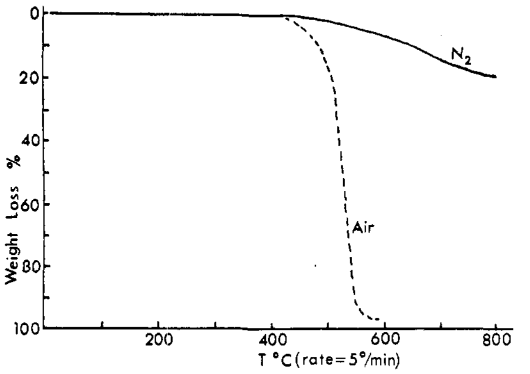

Figure 1.

This poly(p-phenylene) was extremely difficult to burn in order to obtain an elemental analysis; however, the lower limit of molecular weight by carbon analysis is an undecaphenyl, $n = 2$. (*Anal.* Calcd for **6**, $n = 2$: C, 91.59. Found: C, 91.20.) The infrared spectrum showed only a very weak carbonyl absorption (pyrone and/or carboxylic acid) and a strong C–H out-of-plane deformation characteristic of the p-phenylene moiety at 800 cm^{-1}. It has been claimed[6] that an increasing degree of para phenylation leads to a shift of this frequency to lower wavelengths,[29] and for this reason the polyphenyls prepared from 1,3-cyclohexadiene (811 cm^{-1}) have lower molecular weights than those prepared by benzene polymerization (802–807 cm^{-1}). If this interpretation is correct, the p-polyphenylenes prepared by this 1,4 cycloaddition have the highest molecular weight.

Poly(p-phenylene) (**6**) was insoluble in all solvents and was crystalline, showing d spacings characteristic of p-quaterphenyl and poly(p-phenylene) obtained from 1,3-cyclohexadiene and benzene (Table I).

By contrast to those poly(p-phenylenes) prepared by other methods, the polymer **6**, obtained from the 1,4 cycloaddition, was yellow with $\lambda_{\max(\mathrm{refl})} = 340$ nm, more in agreement with the theroetical value.[17–21]

Finally, we observed that whereas the phenylated polyphenylenes (**1**) had a break in the tga at 550° in air and decomposed rapidly, they lost about 30–35% of their weight rather sharply under a nitrogen atmosphere at about 550°; we had attributed this to the loss of some of the pendant phenyl groups.[1] The tga analysis of poly(p-phenylene) (Figure 1) reinforces this interpretation in that although a similar decomposition (tga ~ 500°) of **6** in air is observed, under nitrogen, **6** loses 10% of its weight at 650° and only 20% at 800°.

Thus, poly(p-phenylene) is indeed a highly crystalline, insoluble, thermally stable polymer, but is not highly colored.

Acknowledgment. This research was supported in part by the U. S. Army Research Office, Durham, N. C. The authors wish to acknowledge the assistance of Mr. L. Stoel in obtaining the reflectance spectra, Dr. N. C. Baenziger for the X-ray data, Mr. L. Mathias for the tga, and Mr. G. K. Noren for assistance.

---

(29) p-Quaterphenyl, p-pentaphenyl, and p-sexiphenyl show bands at 825, 818, and 812 cm^{-1}, respectively.

J. K. Stille,* Y. Gilliams
Department of Chemistry, University of Iowa
Iowa City, Iowa 52240

Received January 8, 1971

Electron Microscopy of Poly(vinyl chloride) and Ethylene–Vinyl Acetate Rubber Systems

Commercially available rubber-modified plastics such as ABS polymers generally contain unsaturated rubbers. Attempts to utilize saturated rubbers for obtaining better weatherability characteristics have been conducted in many laboratories. One of the interesting systems is a graft copolymer composed of poly(vinyl chloride) (PVC) and ethylene–vinyl acetate rubber (EVAc).

For the electron microscopic observation of the micromorphology of rubber-modified plastics having unsaturated rubbers, Kato's osmium tetroxide (OsO_4) procedure[1] has been effective. However, this technique is not applicable to the PVC–EVAc system, because neither the PVC nor the EVAc phase is susceptible to the staining agent, OsO_4.

