The Effect of Process Factors on the Mechanical Properties of Styrene-NR Elastomers Containing Natural Rubber-Graft-Polystyrene

Tarinee Nampitch1* and Polchit Buakaew2

ABSTRACT

Styrene-NR elastomers containing natural rubber-graft-polystyrene were prepared by an emulsion polymerization using potassium persulfate as an initiator. The effect of process factors on tensile strength was investigated by varying the temperature, rubber-to-monomer ratio, and initiator and emulsifier contents from 50 to 64 °C, 1.5 to 9, 0.8 to 1.4 g, and 4.5 to 6.5 g, respectively. Experimental results indicated that the tensile strength increased with an increase in reaction temperature, rubber to monomer ratio, and initiator and emulsifier contents.

Key words: natural rubber modification, styrene, emulsion, graft copolymerization, synthesis

INTRODUCTION

Polymerization of two polymers usually gives rise to new material having a better balance of properties than obtainable with a single polymer and are currently wildly accepted methods in order to attain the desired characteristics for new materials. However, blending of two polymers usually results in immiscibility, and the properties are not desirable without a third component such as a compatibilizer, which is able to mediate an attractive interaction between the phases (Hanafi and Hairunezam, 2001). Graft copolymer is one kind of compatibilizers that can be produced from copolymerization (Prasassarakich et al., 2001). Graft copolymerization effectively combines the desirable properties of natural rubber with vinyl monomers in order to produce tough, hard and impact resistance materials with easy processibility (Fayt et al., 1981; Baetzold et al., 1994; Chattopadhyay and Sivaram, 2001; Arayapranee et al., 2002). The natural rubber serving as a base for the graft copolymer has a glass transition temperature of –65 °C and the particle size diameter of rubber latex is in range of 0.5-2 mm.

Some investigators studied the copolymerization of natural rubber and vinyl monomers and has achieved considerable outcome in modifying properties of natural rubber (George and Swift, 1955; Cameron and Qureshi, 1980; Lenka et al. (1986) Prasassarakich et al., 2001; Arayapranee et al., 2002; Nampitch and Vattanatham, 2004 and 2005). The preferred processes used latex emulsion technique to obtain

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the particle size of smaller than 0.6 micron with effective heat removal (Mark et al., 1966; Rodriguez, 1970).

In our earlier publication (Nampitch and Vattanatham, 2005), the kinetics of styrene-NR emulsion copolymerization with high rubber content was reported. In this work, the processing factors of polymerization on mechanical properties of styrene-NR elastomers containing natural rubber-graft polystyrene were studied. The processing factors used in this study, the temperature, rubber-to-monomer ratio and initiator and emulsifier contents, were varied in order to observe the effects of these variables on mechanical properties and tensile strength. The presence of natural rubber-graft polystyrene in the polymerization would enhance miscibility between two polymers, polystyrene and natural rubber. Thus, the incorporation of natural rubber-graft polystyrene improved tensile strength and stiffness.

MATERIALS AND METHODS

1. Materials

High ammonia type commercial concentrated latex, 60% of dry rubber content (DRC) was used. Reagent-grade styrene monomer (purity ≥99%; Fluka) was purified prior to use in the procedure. Polymerization used sodium dodecyl sulphate (SDS, purity ≥99.8%; APS Ajax Finechem) as an emulsifier and potassium persulfate (purity ≥97%; Asia Pacific Specialty Chemicals Limited) as an initiator. Distilled water was used throughout the work.

2. Preparation of styrene-NR emulsion copolymerization

The graft polymerization was conducted in a 4-necked round bottom reactor of 1000 cm³, equipped with a two-blade impeller, a condenser, and a thermometer. Natural rubber latex and an aqueous solution of emulsifier and initiator were introduced to the reactor and the dissolved oxygen in the ingredients was removed by nitrogen purging for at least 30 min. The polymerization temperature was maintained constantly using a temperature controlled water bath. Reaction time was recorded using a stop watch. The gross polymer product was recovered and dried to constant weight in a vacuum oven. The recipe for the copolymerization is shown in Table 1. Blended samples were dried in a vacuum oven to remove water and styrene monomer.

