Evaluation of the Potential Use of Ultrasound during the Industrial Manufacturing of High Impact Polystyrene

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ABSTRACT: During the production of high impact polystyrene the rubber particle formation process is very important to control the final physical property balance. Besides the rubber viscosity, the presence of a copolymer to reduce the interfacial tension between the rubber and polystyrene phase is central. Such a copolymer can be added or can be made during the polymerization. In this study, it was attempted to create a block rubber *in situ* using ultrasound. Polybutadiene dissolved in styrene has been sonicated to create macroradicals. It was anticipated that these macroradicals would initiate the polymerization of styrene thus generating a poly(butadiene-*block*-styrene) acting as emulsifier during the production of high impact polystyrene. No evidence was found for the formation of a block copolymer but the higher reactivity and the resulting rubber particles indicate that besides rubber molecular weight reduction extra functionality was introduced on the rubber. No attempts were made to define the nature of the functionality. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1546–1551, 2009

Key words: sonochemistry; grafting; HIPS

INTRODUCTION

High impact polystyrene (HIPS) is a rubber impact modified polymer. Polystyrene is a brittle material but it can be made ductile by the addition of rubber. The commercial success of HIPS is largely due to the ease of developing polymer systems that meet the application needs of toughness, rigidity, heat distortion, and flow behavior. The balance of these properties is partly determined by the rubber particle size (RPS) and its morphology.[1] The RPS and the morphology is dependant on a large variety of product and process parameters. A detailed description of the particle formation process during the mass acrylonitrile-butadiene-styrene (ABS) process (similar to HIPS) is available.[2] One of the key features is the grafting process. Before the grafting process can be explained it is required to briefly describe the key steps in the mass process to make impact modified styrenics (HIPS and ABS). The first step in the process is to dissolve the rubber into the mixture of monomer(s) and solvent. When the rubber is completely dissolved an initiator (in most cases a peroxide) can be added and applying heat results in polymerization. By applying shear the rubber particles are formed. The rubber particle formation is favored by reducing the interfacial tension between the two phase (styrenic and rubber phase) which are not miscible. The interfacial tension can be reduced by creating styrenic grafts on the rubber backbone. The grafting process is initiated by a radical that generates (by abstraction or addition) radical on the rubber backbone. Peroxy radicals typically generate a large amount of rubber macroradicals. This would be a perfect solution to increase the amount of grafting; however, the peroxy radicals are not very selective and also initiate the styrene polymerization which imposes an upper limit on the amount of peroxide that can be used. Excessive amount of peroxide would create a system that is hard to control (heat transfer problems) and also the resulting molecular weight would be too low for certain applications.

Therefore it is interesting to explore alternative routes to increase the grafting level without interfering too much with the overall polymerization and matrix properties. The idea explored in this work is the combination of sonochemsitry with the mass process to make rubber modified styrenic resins. Sonochemistry is the application of ultrasound to chemical reactions and processes.[3] The origin of sonochemical effects in liquids is caused by acoustic cavitation. Cavitation is the formation, growth, and implosive collapse of bubbles in a liquid. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and

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low-pressure (rarefaction) cycles.[4] During the low pressure cycle, high-intensity ultrasonic waves create small vacuum bubbles or voids in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently during a high pressure cycle. This phenomenon is called cavitation. As different parts of the polymer chain are located at varying distances from the collapsing bubble, the difference of the forces applied on the chain segments can result in the breaking of some bonds. Evidence for the homolytic scissioning of macromolecules has been given by various research groups.[5–7] The mechano radicals created in this process are potential grafting sites and are expected to behave similar to the radicals generated by peroxy radicals.

