A method for examining rubber particles from impact polystyrene

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INTRODUCTION

Rubber particle morphology of impact polystyrene (IPS) and ABS polymers is customarily determined by examining ultra-thin cross-sections by phase contrast or transmission electron microscopy (*TEM*). The general outline and the internal features of the rubber particles can be readily studied by *TEM* of stained sections[1]. No relatively simple technique has been available for the examination of the external features of the rubber particles.

This work describes a simple new technique and points out some of its applications for the examination of the
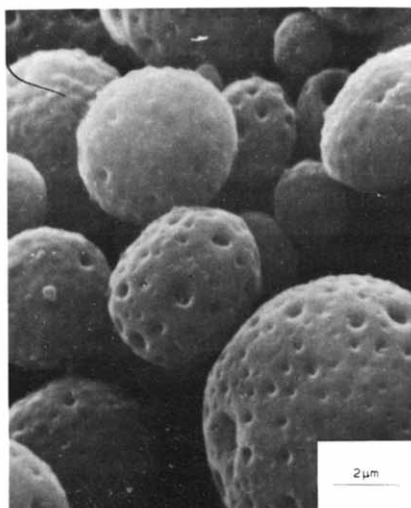

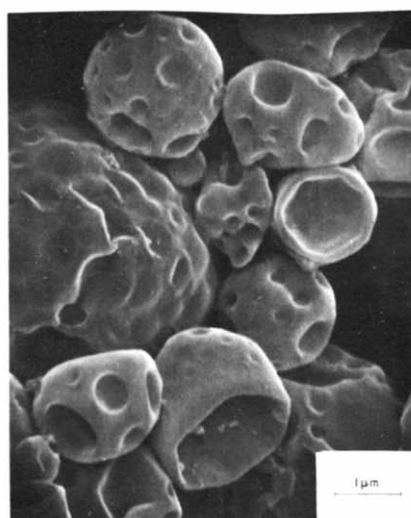*Figure 1* Rubber particles from IPS, separated from methylene chloride

Figure 2 Rubber particles exposed to toluene for 48 h

topography of the rubber particles from IPS.

EXPERIMENTAL

A small piece of polymer, usually a moulding granule, (about 0.02 g) is used for this procedure. It is brought into contact with a 1% OsO_4 solution in cyclohexane (for IPS) in a vial which is placed on a steam-bath and occasionally shaken to effect the matrix polymer solution. The supernatant polystyrene (PS) solution is separated from the hardened particles by decantation after a mild centrifuging. The particles are twice washed with fresh cyclohexane. The effectiveness of this wash is increased by placing the dispersion in an ultrasonic bath to assure a thorough separation of the particles. Finally, this washing is repeated twice in isopropanol. In order to obtain sharp surface details of these particles, chemically unattached PS has to be removed completely.

The fixed rubber particles are viewed by scanning electron microscopy (*SEM*) after they are given a conductive coating of carbon and gold—palladium.

DISCUSSION AND RESULTS

The osmium tetroxide solution in cyclohexane is used to accomplish simultaneously the dissolving of the PS matrix and fixing and staining of the complex grafted rubber particles. As the IPS comes into contact with this solution, the penetration of OsO_4 is immediately enhanced by the solvent action of cyclohexane on PS. In this fashion, the fixation of the particles is apparently very quick and effective.

It is important that the contact time with the solvent is kept to a minimum and that a relatively poor solvent for the matrix polymer is chosen, otherwise rubber membranes of the particle are likely to rupture and the removal of free PS from the occlusions may take place.

