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# Measurement of rubber particle fraction in high-impact polystyrene

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The rubber particle fraction in high-impact polystyrene (HIPS) can be separated efficiently from the polystyrene matrix if the rubber phase is cross-linked using heat-treatment. A conventional gel test to measure the rubber particle weight fraction has been used on HIPS, which has been heat-treated to cross-link the rubber phase. The rubber particle fraction results obtained by the gel test method are shown to agree with results from an alternative method where the rubber particle fraction is calculated using measurements taken directly from transmission electron photomicrographs.

## 1. Introduction

The fraction of the rubber phase in HIPS is an important characteristic which, along with rubber particle size distribution and other parameters, affects the physical properties of the material. A method typically used to determine the HIPS rubber particle fraction is the Ruffing gel test [1]. In this procedure the rubber phase is isolated by centrifugation of a suspension of rubber particles in toluene. It has been demonstrated in our lab that even at high centrifugal force rubber particles may remain suspended depending on the rubber particle size and rubber phase cross-linking. The more recent Bucknall method provides an accurate measurement of rubber particle volume fraction by calculation of the area occupied by rubber particle images in transmission electron microscopy (TEM) photomicrographs of HIPS [2]. The Bucknall method has allowed correlations to be developed using rubber particle volume fraction as an independent variable in HIPS structure–property studies.

An alternative approach is proposed for rubber particle fraction measurement. The procedure involves cross-linking the HIPS rubber phase, centrifugation of the rubber particles from a toluene suspension, and measurement of the dry weight of cross-linked rubber particles.

## 2. Experimental procedure

### 2.1. Materials

Two commercial HIPS resins were selected for the study. Resin A contained 8.40 wt % rubber and 3.42 wt % plasticizer. Resin B contained 7.90 wt % rubber and 0.53 wt % plasticizer. The polystyrene matrix molecular weights (weight average) determined by gel phase chromatography (GPC) were 175 000 and 199 000 for Resins A and B, respectively.

Rubber particle size was measured using laser light scattering and image analysis methods. The rubber particle volume average diameter ($M_v$) for Resin A was 4.24 $\mu$m using a laser light scattering method [3]. A lower $M_v$ of 2.51 $\mu$m was obtained for Resin A using an image analysis method [4]. A similar difference in $M_v$ was obtained for Resin B using the two methods (4.57 $\mu$m using light scattering and 2.80 $\mu$m from image analysis). The differences in $M_v$ for each resin are the result of swelling of the rubber particles in the solvent used to suspend the rubber particles when the light scattering method is used. Using the image analysis method, the rubber particles are not swollen by any solvent and the image analysis method is the more accurate of the two methods.

### 2.2. Microscopy and rubber particle volume fraction measurement

TEM photomicrographs of HIPS were obtained using the method described by Bucknall *et al.* [2]. The magnification of the HIPS in the photomicrographs was 7000 × and the print size was 190 mm × 267 mm. The photomicrographs were used directly for rubber particle volume fraction measurement using an image analysis technique.

The equipment used for the image analysis consisted of a copy stand to securely hold a solid state video camera directly above a TEM photomicrograph. The camera was connected to an image processor manufactured by Image Technology Corporation (ITC), Deer Park, New York, and a personal computer was used to run the ITC image processing software. Feature specific image analysis was performed using the ITC equipment. This equipment has also been used for accurate measurement of HIPS rubber particle size distributions [4].

For each field within an examined TEM photomicrograph, the ITC analyser was used to obtain a binary image of the polystyrene (light regions) in the photomicrograph. A logical "not" function available with the software reversed the image so the rubber phase was detected as the binary image. The binary images of the rubber particles could be overlaid almost exactly on the rubber particles represented in the photomicrographs and the occluded polystyrene was clearly visible, being surrounded by detected rubber in

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the binary images. The ratio of rubber particle area to the total area of the field was taken as the rubber particle volume fraction. The measurement of the rubber particle area was feature specific, so any occluded polystyrene visible in the binary image, but not detected as rubber, was included in the area measurement of the rubber particle fraction. Rarely, the rubber particles in the detected image had to be edited to close artificial breaks in the rubber membrane at the perimeter of the particles. Each rubber particle in the binary image was carefully inspected and edited to insure a good match between the detected binary image and real image.

### 2.3. HIPS heat-treatment

HIPS was placed in a 6-inch section of Teflon tubing (0.25 inch i.d.). After the tubes were purged with nitrogen and capped for the heat treatment, the tubes were transferred to a preheated computer controlled oil bath and held at 210° C. At varying intervals, tubes were removed from the bath, cooled, cleaned, and the contents were cut into small pieces for the rubber phase isolation experiments.