Formation of block copolymers by means of ultrasound has already been described. In some cases, two homopolymers are sonicated and interpolymer radical coupling results in a block copolymer.[8,9] In another study, the degradation of polybutadiene in the presence of acrylic acid has been described showing that a block copolymer is created.[10] Instead of sonicating in the presence of monomer, the macroradicals can also be captured by a stable free radical (e.g., TEMPO) and in a subsequent step the TEMPO terminated polymer is reacted with a monomer resulting in a block copolymer.[11,12]

The aim of the present work was to define conditions to sonicate a rubber solution in the presence of styrene monomer allowing the formation of a block rubber. These conditions should be such that scaling to large plant is feasible (existing hardware, acceptable power consumption, reasonable investment, no excessive noise level) without adding unwanted properties to the final product. During this study, the sonicated rubber solutions were used as starting material in the synthesis of HIPS under conditions that will show the potential effect on the RPS and morphology.

EXPERIMENTAL

Materials

Styrene (STY, purity >99.5 wt %) monomer was used as received from the Dow Benelux manufacturing plant in Terneuzen (The Netherlands).

Ethylbenzene (EB, purity >99.5 wt %) solvent was used as received from the Dow Benelux manufacturing plant in Terneuzen (The Netherlands).

SE PB 5800 rubber, commercial synthetic rubber, linear low *cis* (37%) polybutadiene was used as received from the Dow Deutschland manufacturing plant in Schkopau (Germany). The solution viscosity [ASTM D445] of a 5 wt % solution in styrene is 175 mPa/s.

Dimethylformamide (DMF) was used from Baker.

Ammonium thiocyanate was used from Baker.

OsO_4 was used to stain the samples to be analyzed by transmission electron microscopy (TEM).

Methods

Sonication

The sonication was performed in a glass flow cell (cell content ∼ 80 mL, with probe inserted ∼ 60 mL) provided by Hielscher. The sonic energy was generated by means of a 200 W sonicator (UP200S) operating at 24 kHz from Hielscher using a 14-mm titanium sonotrode. The flow through the cell was provided by a peristaltic pump using silicon tubing. An external device was used to control and measure the power consumption of the sonicator.

Sonication protocol: The solution to be sonicated is made by overnight dissolving of 5 wt % rubber in styrene using moderate agitation. This solution is placed on a balance and is pumped at constant rate into the flow cell via the inlet on the bottom of the cell. Sonication of the solution takes places under constant exposure (not pulsing) and the applied power is adapted to desired level. The sonicated solution exits the cell via the outlet at the top and is collected. The temperature rise is controlled by a constant flow of cooling water through the jacket of the flow cell. During the experiment, at regular intervals, the weight loss of stock solution, temperature of sonicated solution in the cell, and electrical power consumed by the sonicator is recorded. After use all equipment was rinsed and cleaned with ethylbenzene.

Polymerization

Approximately 1600 g of the sonicated rubber solution in styrene is added to a batch reactor (the total content is ∼ 2000 g). The batch reactor is equipped with an Auger type agitator to facilitate mixing and to provide the required shear for the sizing process. The polymerization is done under nitrogen. A temperature profile was applied starting at 120°C ramping up to 150°C in a time frame of 3 h followed by an isothermal part of 1 h at 150°C. No initiator is added as styrene polymerization proceeds spontaneously in the temperature interval. During the run, samples were collected using a drain valve at the bottom of the reactor. The polymerization was stopped at ∼ 50 wt % solids level and at that stage the reaction mixture was drained from the reactor and the unreacted monomer was removed using a vacuum oven (250°C, 1 h, gradually reducing pressure to full vacuum to avoid foaming) equipped with a condensing system.
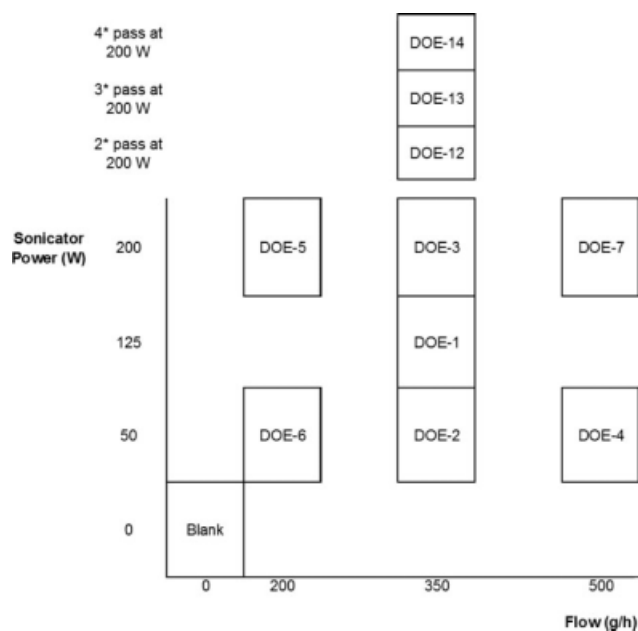
Figure 1 Design of experiments.

