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Dispersing Behavior of Recycled Rubber Particles

*Nima Shahidi, Fouad Teymour, Hamid Arastoopour**

Center of Excellence in Polymer Science and Engineering, Chemical and Environmental Engineering Department, Illinois Institute of Technology, Chicago, IL, 60616, USA
E-mail: arastoopour@iit.edu

Summary: The hydrophobic nature of recycled rubber particles presently limits their use only in non-aqueous media. Recycled rubber particles were chemically modified by preparation of amphiphilic semi-interpenetrating polymer networks using poly(acrylic acid) as the hydrophilic polymer. The resulting composite particles are water dispersible and suitable for various aqueous media applications.

Keywords: composites; dispersibility; recycling; rubber particles; value added material

Introduction

Almost 3 million tons of scrap tire are annually generated in North America and for the most part, these are inefficiently disposed of by landfilling or used as tire-derived fuel (TDF) as shown in Figure 1. [1,2] The environmental concerns regarding disposal of scrap tires are increasing and air emission regulations are impacting their use as TDF.[1,2] It is thus essential to develop a cost effective recycling technology to recover as much as possible of this valuable source of raw materials, for reutilization in new products.

Solid state shear extrusion (SSSE) is a novel non-cryogenic pulverization process which has a potential of providing cost effective recycling technology.[3] The rubber particles produced by the SSSE process have unique properties (e.g., partially devulcanized), which makes them suitable for reuse manufacturing.[4] However, due to the hydrophobic nature of rubber particles, their use has so far been limited to non-aqueous media where they could be better dispersed. Water dispersibility controls the effective use of particulate materials in aqueous media.[5] The addition of a hydrophilic character to hydrophobic rubber particles allows their utilization in aqueous media. Moreover, higher value added materials could be obtained by production of hydrophilic-hydrophobic particulate phase semi-interpenetrating polymer networks (PPSIPNs) with unique properties.[6]

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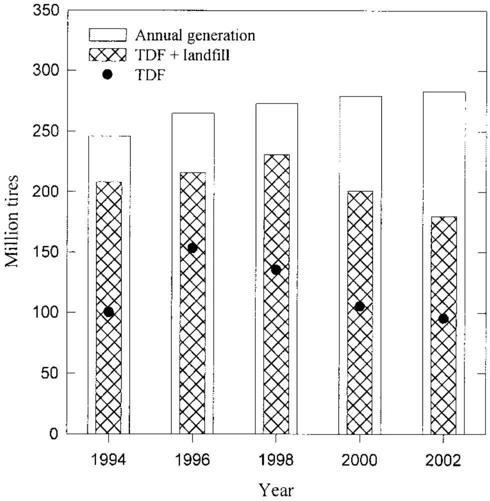

Figure 1. Annual generation of scrap tires in North America [1,2]

The main objective of this work is a) to study the agglomerate structure of recycled rubber particles produced by the SSSE process by measuring their particle size distribution in different organic solvents, b) To develop a process for chemical modification of the rubber particles such that they become dispersible in water.

Solvent-rubber Particle Interaction

The SSSE pulverization process was utilized to obtain a partially devulcanized rubber powder from post-consumer vulcanized natural rubber items.[3] The swelling coefficient of rubber particles in different solvents was measured to determine the solvent-rubber particle interaction. Figure 2 shows that the maximum degree of swelling was obtained in chloroform, indicating a compatibility of chloroform and natural rubber. Swelling behavior of the rubber particles could be predicted by similarity of the Hildebrand solubility parameter (δ_t) of the solvent with that of natural rubber. The Hildebrand parameter indicates the magnitude of the total intermolecular force of a liquid/solid and in the case of chloroform, this value matches favorably with natural rubber. Lower degrees of swelling were obtained in hexane and isopropanol indicating differences between the intermolecular forces of these solvents and that of natural rubber.