Figure 1 shows rubber particles separated from an IPS with methylene chloride as a solvent. In only 20 min, significant breaks in the surface occur-
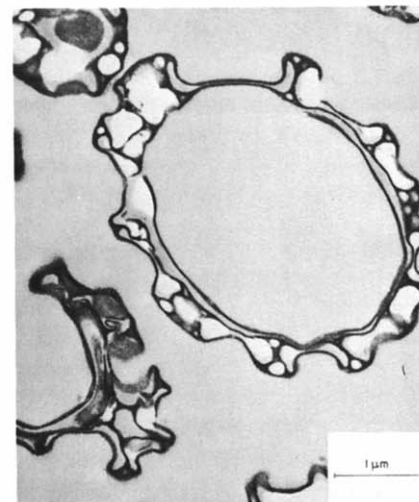

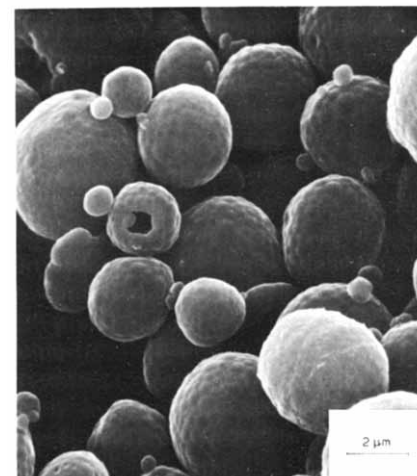*Figure 3* Cross-section of toluene-extracted rubber particle, embedded in epoxy-resin

Figure 4 Rubber particles from IPS—A

red and some free PS was removed from the particles. If the separated particles are kept in contact with toluene for an extended period, large amounts of PS would be removed, as shown in *Figure 2*. This removal of PS is seen more vividly, when these particles are in epoxy resin and ultra-thin sections are viewed by *TEM (Figure 3)*. It is observed in the large central particle of this photomicrograph that while the many outer membranes have been totally collapsed, the central large PS occlusion has maintained its integrity. Some voids are also present without the complete collapse of the membranes.

To illustrate the value of this new technique for the characterization of rubber particle structures in IPS a series of commercial materials were examined by this method, and also by *TEM* for comparison. OsO_4 stained ultra-thin sections were used for the *TEM* work.
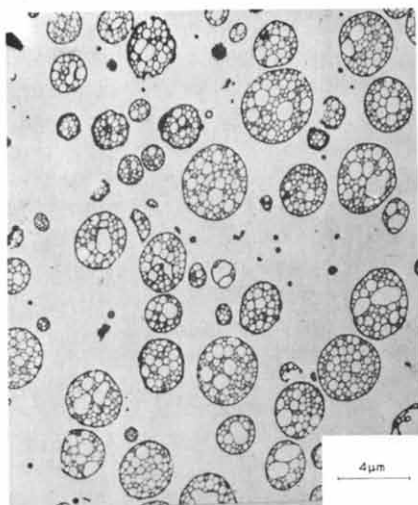
Figure 5 Transmission electron microscopy of IPS—A
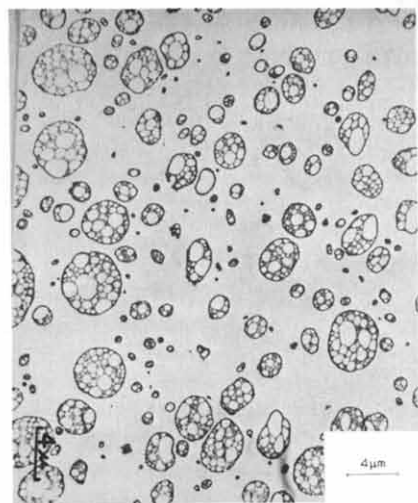

Figure 6 Same as *Figure 4* except IPS—B

Figure 7 Same as *Figure 5* except IPS—B

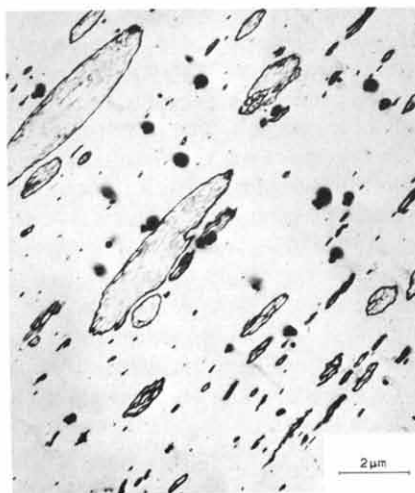Figure 8 Biaxially oriented rubber particles due to vacuum forming