In the present study attempts have been made to overcome this staining difficulty of PVC–EVAc systems by introducing an additional treatment before the application of Kato's method.

Materials. The PVC and EVAc used in the present study were Geon 103EP8 (DP ≈ 800) manufactured by the Japanese Geon Co. and Levaplene-450 supplied by Fabenfabriken Bayer AG. PVC–EVAc systems were prepared by blending and grafting. The blending was carried out by milling a mixture of a formulated PVC powder and EVAc pellets on an 8-in. open roll at 155° for 6 min. Then the resulting 1-mm thick sheets were compression molded at 160°. The grafts, on the other hand, were prepared by dissolving EVAc in vinyl chloride monomer, followed by normal suspension polymerization of the monomer. The composition of PVC–EVAc was varied from 5/95 to 90/10 for the blends and from 5/95 to 50/50 for the grafts.

EVAc Staining Procedure. A specimen block with suitable dimensions for ultramicrotomy was placed in methanol saturated with sodium hydroxide. The solution was heated to boiling and refluxed for 1–2 hr. The specimen was then taken out, washed with water, and dried. The procedure employed thereafter was the same as Kato's method: the specimen was exposed to OsO_4 vapor for about a week and subjected to ultrathin sectioning.

By the treatment mentioned above, it is believed that the acetate groups in the EVAc near the specimen surface were saponified to hydroxy groups, as evidenced by complete disappearance of the C=O band (~1725 cm^{-1}) and an increased intensity of the OH band (~3300 cm^{-1}) in the atr infrared trace (Figure 1). Hydroxyl groups are capable of

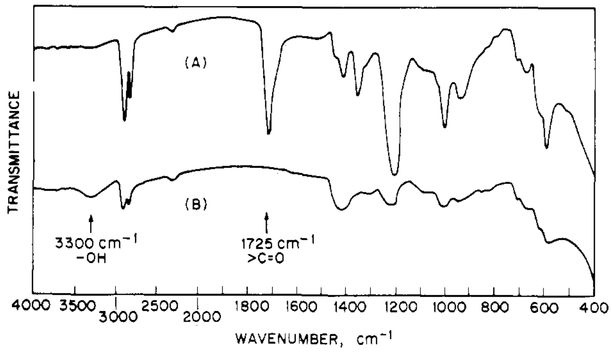

Figure 1. Atr infrared spectra of a PVC–EVAc = 70/30 graft system before (top) and after (bottom) treatment with methanol saturated with sodium hydroxide.

---

(1) K. Kato, *J. Polym. Sci., Part B*, **4**, 35 (1966).

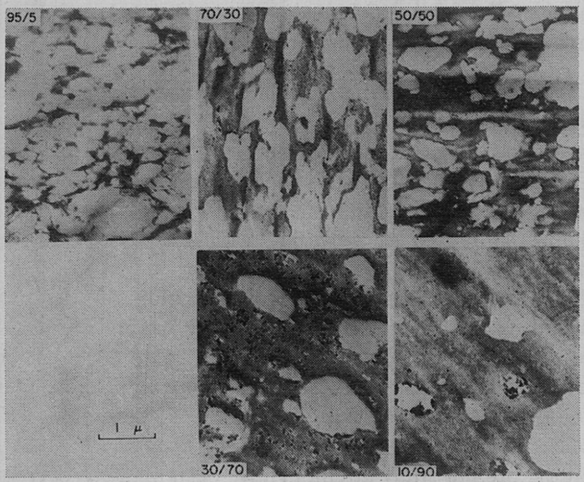

Figure 2. Electron micrographs of ultrathin sections of PVC–EVAc blends. The numbers in the pictures indicate PVC/EVAc ratios by weight.

