Study of the Rubber Particle Size (RPS) distribution of HIPS: comparison between Laser Light Scattering technique and Transmission Electron Microscopy

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1. Summary

The mechanical properties of HIPS depend directly on the particle size and the particle size distribution of the rubber phase. The size and morphology of the rubber particles are established at the phase inversion, where the polystyrene phase becomes the continuous phase. Several methods have been employed to find the moment where phase inversion occurs, being the Transmission Electron Microscopy (TEM) the most commonly used. Using the Laser Light Scattering technique (Malvern Mastersizer 2000), information about the rubber particle size and the particle size distribution was obtained.

2. Introduction

HIPS is a polymeric material toughened by the incorporation of polybutadiene rubber. Basically, HIPS is produced via bulk polymerization of styrene (St) in the presence of polybutadiene (PBd). Initially, the rubber-rich phase is the continuous phase, but after the so-called *"phase inversion period",* the PS-rich phase becomes continuous and the HIPS morphology is developed. This phenomenon takes place at 10-20% St conversion with an abrupt change in the apparent viscosity of the reaction mixture [1, 2]. The phase inversion is a critical point during the polymerization, due to the fact that the rubber particles are established at this moment and the morphology is maintained until the end of the polymerization. Since the mechanical properties of HIPS are affected by the rubber particles size and the rubber particles size (RPS) distribution, it is important to establish the precise moment at which phase inversion takes place.

This study involves the monitoring of rubber particles development during the bulk

polymerization of styrene in the presence of polybutadiene rubber (synthesis of HIPS), by Laser Light Scattering technique in order to determine the moment when the phase inversion takes place. Also, the information obtained by Laser Light Scattering technique was corroborated with Transmission Electron Microscopy micrographs.

3. Experimental

3.1 Materials

Styrene (containing 15 ppm of TBC) and polybutadiene (M_w = 100,000-120,000 g/mol) were supplied by Total Petrochemicals USA and were used as received. AIBN and Methyl ethyl ketone (MEK) (Sigma-Aldrich) were used as received.

3.2 HIPS synthesis

HIPS was synthesized by bulk polymerization of styrene in the presence of polybutadiene (6% w/w) and AIBN (0.1% w/w) as radical initiator, where the synthesis conditions used were 70 ºC and 250 rpm. At different periods of predetermined time, samples were taken from the reaction media and diluted in MEK for Rubber Particles Size (RPS) distribution analysis by Laser Light Scattering. The rest of the sample was heated to 150 ºC for 12 hours, in order to complete the polymerization of the styrene monomer and to crosslink the rubber particles. Once the polymerization was complete, samples were characterized by TEM.

3.3 HIPS characterization instruments

For the HIPS characterization by Laser Light Scattering, a Malvern Mastersizer 2000 was used, using MEK as a solvent. The dilution of the samples (1 g) in MEK (20 mL) was done in order to separate the rubber from the PS matrix. The micrograph was taken using a JEOL TEM. HIPS samples were prepare using a Leyca Ultramicrotome for the sample cuts, and stained with OsO_4.

4. Results and discussion

The Rubber Particles Size (RPS) distribution evolution was followed by Laser Light Scattering and when phase inversion occurs during the polymerization, the presence of only one size of particle can be identified and it is evidenced by a very well defined peak. Then, the samples were polymerized at 150º C to complete the styrene monomer conversion.

From Figure 1, it can be observed that after 2 hours of polymerization, the phase inversion has taken place. For samples taken at 1 hour of polymerization, the RPS curve is not defined as a consequence of rubber particles of different sizes and volumes, since the more abundant phase in the reaction solution at this time is formed by the polybutadiene. Once the phase inversion occurs, the rubber particles are formed and their size and shape is established, reaching a determined value of particle size (HIPS particle size ~9 µm), which will remain constant until the polymerization ends.

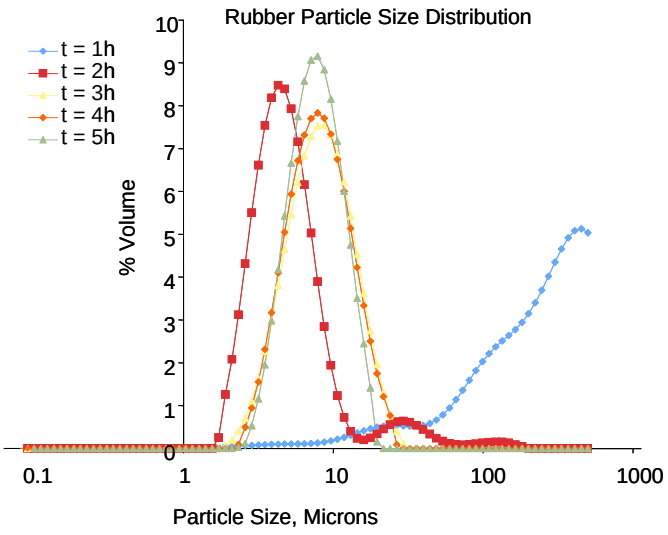

Figure 1: Rubber Particle Size distribution of the synthesized HIPS at different reaction times

Therefore, from the information gathered from Malvern the phase inversion has been established at 2 hours. To corroborate this, TEM micrographs were taken and the morphology of the material was evaluated at different reaction times. From Figure 2, it can be observed that phase inversion is achieved after 2 hours of polymerzation, corroborating the results acquired from the Malvern

data. Moreover, the morphology of the material is not affected as the polymerization time increases, as it can also be observed in Figure 2.

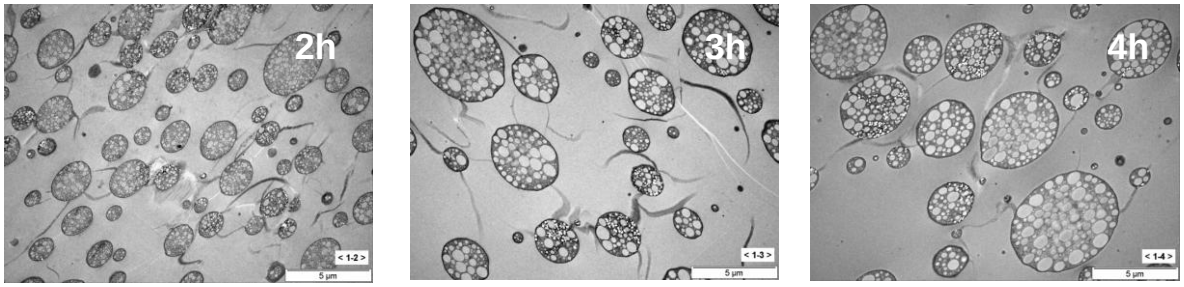

Figure 2: TEM micrographs of the synthesized HIPS for different reaction times

5. Conclusions

The polymerization time at which the phase inversion takes place in the HIPS synthesis was established by Laser Light Scattering technique following the evolution of the Rubber Particle Size distribution. These results were corroborated by TEM micrographs and they are in accord with those obtained through the Laser Light Scattering technique.

4. References

1. Freeguard et al. *J. Polym. Sci* 1971, **15**, 1619-1655

2. Soto et al. *J. Appl. Polym. Sci*. 2004, **92**,1397-1412