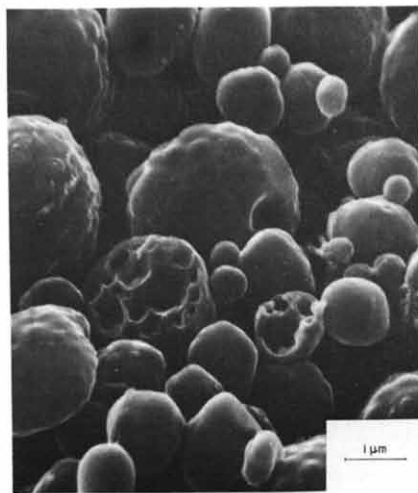Figure 9 Transmission electron microscopy of a vacuum-formed specimen

Figure 10 Rubber particles from a fractured specimen

Following are some examples of the observations made in this approach.

One of these materials, impact polystyrene A (IPS—A) shown in *Figures 4* and *5,* has extra high impact strength. It has a volume-average particle size of 3.1 μm, number-average particle size of 1.3 μm and the gel fraction of 0.42. These data were determined by the Quantimet 720 image analysing system. In *Figure 4,* most of the particles of this material are about 2—3 μm, which is close to the volume-average particle size.

While the details of the surface topography of the rubber particles of this polymer are not easily discernible from *TEM (Figure 5),* the scanning electron microscope technique reveals excellent, three dimensional detail of the grafted particle surface. Comparing IPS—A and IPS—B (*Figures 4* and *6*) the similarities in characteristic surface nodules are readily seen. It is possible that these

regular surface bumps relate to the graft polymer distribution on the particles, or that they develop as a result of the nature of the rubber used.

Considering *Figure 4* further, a doughnut-shaped particle is shown in this picture. Such shapes are not easily recognizable by standard techniques.

Figures 6 and *7,* give another comparison of the techniques. They show IPS—B which has a 1.1 μm number-average diameter, a 3.0 μm volume-average particle diameter, and a 0.31 gel fraction. From *Figure 6* it is apparent that in addition to the characteristic surface of IPS—A, the particles are also unique in that a large number of them are cigar-shaped. Upon examining numerous rubber modified polystyrenes, it was concluded that IPS—B was unique in exhibiting this large number of elliptical particles. Ellipticity of rubber particles cannot be dependably determined from *TEM* photomicro-

graphs, particularly since microtoming is known to cause distortion in some cases.

Apparently with the very quick access of OsO_4 to the rubber particles, its fixation speed is such that very little if any subsequent deformation is possible in the sample preparation work. *Figure 8* shows platelet-shape rubber particles from a vacuum formed article. A comparable *TEM* photomicrograph is shown in *Figure 9.* Here the application is to evaluate rubber particle deformation.

It may be also of interest to examine how the nature of rubber particles varies as a result of deformation and subsequent fracture. For this purpose, a polymer sample from the vicinity of fracture of a whitened stress—strain specimen was examined by this method. In this crazed area, indication of particle fracture and deformation was sought. As seen from *Figure 10,* some

severed particles were detected, while deformed particles were absent. These findings appear consistent with the crazing mechanism of rubber reinforcement[2], where the crazes are initiated by the rubber particles and where the specimen deformation is primarily due to the extension of the crazes. In this fashion, the craze fracture would produce fractured particles but no permanently deformed whole particles. Deformed particles may be expected, however, with polymers, where shear yielding is a predominant mechanism.

