

Electron Microscope Observation of Microtexture and Craze Formation of Acrylonitrile-EPT-Styrene Copolymer

Microtextures of various rubber-plastic copolymer systems have been observed by electron microscopy using the Kato's osmium tetroxide staining method.¹ Most of them contain polybutadiene or polyisoprene unit as rubber component.¹⁻⁴ By the reaction with osmium tetroxide, the rubber component becomes hard enough to be microtomed at room temperature. At the same time, it is stained with the reagent and, as a result, gives excellent contrast in an electron micrograph. It is also possible to see the microtexture of a copolymer system if one component contains —OH, —O—, or —NH₂ groups which react with osmium tetroxide. The applications are seen in a hydrolyzed copolymer of PVC and ethylene-vinyl acetate rubber⁵ and an interpenetrating polymer network of poly(urethane-urea) and polyacrylate.⁵ No observation has been made of the microtexture of a copolymer system whose rubber component is neither hardened nor stained by osmium tetroxide. This note refers to an application of Kato's method to an acrylonitrile-EPT-styrene copolymer (AES) whose rubber component does not react with osmium tetroxide. (EPT means ethylene-propylene terpolymer, which is a kind of synthetic rubber.)

Latex of a commercial EPT (JSR EP 93, Japan Synthetic Rubber Co., Ltd.) was used in order to prepare AES. Detail of the method of preparation and characterization will be reported elsewhere. Briefly, an emulsion of acrylonitrile (AN), styrene (ST), polymerization initiator, and activator was added dropwise to the latex kept at a temperature between 50° and 80°C. Polymerization was stopped after 5 to 6 hr both by lowering the temperature and by adding a termination reagent. About 1 part of EPT in weight was reacted with 4 parts of the monomer mixture of AN and ST. AN and ST are believed to be copolymerized and grafted to EPT particles by this procedure. EPT itself contains about 0.9 mole-% of ethylidene norbornene unit which has one double bond in one unit. Some of the double bonds of EPT are consumed during the graft reaction. Thus, the double bond content in AES is negligible.

A blend sample of AES and ABS (JSR ABS 10, Japan Synthetic Rubber Co., Ltd.) (80/20 in weight) was prepared by using a mixer and a 5-oz injection machine at 230°C. Test pieces of pure AES were also made as the same way. Several hundred angstrom-thick sections of the specimen were obtained at -100°C by using a LKB Ultratome III microtome combined with a LKB Cryokit 14800. This technique enables one to make ultrathin sections of any soft materials which are not hardened by osmium tetroxide. After the ultrathin sections were exposed to osmium tetroxide vapor at room temperature for 12 hr, they were examined on a Hitachi HU-12 electron microscope.

Figure 1 shows a section of AES. White honeycomb structures whose diameter is less than 2 μ are seen in the slightly stained matrix. They make a marked contrast with the well-known texture of ABS or high-impact polystyrene (HIPS)¹⁻⁴ in which honeycomb structures are highly stained with osmium tetroxide. However, their size, shape, and internal structure are very close to those of ABS. The small, dark particles in the figure are carbon black powder which was mixed in for some other purpose.

Figure 2 shows a stained section of the blend. It clearly demonstrates the difference in reactivity of the three phases with osmium tetroxide. Since the double bond content of EPT particles is very small, it will be concluded that the white honeycomb is the EPT phase, the slightly stained background is the matrix phase of the copolymer of AN and ST, and the black honeycomb is the polybutadiene phase which comes from ABS. The diameter of the polybutadiene honeycomb ranges from 0.2 to 1.3 μ , while the EPT honeycomb is larger. Since the specimens were stained for a much longer time than usual, the inner structure of a small polybutadiene particle is almost smeared out in the figure. Polystyrene and/or polyacrylonitrile may be responsible for the slight staining of the matrix phase.

AES resin shows stress-whitening behavior upon deformation and has excellent impact-resistant property. The Izod impact strength of the resin is 80 kg-cm/cm or more at 23°C,⁶ which is about two to four times larger than that of a general purpose-grade ABS. These facts suggest that craze formation may take place upon deformation as is observed in the case of ABS and HIPS.^{2,7,8} In order to investigate it, test pieces of both the blend and the pure AES were bent to generate stress-whitening portions. These portions were microtomed at -100°C, stained, and observed the same way as the above. Figure 3 shows an example of a deformed AES. Well-