3. Mechanical tests

Samples for mechanical testing were punched from the sheet according to ASTM D-412-Die C. Tensile testing used an Instron tensile tester (Model 1011) according to ASTM D-412-Die C. The readings were taken from an average of the best three measurements.

RESULTS AND DISCUSSION

1. Effect of initiator

The effect of the amount of initiator on the tensile strength was studied over the range of 0.8 to 1.4 g while keeping the concentration of all other reagents constant. The result of the experiment is shown in Figure 1.

Table 1  Emulsion polymerization recipe.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber to styrene ratio</td>
<td>60/40, 70/30, 80/20, 90/10</td>
</tr>
<tr>
<td>Water</td>
<td>200</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>4.5, 5, 5.5, 6</td>
</tr>
<tr>
<td>Initiator</td>
<td>0.8, 1, 1.2, 1.4</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>50, 55, 60, 65 °C</td>
</tr>
</tbody>
</table>

1 In organic compound 100 parts
Tensile strength increase was directly related to the amount of initiator. The higher initiator content can produce more radicals that can transfer to either rubber or monomer, producing macroradicals, which enhanced the generation of both polystyrene and graft polystyrene-rubber particles, thus resulting in an increase in graft copolymer and polystyrene in the system. A graft copolymer is known to be very effective in improving interfacial adhesion by entanglement or bridging of different polymer chains near the interface. Then an increase in graft copolymer (NR-g-PS) has improved the tensile strength. Moreover, an increase in polystyrene will enhance tensile strength of the product due to the stiffness of polystyrene.

2. Effect of polymerization temperature

The effect of temperature on tensile strength is shown in Figure 2. The rate of decomposition of the initiator depends on reaction temperature. An increase in reaction temperature can produce more radicals, thereby enhancing the propagation rate as well as the solubility of monomer and its diffusion rate. Thus, more radicals transfer to the rubber chain and monomer-swollen latex particles to produce more graft copolymer and polystyrene leading to an enhanced tensile strength. Moreover, it was found that the value of tensile strength was extremely high at 65 °C because autoacceleration effect occurred and the reaction rate increased rapidly. This leads to a surge in heat generation (Rodriguez, 1970) and a significantly enhanced tensile strength.

3. Effect of emulsifier

The emulsifier added to the system formed micelles. These micelles were present in interval I of the polymerization. At high emulsifier concentration, the number of micelles is high, thus increasing the number of polystyrene particles, which is in agreement with the work done by Smith and Ewart (1948). This leads to enhanced tensile strength. Figure 3 shows results for the effect of emulsifier content on tensile strength.

4. Effect of rubber to monomer ratio

The effect of the rubber to monomer ratio on tensile strength is shown in Figure 4. As the rubber to monomer ratio increased, the number of the graft polystyrene-rubber particles increased and they captured more of the hydrophobic
Figure 2  Effect of temperature on tensile strength at rubber/monomer ratio of 60/40 in 100 g of organic compound, 5 g of emulsifier, and 1 g of initiator.

Figure 3  Effect of emulsifier on tensile strength at rubber/monomer ratio of 60/40 in 100 g of organic compound, 1 g of initiator, and a 60 °C reaction temperature.

oligomer radicals produced in the water phase as a result increased in amount NR-g-PS in the system. This leads to enhance tensile strength.

CONCLUSIONS

Styrene-NR elastomers containing natural rubber-graft-polystyrene was prepared by an emulsion polymerization using potassium persulfate as an initiator and sodium laurylsulfate as an emulsifier. The polymerization results in a product system with three components: ungraft polystyrene, ungraft natural rubber, and graft polystyrene-rubber. Ungraft polystyrene and
Experimental results indicated that the tensile strength increased with reaction temperature, rubber-to-monomer ratio, and initiator and emulsifier contents.

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LITERATURE CITED


