direct addition of the reagent to the *dry* resin constitutes a much more sensitive test for methylcellulose.

When reagent was added, and dry PVC was polymerized with poly(vinyl alcohol) (Mowiol from Heochst) or with poly(vinyl pyrrolidone) (from G.A.F.) and the mixture refluxed, only a faint reddish-violet color developed. A dark-blue color developed when the above test was performed on powder of ethylcellulose, filter paper, and, surprisingly, dry gelatin. A light-violet color was formed by the action of the reagent on dry poly(vinyl alcohol), poly(vinyl pyrrolidone), and glyceryl monostearate, and a yellow color by action on a copolymer methyl vinyl ether and maleic anhydride (Gantrez AN. 119). The action on sorbitan monostearate (Span-40 from Atlas), and even on a very pure sample of sorbitan, produced the same dark-blue color as with methylcellulose. This observation, which does not agree with the opinion[3] that the blue color is formed only in polyols containing on aldehyde group, cannot be studied further within the scope of the present investigation. (Glycerin forms no color with the reagent.) A blue color was formed by the action on PVC resin, which contained no methylcellulose but into which some sorbitan monostearate had been worked before dryng.

Thus the presence of traces of carbohydrates, sorbitan derivatives, or gelatin can be rapidly determined by warming dry resin with the Dische reagent. (Erroneous conclusions may be drawn in the presence of nitrates.) Indeed, when commercial PVC samples of various origin were examined by this method, some produced the dark-blue color, some the light violet, and some, the yellow.

References

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Received April, 1972