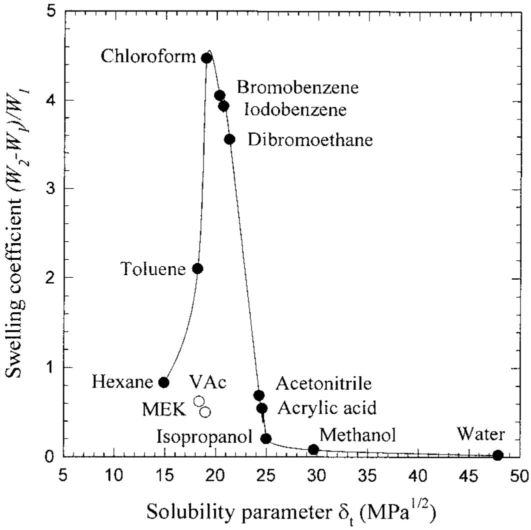

Figure 2. Swelling degree of unmodified rubber particles in different organic solvents. (W_2 is the weight of swollen particles and W_1 is the weight of dry particles)

Swelling behavior can be adequately described using Hildebrand parameter, despite the fact that in some cases (e.g. methyl ethyl ketone, MEK) differences in polar character give unexpected results as shown in Figure 2. Swelling predictions become more consistent if the Hildebrand value of a solvent is further decomposed into its Hansen solubility components. The Hansen parameters represent the components contributing to the Hildebrand parameter, namely: the dispersion force component, δ_d, the polar component, δ_p and the hydrogen bonding component, δ_h,

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

Table 1 summarizes the Hildebrand and Hansen solubility parameters of a number of solvents and natural rubber. The intermolecular forces between natural rubber molecules are primarily due to dispersion force (δ_d), with practically no polar forces involved. These polar configurations are matched with the intermolecular forces of chloroform and toluene molecules, thus encouraging interpenetrating and swelling of the rubber particles.

Table 1. Solubility parameters of selected solvents.

Solvent	Solubility parameters [7] (MPa$^{1/2}$)				H-bonding group[7]
	δ_d	δ_p	δ_h	δ_t	
Water	15.5	16.0	42.4	47.9	strong
Isopropanol	15.8	6.1	16.4	23.5	strong
Hexane	14.9	0	0	14.9	poor
Toluene	18	1.4	2	18.2	poor
Chloroform	17.8	3.1	5.7	19	poor
Methyl ethyl ketone	16	9	5.1	19	moderate
Natural rubber[8]	18.4	2.1	7.2	19.8	

Particle-particle Interaction

Size distribution measurement of the rubber particles in different solvents was conducted to study the interaction forces between rubber particles. A narrow size fraction of the produced rubber particles in the range of 90-250 micron was collected using sieving method. The particles were dispersed in different suspension fluid (shown in Table 2) and laser diffraction technique was used to measure their size distribution using a Microtrac SRA-150. The median diameter of the suspended particles was determined as a measure of dispersibility in that specific medium. The results indicate the swollen size of the particles; therefore, the volume fraction of solvent in the swollen particles was measured to estimate the equivalent median size of unswollen particles as shown in Table 2. The flow rate of the suspension is crucial in this measurement in terms of measuring the size of primary particles.[7] Therefore, the prepared suspensions were sonicated to induce a high shear on the agglomerates prior to size measurement.

The effect of mobile phase on dispersing behavior of the rubber particles was studied using the suspending media of Table 2. Except for toluene, a narrow normal distribution was obtained when measuring the size of particles in the selected dispersing media. This is evident from the relatively smaller standard deviation reported. In the case of toluene a much broader distribution is obtained with a standard deviation exceeding 50% of the median size reported. Inspection of the particle size distribution curve (not shown) shows that this broadening is a result of a considerable shouldering on the low end of the distribution. It is believed that, because of its high ability at dispersing the rubber, toluene results in the observation of a substantial amount of fine particles in the range of 20 microns to 70 microns. In other media, these are usually present as part of large agglomerates.

Table 2. Median size of the unmodified rubber particles in different suspending mediums.

Dispersing medium	Median Size of swollen particles (microns)	Standard deviation (microns)	Volume fraction of solvent	Equivalent median size of unswollen particles (microns)
Isopropanol	239	55	0.1	230
Hexane	255	78	0.41	214
Toluene	246	126	0.71	161
Water	>>1000	-	0.02	>> 1000
SDS*+ water	215	53	0.02	214

*Sodium decyl sulphate

The equivalent median size of unswollen rubber particles in hexane and isopropanol was larger than that obtained in toluene. The reason is that a majority of the rubber particles remained in the form of agglomerates in hexane and isopropanol even after ultra-sonicating of the suspensions. Conversely, swelling of the rubber particle agglomerates in toluene resulted in disruption of the aggregated structures and subsequent deagglomeration of the particles. During the SSSE process, high compression and shear forces are applied for pulverization of the rubber particles and the resulted particles have irregular shapes.[4] In addition, the applied compression force results in interlocking of the irregular fine particles during the pulverization process. Our results indicate that the particles interlock and bind strongly. Furthermore, swelling of the particles in a good solvent such as toluene could break up the agglomerated particles.