ACKNOWLEDGEMENTS

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Elastomer structures and 'cold crystallization'

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INTRODUCTION

In a great number of applications an ideal elastomer should satisfy, to a certain extent, both of the following requirements: (i) nearly instantaneous crystallization upon application of strain (strain induced crystallization) and (ii) slow or no crystallization when cooled at the temperature of maximum crystallization rate (cold induced crystallization). A noteworthy case of (ii) is elastomer crystallization in a strained state.

The connection between the points (i) and (ii) has not been clearly understood up to now, but it is known that some crystallizable elastomers fulfil the requirements of both (i) and (ii) better than others. From an experimental point of view, cold induced crystallization kinetics are substantially easier to measure than those of very fast strain induced crystallization.

The phenomenon of cold induced crystallization in natural rubber, NR, has been known since the very beginning of elastomer technology and the tendency of natural rubber to crystallize by cooling has been overcome by crosslinking it with sulphur (vulcanization) without impairing its ability to crystallize by stretching (Goodyear 1836).

The synthesis of *cis*-polyisoprenes, IR, and *cis*-polybutadiene, BR, of different microstructural purity (different *cis* content) gave the possibility of changing the crystallization rate[1]. It has also been reported that the very

fast cold crystallization of *trans*-polypentenamer, TPA, could be reduced by lowering the *trans* content[2]. The same fact had been observed earlier for *trans*-polychloroprene[3].

There is a general agreement in postulating that the reduction of the crystallization rate, obtained either by crosslinking or by chain regularity reduction, can be linked with the lowering of the melting point[4]. In both cases the low level of structural defects introduced in the chains does not affect the glass transition temperature in such a way as to vary the crystallization rate.

The aim of this paper is to emphasize the importance of the variations of the glass transition temperature and melting point on the elastomeric cold crystallization rate and the way these may be used in planning new elastomer structures.

DISCUSSION

We have shown[5] that the crystallization rate of several different uncrosslinked elastomers, expressed in terms of crystallization half time $t_{1/2}$, essentially depends on three variables. Two of these are peculiar to the elastomer structure, i.e. the glass transition temperature (T_g) and the 'melting temperature' T_m^0, defined below. The third is the experimental crystallization temperature (T_c).

The expression connecting $t_{1/2}$ with these variables is:

$$\log_{10} \frac{t_{1/2}}{a_T} = a + b \frac{T_m^0}{T_c(T_m^0 - T_c)} \quad (1)$$

with $a = -4.61$ and $b = 338$. a_T is a reduction factor to refer all elastomers to a state of uniform segmental mobility. The reduction factor employed is the Williams, Landel and Ferry relation:

$$\log_{10} a_T = -8.86(T_c - T_s)/$$
$$(101.6 + T_c - T_s)$$

with $T_s = T_g + 50K$.

T_m^0 is an adjustable parameter which we call 'melting point', chosen so that all the experimental results lie on the same straight line when equation (1) is plotted as $\log_{10} t_{1/2}/a_T$ *versus* $T_m^0/T_c(T_m^0 - T_c)$. The T_m^0 found in this way are related to the experimental ones, although they are slightly higher[9].

Equation (1) is similar to that obtained by Hoffman[6] in which b is a function of the melting enthalpy and the interfacial free energy for lateral and end surfaces of the crystal. The novelty, in our approach, lies in the
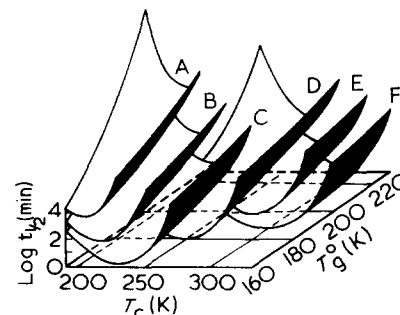

Figure 1 Plot of log $t_{1/2}$ vs. T_c and T_g for different values of T_m^0. T_m^0 values: A, 260K; B, 280K; C, 300K; D, 320K; E, 340K; F, 360K