### 2.4. Gel phase isolation and rubber particle weight fraction measurement

A modification of the Ruffing gel test was used in the isolation of the rubber phase [1]. The material obtained from each heat treatment experiment (1.000 g) was dissolved in toluene (25 ml), and the mixture was agitated for 2 h. The toluene suspension of rubber particles was centrifuged at 27 000 relative centrifugal force, for 1 h and the supernatant toluene–polystyrene solution was decanted. The toluene was removed from the isolated wet gel at conditions of 100° C and 1.0 mm Hg pressure overnight. The swelling factor (measurement of rubber cross-linking) was the weight ratio of toluene-swollen gel to dry gel. The weight ratio of the dry rubber phase to weight of the sample was the rubber particle weight fraction. The supernatant liquids were inspected for the presence of rubber particles using a phase contrast microscope at magnifications of 400 × and 1000 ×.

## 3. Results and discussion

The conventional gel test for determination of the rubber particle weight fraction in HIPS is an approximation. The amount of rubber particles centrifuged in this procedure depends on the rubber phase cross-linking and the rubber particle size. Small particles are more difficult to centrifuge and the centrifugation efficiency increases as the rubber phase cross-linking increases.

Commercial HIPS resins vary over a wide range in average rubber particle size and rubber phase cross-linking. Use of the conventional Ruffing gel test provides a way to measure cross-linking on a relative basis. However, the gel test for determination of the rubber particle weight fraction (gel fraction) is accurate only when nearly all of the rubber particles are centrifuged from the toluene suspension. In comparing the gel fractions of two samples the test is only valid when both resins have the same rubber phase cross-linking and the same rubber particle size distribution. Incorrect conclusions about relative gel fractions within a group of HIPS resins can be reached if differences in cross-linking and rubber particle size are not taken into account.

Figure 1 shows a correlation between the measured per cent gel phase and rubber phase cross-linking for a group of HIPS resins evaluated using the conventional get test. The resins were prepared in the laboratory

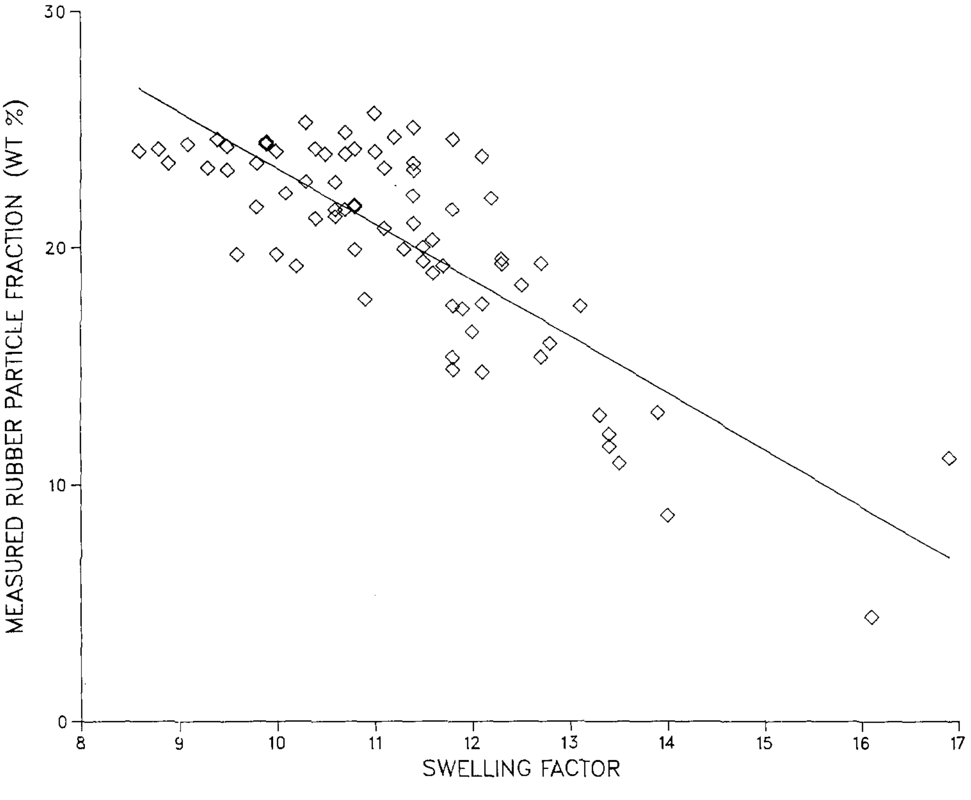

*Figure 1* Influence of cross-linking on measured rubber particle fraction.