The median size obtained from dispersion of rubber particles in water shown in Table 2, was much larger than 1000 microns, indicating extended poor dispersibility of the rubber particles in water. Addition of sodium decyl sulfate (SDS) as a cationic surfactant resulted in better dispersion of rubber particles in water, but the suspension still contained a considerable amount of agglomerates (see Table 2). The median size of rubber particles was measured in the swollen form, in solvent mixtures containing hexane and toluene as shown in Figure 3.

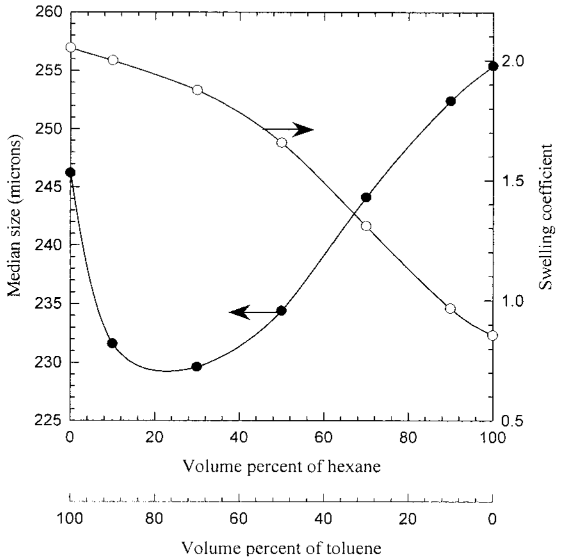

Figure 3. Dispersing behavior of unmodified rubber particles in mixtures of toluene/hexane

Rubber particles disperse better in toluene but considerably swell, resulting in a large particle median size. Addition of hexane in the suspending medium, reduces the degree of swelling, yet does not initially induce considerable agglomerates. Thus, the median size of the particles decreases to a minimum of 230 microns at 30 volume% hexane. Further increasing the amount of hexane to more than 30 volume%, affects the dispersibility and results in more agglomerates, thus the median size increases.

Therefore, the choice of mobile phase for measuring the particle size distribution of agglomerated particles is crucial when the shear rate induced on the suspension is not sufficient to break all the agglomerates. The best choice of suspending medium for particle size measurement is a liquid with similar intermolecular forces (Hansen solubility parameters) as of the molecules of the particles. In the case of rubber particles, these choices are toluene, chloroform, bromobenzene, iodobenzene and dibromoethane among the solvents shown in Figure 1.

Modification of the Rubber Particles

Amphiphilic composite rubber particles were obtained by swelling and then polymerization of acrylic acid monomer in the rubber particles to create PPSIPNs.[10] This modification process was conducted such that poly acrylic acid (PAA) chains partially interpenetrate in the rubber network. The other portion of the PAA chains were formed on the surface of the rubber particles (core-shell structure), which results in reagglomeration of particles in dry form, as evident from the Scanning Electron Microscopy (SEM) picture of Figure 4.

By soaking the prepared composite particles in water a swelling coefficient of 2.2 was obtained indicating a compatibility of the produced composite particles with water. The reason is that the polarity of rubber particles increases by addition of PAA. The polar interaction forces of PAA molecules match with that of water molecules and that results in dispersibility of the composite particles in water containing small number of agglomerates. Water dispersibility of the produced composite particles enables their use in any aqueous media applications, and provides a broader range of applications for the recycled rubber particles beyond their use as non-reactive fillers.