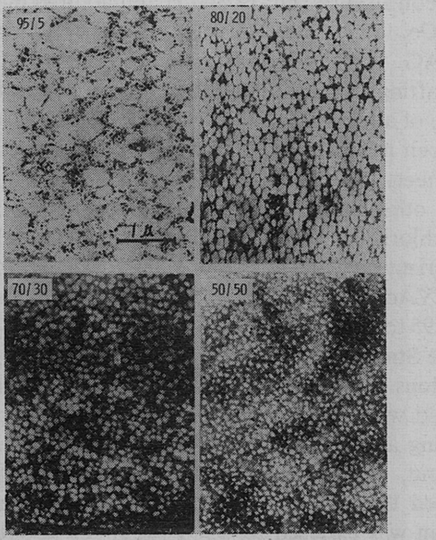

Figure 3. Electron micrographs of ultrathin sections of PVC–EVAc graft copolymers. The numbers indicate PVC/EVAc ratios by weight.

reacting with OsO_4 because polymers containing OH groups such as poly(vinyl alcohol) are known to be susceptible to staining with OsO_4.[2] Curve B is more diffuse than curve A in Figure 1 presumably because light scattering may have occurred at the surface of the former specimen due to surface roughness which developed during the treatment described above.

Figure 2 shows the electron micrographs of ultrathin sections of PVC–EVAc blends with varying EVAc contents. It is apparent that the proportion of dark phase increases with the increase in EVAc content, indicating that the EVAc phase is selectively stained by OsO_4. In the sample containing 5% EVAc, the EVAc phase forms a network which separates the PVC matrix into particles about 1 μ in diameter. This pattern is very similar to that of the blend of PVC and acrylonitrile–butadiene rubber containing 20% acrylonitrile, which was classified as a semicompatible blend in a previous paper.[3] It is interesting to note that PVC particles of *ca.* 1 μ diameter still exist in the samples containing much higher percentages of EVAc. This result clearly indicates that the original particle structure of PVC powder[4] was not destroyed by milling. It is also important to point out that extremely fine bright spots appear in the dark phase, particularly in the samples containing 30 and 90% EVAc. It is possible, therefore, that the EVAc phase is contaminated with PVC to some extent.

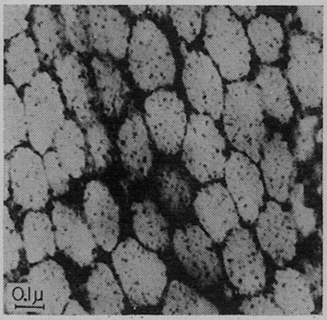

Figure 4. Magnified picture of a portion of Figure 3 (PVC/EVAc = 80/20), indicating that the EVAc phase disperses in the PVC phase in a radial direction from the center of the PVC phase.

The graft systems, on the other hand, exhibited different structures, as shown in Figure 3. In the sample containing 5% EVAc, the structure is very similar to that of the blend, except that the PVC particles are a little smaller. However, as the EVAc content increases from 5 to 50%, the size of PVC particles or, in other words, the mesh of the EVAc network decreases from 0.5 to 0.05 μ. The structure of the sample containing 50% EVAc can be described as an EVAc matrix containing dispersed PVC particles of *ca.* 0.05-μ diameter. It is interesting to note that in the 20% EVAc sample, the dark EVAc phase aligns in a radial direction from the center of the PVC (Figure 4). The origin of this alignment is not known. Further studies especially on the dynamic mechanical and tensile properties are being carried out.

---

(2) K. Kato, private communication

(3) M. Matsuo, C. Nozaki, and Y. Jyo, *Polym. Eng. Sci.*, **9**, 197 (1969).

(4) D. N. Bort, E. E. Rylov, N. A. Okladnov, B. P. Shtarkman, and V. A. Karign, *Vysokomol. Soedin.*, **7**, 50 (1965).

* Address correspondence to this author at Bell Laboratories, Murray Hill, N. J. 07974.

Y. Jyo, C. Nozaki, M. Matsuo*
The Japanese Geon Company, Ltd.
Central Research Laboratory
1-2-1 Yako, Kawasaki, Japan

Received April 27 1971