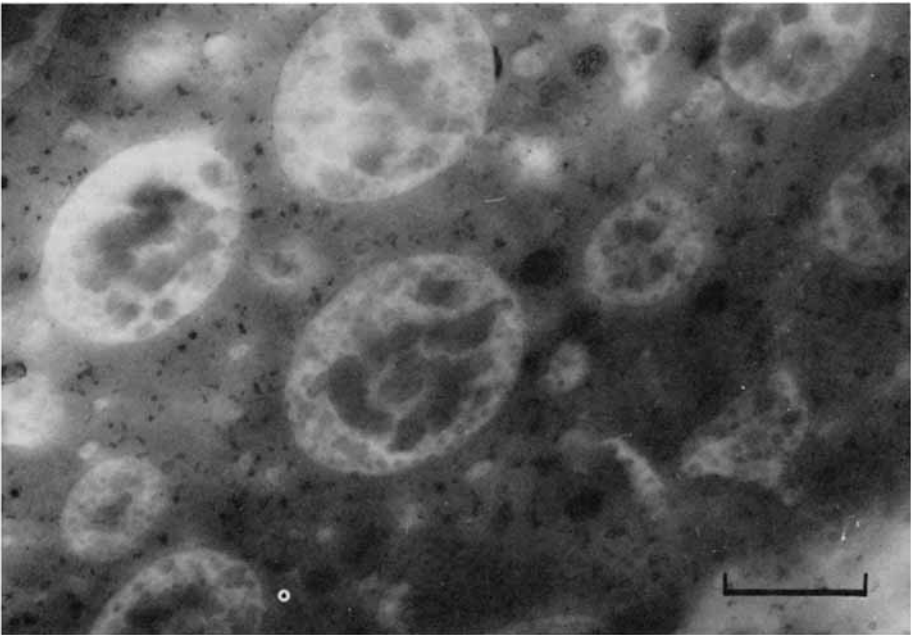


Fig. 1. Electron micrograph of an ultrathin section of AES stained with OsO_4 . All the scale bars represent 1μ .

stained strands whose diameter is about 300 \AA and length about 0.2μ are developing from EPT rubber particles. The feature is very close to the craze in deformed ABS or HIPS.^{2,8} Thus, the strands in Figure 3 may come from craze which is composed of oriented molecules of the copolymer of AN and ST with microvoids. Osmium atom may be adsorbed by the void. The number and the size of the crazes in Figure 3 are smaller than those in published micrographs of de-

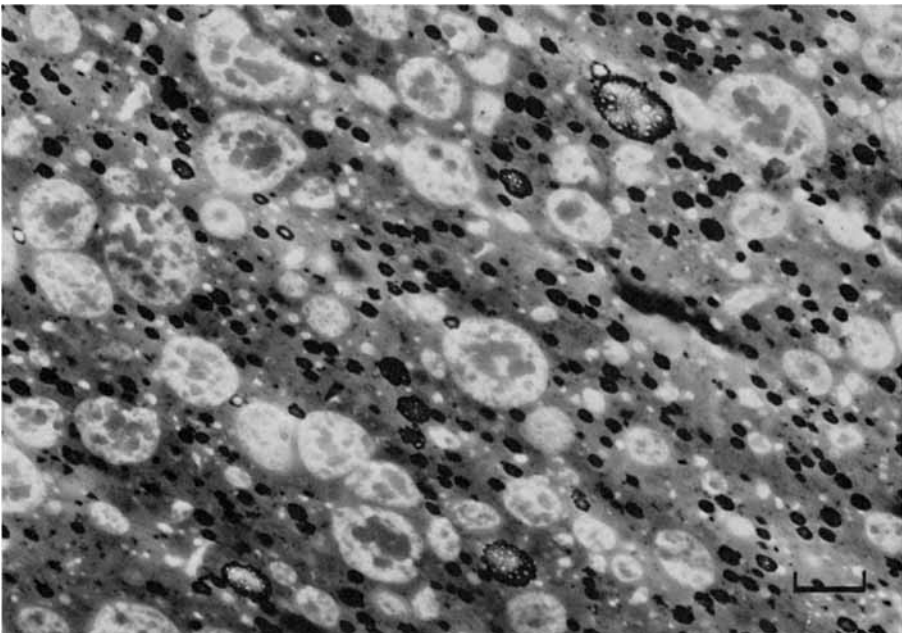


Fig. 2. Electron micrograph of an ultrathin section of AES/ABS blend stained with OsO_4 .