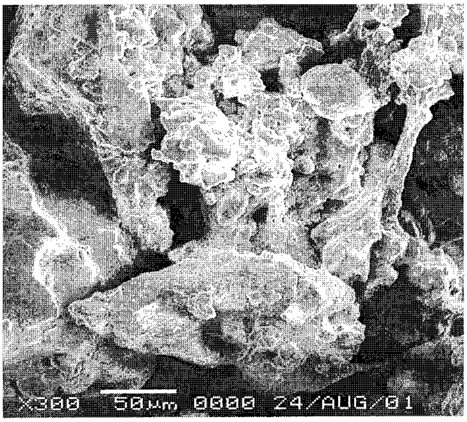

Figure 4. A typical SEM micrograph of the prepared composite particles

Thermal Characterization

The composition and structure of the composite particles produced can be inferred by thermal analysis of the sample. Figure 5 and 6 show the thermal degradation behavior of unmodified rubber particles and the produced composite particles. Differential scanning calorimetry (DSC) results showed that the thermal degradation of PAA occurred in the temperature range of 200 to 300 °C, and the rubber phase in the temperature range of 350 to 450 °C. Thermogravimetric analysis (TGA) indicates two major weight losses due to degradation of PAA and rubber, which also indicates that the prepared composite particles contained almost 45 to 50 % PAA as shown in Figure 6. Differential thermogravimetric (DTG) results showed that the weight percent change of rubber decreased from – 0.8 wt.%/°C in the unmodified rubber, to – 0.6 wt.%/°C in the composite particles. This indicates thermal stabilization of the rubber phase in the composite particles by interpenetration of PAA in the rubber networks.

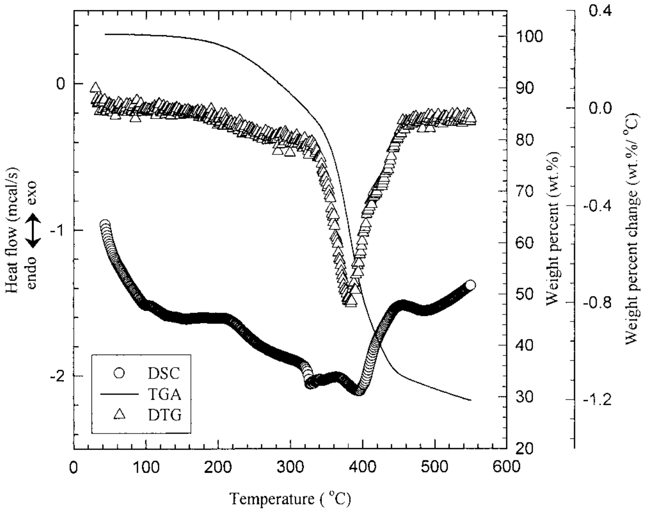

Figure 5. Thermal analysis of the unmodified rubber particles

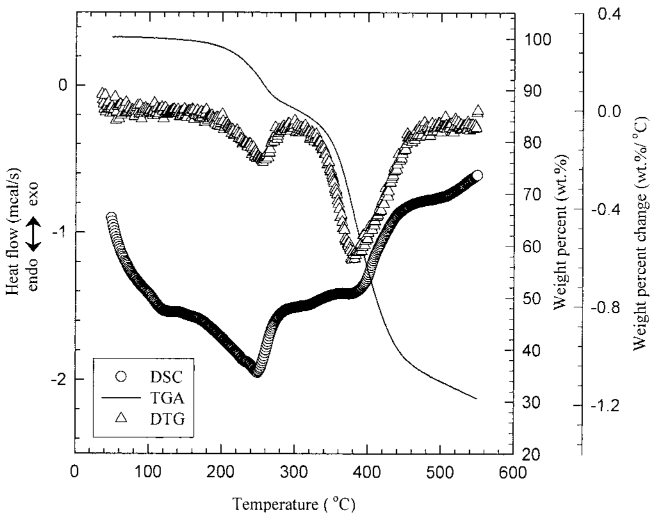

Figure 6. Thermal analysis of the modified rubber particles with PAA

Conclusions

The effect of mobile phase on particle size distribution measurement using laser diffraction technique was investigated for pulverized rubber produced from recycled materials. The rubber particles produced by the SSSE pulverization process were found to contain a large amount of agglomerates. It was found that measuring the size distribution of these particles with laser diffraction technique is more accurate if the particles are suspended in a liquid with similar interaction forces as of rubber molecules. Using such a suspending medium results in swelling and deagglomeration of the particles. Addition of a hydrophilic character to the rubber particles increases their surface polarity that could be matched with the interaction forces of water molecules. Therefore, the produced composite particles are water dispersible and suitable for use in any aqueous media applications. This results in a broader range of application for recycled rubber materials and avoids the limited use of recycled rubber particles.

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