Characterization

Solids level

The solids level was obtained by evaporating the unreacted styrene in a vacuum oven at full vacuum and 250°C for 600 s. The solids level (wt %) is the ratio of the weight of the dried sample to the undried sample multiplied by 100.

Molecular weight

Gel permeation chromatography (GPC) was done with tetrahydrofuran (THF) as solvent using a Polymer Laboratories 5 μm Mixed-C column in combination with an ultraviolet detector (254 nm). The calibration is done using narrow molecular weight polystyrene standards. The sample is partially dissolved in DMF (rubber is not soluble in DMF).

Rubber particle size

The RPS was measured with a Coulter Multisizer III equipped with a 30 μm aperture tube. A 1.0 wt % ammonium thiocyanate solution in DMF was used as sample solvent and electrolyte.

Rubber particle morphology

The rubber particle morphology was determined based on TEM pictures obtained after staining the rubber phase.

RESULTS AND DISCUSSION

Design of experiment

To determine the effect of sonication on rubber molecular weight, grafting, and RPS and morphology a

set of experiments were designed varying the flow through the cell and the acoustic power as schematically represented in Figure 1. These parameters are easy to control/vary in an industrial environment and are expected to have a significant effect on the above described properties. The original design ranged from DOE-1 to DOE-7, but because the magnitude of reduction in rubber molecular weight was not as expected, three extra experiments were added where a sample was submitted to a number of extra treatments at full power (DOE-12 to DOE-14).

Sonication of the rubber solution

The sonicated samples were analyzed with GPC. In case a block rubber is formed during the sonication process the polymer should be UV active as the phenyl ring absorbs UV with a 254 nm wavelength. No evidence was seen for the presence of styrene units in the polymer backbone for any of the performed experiments. This is unexpected and suggests that no homolytic chain scissioning is occurring under the conditions used. To verify this, the molecular weight of the polybutadiene after sonication was measured. As X-axis the specific energy (E_{sp}) will be used [see eq. (1)].

$$E_{sp} = P/Q_m \tag{1}$$

P: Power during sonication (W or J/s)
Q_m: Flow through cell (g/s)

Figure 2 shows a linear relation between the obtained weight average molecular weight (M_w) and the applied specific energy. Increasing the specific energy results in a lower M_w. This proves that the rubber backbone is cleaved using ultrasound. It is not understood why the generated radicals do not react with the styrene to yield poly(butadiene-b-styrene). Here the effect of temperature needs to be discussed. To be able to propagate at a reasonable rate
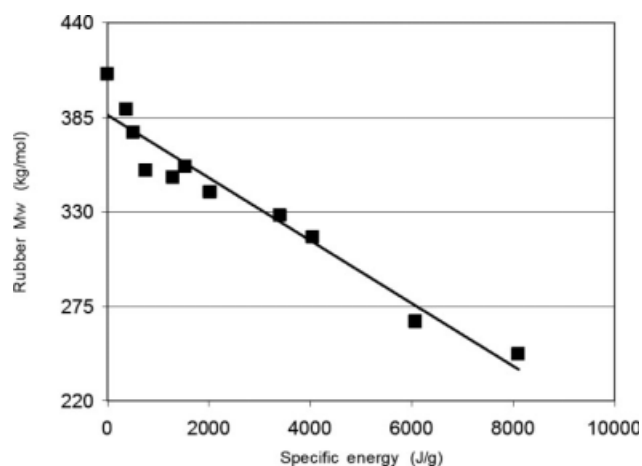

