Synthesis of High-Impact Polystyrene Fibers using Electrospinning

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Abstract. Synthesis of fibers from waste high-impact polystyrene (HIPS) have been successfully done using electrospinning method. The HIPS solutions were made with a single solvent (DMF or d-limonene), a mixed solvent (d-limonene/DMF), and with the addition of acetone to the previously stated solvents. The effects of HIPS concentration, a mix of solvent, and the addition of acetone on the morphology and the diameter of fibers were observed. The morphological change from particles to fibers took place along with the increasing concentration of HIPS in d-limonene. For other precursor solutions using DMF solvent, bead free fibers could be obtained even at low levels. The average diameter of fibers increased along with the increase of the HIPS concentration in DMF. At the concentrations of 15, 20, 25, 30, and 35 wt.%, the average diameters were 1.85, 2.09, 2.66, 3.59, and 7.38 μm, respectively. For the precursor solutions with the combination of different solvents (HIPS/DMF), the existence of beads was influenced by the ratio of solvents. When the ratio of d-limonene/DMF was 75:25, the obtained beaded fibers had a relatively large amount of beads. At the ratio of 50:50, fewer beads were found. Bead-free fibers were finally reached when the ratio of HIPS / DMF was 25:75. The addition of acetone reduced the diameter of the produced fibers. However, too much addition of acetone caused the fibers to be wet. Additionally, the diameter became larger if the addition of acetone surpassed a certain amount of volume.

1. Introduction

Nanotechnology has become a rapidly growing field in recent years. One area of great interest in nanotechnology is the synthesis and application of nanofibers. Nanofiber is a one-dimensional material which shaped like a fine thread [1]. It has a broad range of applications due to its unique physical properties, such as great ratio between the surface area and the volume. Nanofibers are elastic, and they have superior mechanical properties such as having high flexibility, high ultimate tensile strength and high porosity [2,3]. By acquiring these properties, nanofibers can widely be used in various applications e.g. as sensors, catalysts, and filters [4–6].

One technique to synthesize nanofibers is electrospinning. It is a simple approach to producing fibers with a relatively uniform diameter and various compositions using a high electric field. A high voltage source, a collector, a syringe pump, and a syringe with a metal needle are parts of the electrospinning apparatus [1]. The fibers produced are long and continuous while the diameters of fibers can be controlled by changing the polymer parameter (type and molecular weight), the solution parameter (polymer concentration, viscosity, conductivity and surface tension), the processing parameters (applied voltage, distance of needle tip to collector, flow rate, and diameter of needle tip), and the environmental parameters (temperature and humidity) [6].
Polystyrene is one of the commodity polymers that are widely used and an amorphous thermoplastic polymer that can easily be produced [7]. Recently, electrospun polystyrene fibers have been applied as biocatalysts and formalin sensors [8,9]. High-impact polystyrene (HIPS) and styrofoam are further developments of polystyrene. HIPS is a graft copolymer consisting of a small amount of butadiene rubber dispersed in a matrix of polystyrene [10]. Due to the special structure, HIPS has a series of advantages, such as excellent toughness, processability, and low production cost. Therefore, it is widely used in many fields, such as for furniture, household appliances, packaging materials, transportation, automobile, and so on [11].

The increasing use of HIPS does in turn increase the waste problem of HIPS. Usually, HIPS is recycled by transforming it into pellets using an extruder that will ultimately result in lower grade products [12]. Several studies have described the transformation of waste styrofoam into nanofibers using electrospinning and rotary force spinning methods [13–15]. In the case of electrospinning of HIPS, there is only one report in which HIPS was dissolved in a mixture of 1,2-dichloroethane (DCE) and N, N-dimethylformamide (DMF) [16].

The purpose of this present study was, therefore, to provide an alternative solution in the treatment of waste HIPS by converting it into fibers using electrospinning. The mixture of DMF and d-limonene was used as the main solvents, while acetone was employed as the additional solvent for d-limonene. The morphologies of produced fibers were observed using a digital microscope. Microscopic images of the fibers were analyzed for obtaining their average diameters and standard deviations so that their uniformity could be determined.

2. Experimental Method

Waste HIPS was collected from covers of broken compact discs. The main solvents used were N, N-dimethylformamide (DMF) and d-limonene, which were purchased from Sigma-Aldrich and Bratachem, Indonesia, respectively. Additionally, acetone, which was also obtained from Bratachem, Indonesia, was used as a supplementary solvent for the d-limonene solvent.