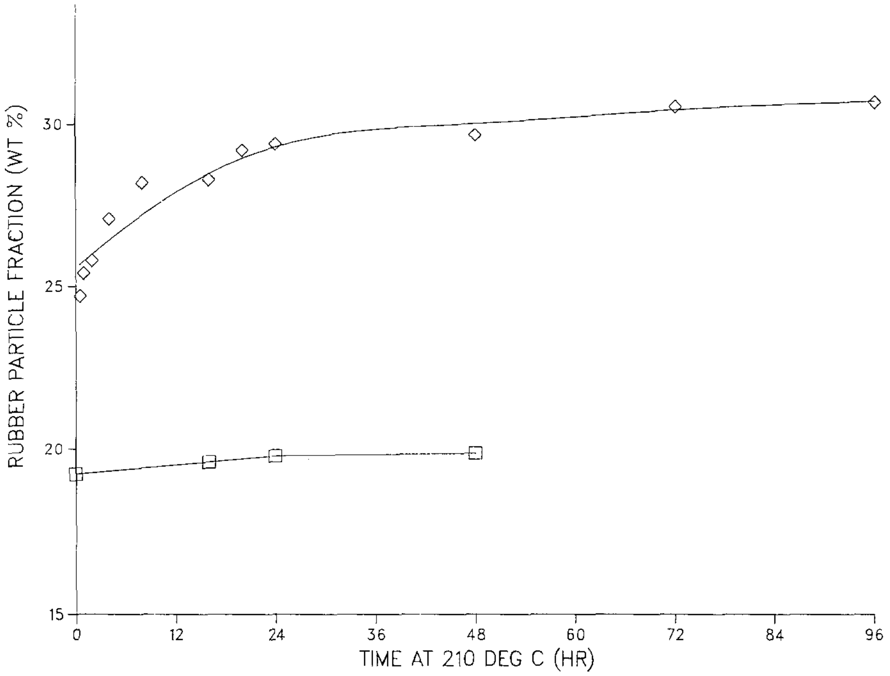

*Figure 2* Effect of heat treatment on measured rubber particle fractions isolated from Resins A and B (◇) Resin A; (□) Resin B.

using a single bulk polymerization reactor with 6–8% rubber in the feedstocks. Inspection of supernatant from the conventional gel test shows many rubber particles to be present and the correlation in Fig. 1 can be explained by more efficient centrifugation of rubber particles when the rubber phase cross-linking is high. It is proposed that when the rubber phase cross-linking is high, the measured per cent gel phase is closer to the true rubber particle fraction.

Increasing the rubber phase cross-linking in the HIPS through heat treatment produces rubber particles, which can be centrifuged efficiently at a reasonable force. Figure 2 shows an increase in rubber particle weight fraction as the length of the heat treatment time at 210° C is increased for Resin A. After Resin A was heat treated for 96 h, only a few very small particles (less than 1 $\mu$m) were left in the supernatant after centrifugation. The curve for Resin A in Fig. 2 is probably asymptotic to a line corresponding to the true rubber particle weight fraction for that resin.

There is a difference between Resins A and B in measured rubber fraction. Also, the response of Resin B to heat treatment is different from Resin A. The resins have different rubber levels and amounts of polystyrene occluded in rubber particles, which accounts for the ordering of the resins in measured rubber particle fractions after the 96 h heat treatment (see Table I). The resins also had different degrees of cross-linking before the heat treatment.

The rubber particles in Resin B, being highly cross-linked before the experiment, are centrifuged efficiently without the heat treatment.

The hypothesis that highly cross-linked rubber particles can be efficiently centrifuged from a toluene suspension is supported by rubber particle volume fraction data obtained using the alternative TEM image analysis method (see Table II).

When the HIPS rubber phase is sufficiently cross-linked, the rubber particles can be centrifuged efficiently from a toluene suspension. The weight ratio of the centrifuged, cross-linked rubber phase to total weight of the HIPS sample, used in the evaluation, is the rubber particle weight fraction. The weight fraction value is about the same as the volume fraction because the specific gravities of polystyrene and polybutadiene are near 1.0. It has been calculated that a weight fraction of 0.300 corresponds to a volume fraction of 0.306, assuming rubber particles are 75% polystyrene by weight, and the polystyrene and polybutadiene specific gravities are 0.92 and 1.03, respectively.

Determination of the rubber particle weight fraction in HIPS using the heat treatment approach provides an alternative to obtaining TEM photomicrographs for measurement of rubber phase volume fraction. The disadvantage of the heat treatment

TABLE I

| Resin | Initial rubber particle weight fraction | Swelling factor |
|---|---|---|
| A | 0.256 | 12.4 |
| B | 0.192 | 9.9 |

TABLE II

| Resin | Weight fraction (gel after 210° C heat-treatment) | Volume fraction (image analysis of TEM photomicrographs) |
|---|---|---|
| A | 0.308 | 0.307 |
| B | 0.199 | 0.202 |

method is the time required to cross-link the rubber phase. Other means for rubber phase cross-linking are being explored to shorten the time.

## 4. Conclusions

The rubber particle fraction in HIPS can be accurately measured by centrifugation of the rubber particles suspended in toluene if the rubber is sufficiently cross-linked. The heat treatment time required to sufficiently cross-link the rubber depends on the heat history the HIPS experienced during manufacturing. A heat cycle of 96 h at 210° C cross-links the rubber phase in most HIPS resins to the extent that isolation of the gel phase will provide an accurate measure of the rubber particle fraction.

The rubber particle fraction results obtained using the modified gel test agree with results from the method used by Bucknall, where the area occupied by the rubber particles in a TEM photomicrograph is measured. Measurement of this area is made easier using an image analyser. Regardless of how the area is determined, many representative TEM photomicrographs are required for each HIPS resin.

The modified gel test for determination of rubber particle fraction has a disadvantage, the 96 h heat treatment. Other ways to cross-link the HIPS rubber phase are being explored.

## Acknowledgement

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