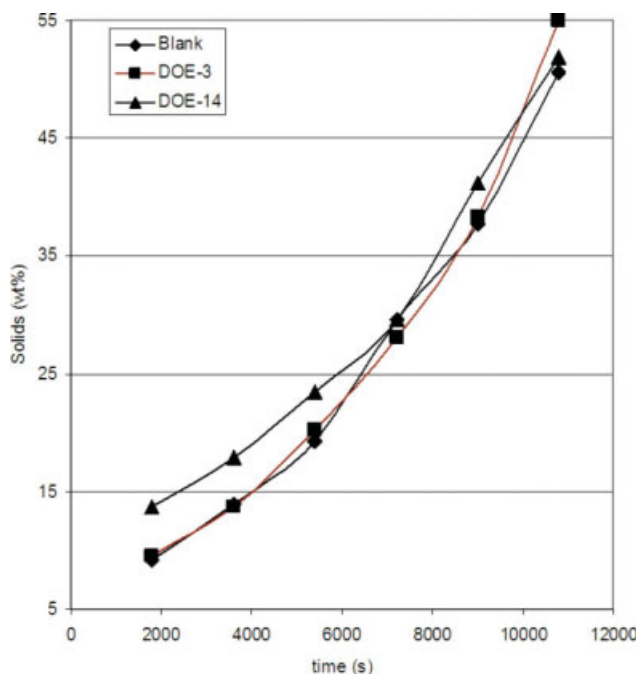**Figure 2** Rubber M_w reduction as function of specific energy.

Figure 3 Reactivity as function of rubber treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

styrene needs a certain minimum temperature. During the sonication the temperature in the flow cell was monitored. The temperature varied between 50°C (50 W setting) and 90°C (200 W setting). This range of temperature should be sufficient to allow styrene propagation. This is the macroscopic temperature and it is known that the temperature during the cavity implosion will be much higher.[13] The potential effect of higher temperatures was not investigated because the vapor pressure of the solution would become too high and also the efficiency of the cavitation is expected to become less. As the temperature is raised, the equilibrium vapor pressure is increased. This leads to easier bubble formation due to the decrease of the cavitation threshold. However, the cavitation bubbles contain more vapors which cushion the implosion in addition to using enthalpy generated in the implosion for the purpose of condensation. This decrease in the violence of the implosion results in a lower production of radicals. The only explanation left at this time it that the generated macro radicals can perform some kind of side reaction facilitating consumption of the radicals without producing a crosslinked system. As a conclusion of these sonication experiments we can say that it is possible to reduce the rubber molecular weight by chain scissioning but it has not been possible to use the generated macro radicals as initiator for the styrene polymerization.

The aim of the present work was to create a block rubber starting from polybutadiene. To achieve this

each rubber molecule needs to be scissioned resulting in two block copolymers. As the breakage of the polymer achieved by applying ultrasound is around midpoint,[14,15] a M_w reduction of $\sim$ 50% needed. To achieve this energy levels in the range of 8000 to 10,000 J/g are required. Processes such as compounding typically use energy levels in the range of 500–1500 J/g which are considered already significant. Therefore it has to be concluded that this sonication process is a high energy consuming technique and therefore will add unacceptable costs to manufacturing.

Polymerization of the rubber solution

Despite the absence of polystyrene fragments on the sonicated rubber and the low energy efficiency of the sonication process, some rubber solutions were submitted to thermal polymerization in a batch reactor. A comparison will be made for the results (reactivity, molecular weight, and RPS and morphology) obtained for the blank DOE-3 (E_{sp} = 2028 J/g) and DOE-14 (E_{sp} = 8113 J/g).