To observe the effect of HIPS polymer concentration on the produced fibers, the precursor solutions (15, 20, 25, 30, and 35 wt.%) were prepared by dissolving HIPS in a single solvent (DMF or d-limonene). Then, for the observation of the effect of solvent, the mixtures of solvents (d-limonene/DMF) with ratios of 75:25, 50:50 and 25:75 wt.% were prepared and then used to make HIPS solution with a concentration of 20 wt.%. Lastly, to observe the effect of acetone addition, a solution of HIPS/d-limonene with a concentration of 40 wt.% was made and then added by acetone forming 10, 20, and 30 wt.% solutions.

The schematic diagram depicting the synthesis process of fibers using electrospinning apparatus (Nachriebe 600, Indonesia) is shown in Figure 1. The precursor solution was placed in the plastic syringe with metal needle diameter of 0.8 mm. The syringe was mounted on the syringe pump to control the flow rate of the ejected solution. The metal tip of the needle was then connected to the positive pole of the high voltage source. The grounded collector plate was coated with aluminum foil to collect fibers and located as far as 20 cm from the metal tip.

![Figure 1. The schematic diagram of electrospinning](image-url)
The characterization of the fibers was done by using a digital microscope (National DC3-163) with 200×, 400×, and 1000× magnifications. Then, the microscopic images were processed to obtain the average and distribution of the diameter of fibers. The observations were taken at different locations of up to 100 points. The determination of the uniformity of fibers was done by calculating the coefficient of variation (CV) using Equation (1) [17].

\[
CV = \frac{\sigma}{\mu},
\]

where \(\sigma\) represents the standard deviation and \(\mu\) represents the average diameter of fibers.

3. Results and Discussion

By adjusting the electrospinning parameters, the morphology of nanofibers can be changed. It consists of the structures of simple beads (nanoparticles), beaded fibers, and bead-free fibers [18]. In this study, the effects of the concentration of HIPS polymer in a single solvent (d-limonene or DMF), in mixed solvents with certain ratios (d-limonene and DMF), and of acetone addition are given as follows.

3.1. Morphology of fibers from precursor solution using a single solvent (d-limonene or DMF)

HIPS solutions with various concentrations of 15, 20, 25, 30 and 35 wt.% were created by using a single solvent (d-limonene or DMF). Figure 2 shows the microscopic images of the HIPS fibers with DMF solvent under a digital microscope with 400× and 1000× magnifications and their respected fiber size distribution. During the syntheses, the process parameters, such as the flow rate of 0.5 mL/h, the high voltage of 15 kV and the distance of the collector-the needle tip of 20 cm, were kept constant.

As can be seen in Figure 2, the average diameter of fibers changed because of the change of HIPS concentration. For the concentrations of 15, 20, 25, 30, and 35 wt.%, the average diameter of fibers of were 1.85, 2.09, 2.66, 3.59, and 7.38 µm, respectively. The average diameter of fibers increased together with the increasing concentration of HIPS polymer since the viscosity became higher as a result of the enhancing HIPS polymer concentration. As the viscosity increased, it hindered the deformation process of the jets into fibers and a longer time was needed for the process to produce a perfect result. Therefore, by keeping all other parameters constant, the average diameter of fibers will
be larger when the concentration of HIPS polymer is higher [19–21]. To determine the uniformity of fibers, the coefficient of variation (CV) was calculated using Equation (1). If the calculated CV was greater than 0.3, the diameters of fibers were then nonuniform [17]. From the fiber size distribution, it could be seen that the CVs were less than 0.3. Therefore, the HIPS fibers made from the precursor solution with DMF solvent produced fibers with a uniform diameter.

![Figure 3](image-url)  
**Figure 3.** Microscopic images of HIPS fibers made from waste HIPS solution with d-limonene solvent under 400× and 1000× magnifications along with their respected fiber size distributions, (a) 15 wt.% HIPS, (b) 20 wt.% HIPS, (c) 25 wt.% HIPS, (d) 30 wt.% HIPS, and (e) 35 wt.% HIPS.
1.59, and 2.86 µm, respectively. From the fiber size distribution, it was found that the CVs for all the obtained fibers were below 0.3 and therefore, they were uniform.