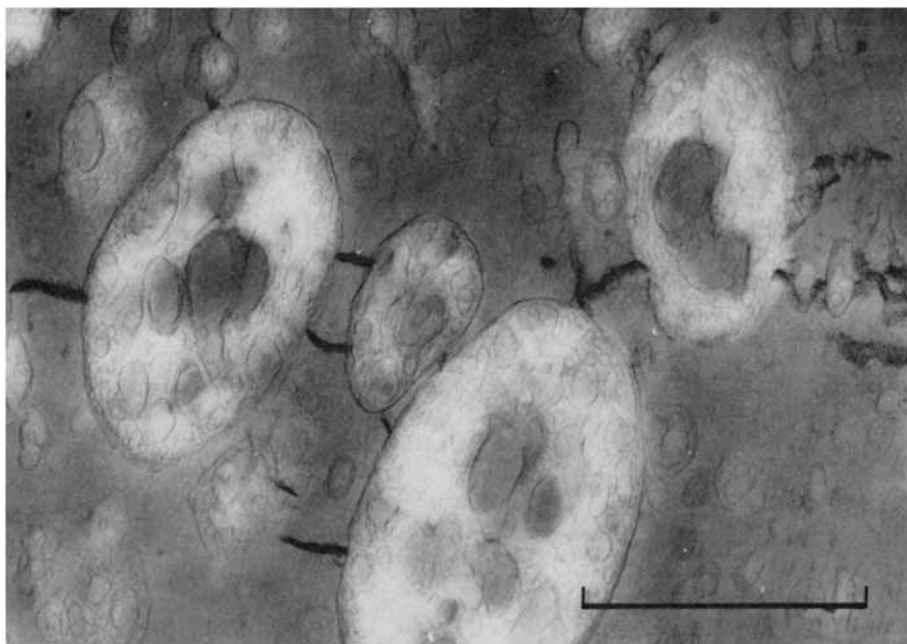


Fig. 3. Electron micrograph of an ultrathin section of deformed AES stained with OsO_4 .

formed ABS and HIPS.^{2,8} This may be simply attributed to the lesser amount of the deformation of the test pieces in this study.

Figure 4 shows a stained section of a deformed blend. The amount of the deformation is similar to the above. Crazes are generated from both EPT and polybutadiene particles. The particles are elongated along the direction of the bulk deformation. The direction of the craze devel-

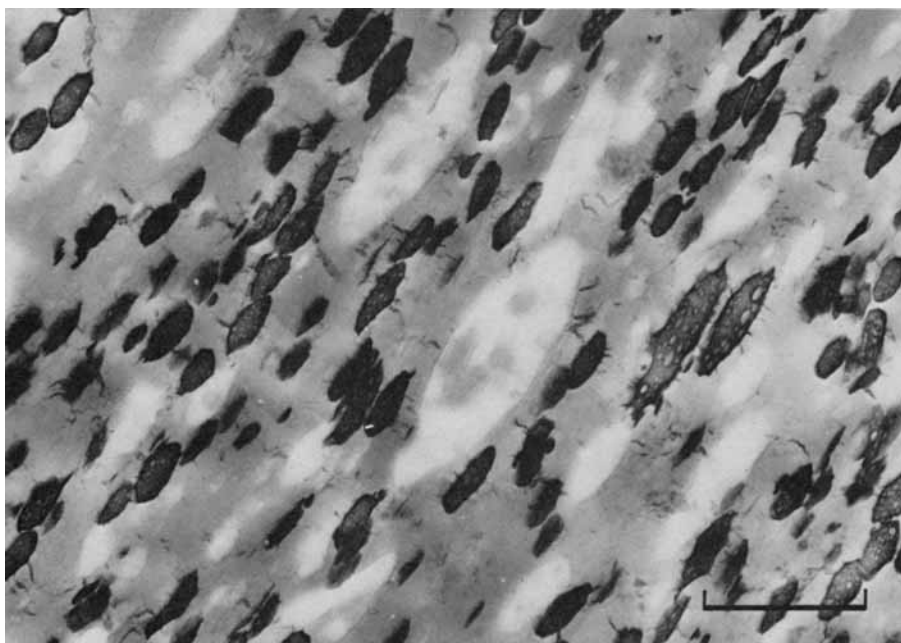


Fig. 4. Electron micrograph of an ultrathin section of deformed AES/ABS blend stained with OsO_4 .

opment is normal to it. There seems no significant difference in the ability of craze formation between ABS and AES. Thus, the tough property of AES can be elucidated by craze formation upon deformation.

In conclusion, a honeycomb structure was observed in AES resin by an osmium tetroxide "negative" staining method, in which EPT rubber particle is not stained and the matrix is slightly stained. The high-impact property of AES was attributed to generation of crazes upon deformation.

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