Reactivity

A significant difference ($\sim$ 5 wt %) in reactivity is observed between the blank and DOE-14 (Fig. 3). A small part of this deviation can be explained by the evaporation of the monomer during the sonication process ($\sim$ 0.5 wt %). It is clear that the highly
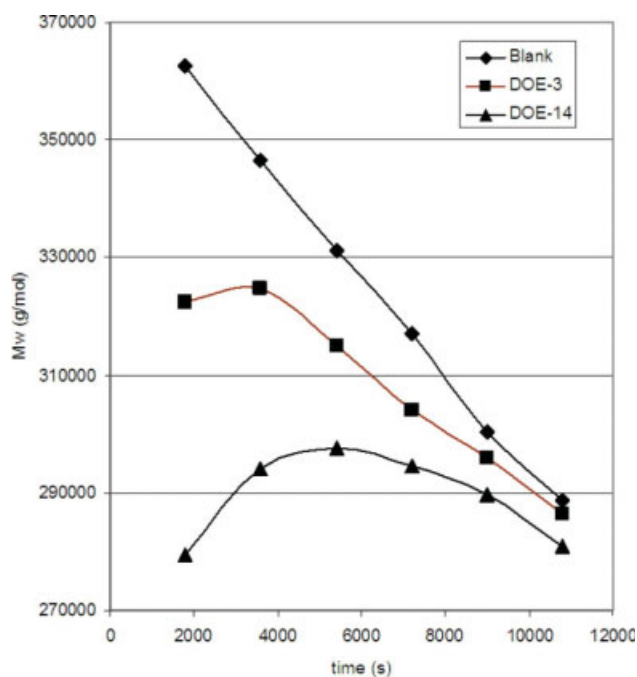

Figure 4 Molecular weight as function of conversion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
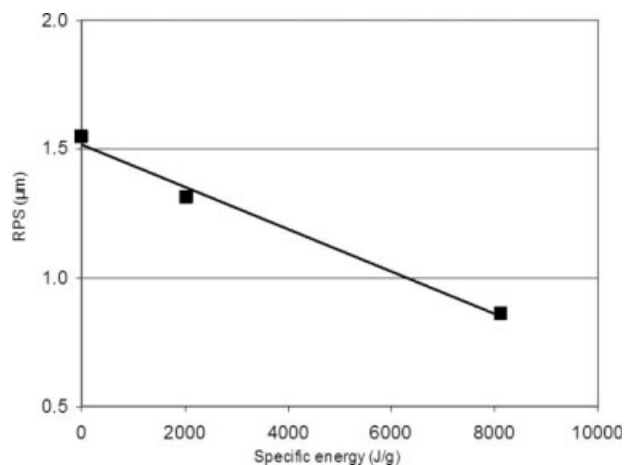
Figure 5 Rubber particle size as function of E_{sp}.

sonicated feed has a higher intrinsic reactivity which cannot be explained. It seems reactive groups have been formed on the rubber during the sonication process. Further confirmation for this statement might be found when comparing the molecular weight of the DMF soluble fraction.

Molecular weight

Figure 4 shows there is a distinct difference in 'starting-point' data for the different batch runs. For the blank the 'standard-behavior' where molecular weight decreases as function of increasing conversion is observed. This is a logical relation since the first polystyrene is formed at lower temperatures and high monomer concentration hence a higher molecular weight is expected.

For DOE-3 and DOE-14 the starting point is at a lower molecular weight, followed by an increase and then switching to normal behavior. There is no logical explanation for this phenomenon except the hypothesis mentioned earlier that there are reactive groups present on the rubber which generate, in the

early stage of the polymerization, a low-molecular weight grafted/block rubber that is soluble in DMF. Polybutadiene itself is not soluble in DMF and therefore does not contribute to the molecular weight measurement. No further work was done to identify the nature of these reactive groups.

RPS and morphology

The presence of a block rubber should be reflected in the RPS and morphology. When the RPS is plotted versus E_{sp} a linear trend is observed (Fig. 5). As the rubber molecule is inversely proportional to E_{sp} (see Fig. 2) it can be concluded that RPS is smaller when a lower molecular weight rubber is used. This is in line with previous results that a low rubber molecular weight generally results in smaller RPS and is not related to extra grafting.[16]

The final step in the evaluation of the experiments is the analysis of the particle morphology by TEM. On the basis of the absence of block rubber after sonication and the results obtained for the RPS measurements it is to be expected that no fundamental different morphology will be present. This is not in line with the data in Figure 6. The reference sample is showing the typical cellular/salami type of rubber structures obtained when polybutadiene is used. When the samples were sonicated, a gradual decrease of this structure is seen as a function of sonication level. Core-shell and/or rods and dots become more important. For the four times sonicated sample (DOE-14), hardly any cellular is observed and only the small core-shell like particles remain. It has been described that high levels of grafting would be needed to achieve this type of morphology, only reducing the rubber molecular weight is not sufficient to induce this change in morphology.[16] The only explanation that can be given, in line with our observations, is that during the sonication process the rubber molecular weight is
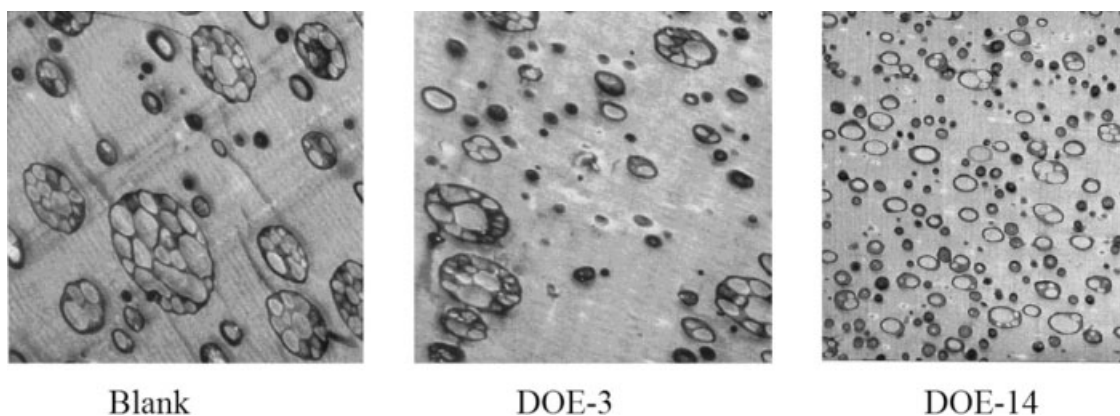

Figure 6 TEM of HIPS made with different rubbers.

reduced by scissioning and at the same time some active groups are created on the rubber. They are responsible for the higher reactivity (see Section "Reactivity") and can result in a higher grafting degree during the polymerization.

CONCLUSIONS

1. Rubber molecular weight can be reduced and controlled by sonication. There is a relationship between obtained rubber molecular weight (M_w) and specific energy (E_{sp}). The reduction of the molecular weight is caused by chain scissioning.

2. Extremely high levels of E_{sp} are required to obtain the desired molecular weight reduction allowing a significant change in RPS and morphology. This implicates that scale-up is almost impossible as long as this process is not optimized.

3. No polystyrene blocks are formed during the sonication of the rubber in presence of styrene. The hypothesis that the mechanoradicals on the end of a scissioned rubber molecule—created by the cavitation—would function as initiating site for the grafting reaction is not confirmed.

4. The shift in rubber particle morphology cannot be explained by the reduction of the rubber molecular weight. It is assumed that active groups are created on the rubber during the sonication process that generate more grafting during the polymerization process. An indication for this can be found in the higher reactivity and different molecular weight build-up observed for the feeds that were sonicated intensively.

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