3.2 Morphology of fibers with mixed solvent (d-limonene/DMF)

The precursor solution with mixed solvents of 20 wt.% HIPS was prepared by using a mixture of solvents with various ratios of d-limonene/DMF to be 75:25, 50:50, and 25:75 wt.%. The viscosity and surface tension of the precursor solution were then measured, and the results are shown in Table 1. During the syntheses, the process parameters were kept constant. The flow rate was 0.2 mL/m, the applied high voltage was 9.2 kV, and the distance between the plate collector and the needle tip was 20 cm. Figure 4 shows the microscopic images of the HIPS fibers made from different ratios of solvent mixture (d-limonene/DMF).

| Table 1. Properties of HIPS solution*. |
|---------------------------------------|
| Solution | Concentration (wt.%) | Viscosity (centi Poise) | Surface Tension (dyne/cm) |
|----------|----------------------|------------------------|------------------------|
| HIPS/d-limonene/DMF(75:25) | 20 | 309 | 34.2 |
| HIPS/d-limonene/DMF(50:50) | 20 | 312 | 33.5 |
| HIPS/d-limonene/DMF(25:75) | 20 | 325 | 32.8 |

*Values reported for 25 °C. The ratio represented the weight ratio of d-limonene to DMF.

Figure 4. Microscopic images of 20 wt.% HIPS fibers made from mixed solvents (d-limonene/DMF) under a digital microscope with 400× and 1000× magnifications and their corresponding fiber size distributions, (a) d-limonene/DMF of 75:25%, (b) d-limonene/DMF of 50:50%, and (c) d-limonene/DMF of 25:75%.

As presented in Figure 4 (a), beaded fibers did appear with varying diameters and in an elliptical shape. By looking at this morphology, the beads were formed before the elongation while the elliptical shape was caused by the pulling effect of the jets during the elongation process [23]. When the percentages of d-limonene and DMF were equal, the diameter of fibers increased while the number of beads decreased significantly as depicted in Figure 4.(b). Lastly, in Figure 4.(c), as the DMF was increased further to 75%, the bead-free and straight fibers were formed. The average diameter of fibers increased as the percentage of DMF was increased. The average diameters were 1.06, 1.73, and 1.86 µm for the precursor solutions with the ratio of solvents (d-limonene: DMF) of 75:25, 50:50, and
25:75%, respectively. As seen from Table 1, along with the increase of the DMF concentration in the mixed solvents, the precursor solution of 20 wt.% HIPS experienced an increase in the viscosity and decrease in the surface tension. The increase in viscosity and the decline in surface tension thus caused the diameter to increase while the number of beads decreased or even disappeared [22]-[24].

From the fiber size distribution, all fibers were evenly distributed and almost all the fibers were uniform as they had below 0.3 CVs. Therefore, by adjusting the ratio of solvents (d-limonene and DMF) and setting a constant amount of polymer concentration, beaded fibers or bead-free straight fibers with uniform diameter can be achieved.

3.3. Addition of extra acetone into HIPS solution

Figure 5 shows the microscopic images of the fibers as a result of acetone addition at 10, 20, and 30 wt.%, on the initial weight of the precursor solution of HIPS dissolved in d-limonene at a concentration of 40 wt.% as well as their fiber size distribution. The process parameters used in the form where the flow rate of 0.2 mL/m, the applied voltage of 9.2 kV, and the distance between the collector and the needle tip of 15 cm. All these parameters were held constant.

![Figure 5](image)

**Figure 5.** Microscopic images of HIPS fibers obtained from the precursor solution of 40 wt.% HIPS in d-limonene with the addition of acetone variation at 200× and 400× magnifications and their corresponding fiber size distributions, (a) from HIPS in d-limonene with no acetone addition, (b) with 10 wt.% acetone, (c) with 20 wt.%, and (d) with 30 wt.% acetone.

Figure 5(a) shows the microscopic image of fibers formed from the precursor solution of 40 wt.% HIPS in d-limonene. The fibers were bead-free with the average diameter of 12.01 µm and the standard deviation of 3.48 µm. From the images in Figures 5(b)-5(c), the addition of acetone solvent in the precursor solution caused the viscosity of the precursor solution to decrease and therefore the diameter of fibers also decreased proportionally [22]. Their average diameters were 9.08, 5.09, and 8.89 µm for the acetone additions of 10, 20, and 30 wt.%, respectively. Moreover, all fibers were evenly distributed and uniform as they had less than 0.3 CVs. However, when the acetone was added up to 30 wt.%, the fibers were wet, and the average diameter went larger as shown in Figure 5.(d). The addition of too much acetone made the molecules of solvent cannot reach the collector since they evaporated too soon [22].

4. Conclusion

High-impact polystyrene (HIPS) fibers have successfully been synthesized from waste HIPS dissolved in the DMF solvent, the d-limonene solvent, the mixture of DMF and d-limonene solvents as well as d-limonene and acetone solvents. Varying concentrations of HIPS polymer in the single solvent (DMF or d-limonene) caused morphological changes in the fibers. When DMF was used as the solvent, all
fibers were free of beads. Meanwhile the diameter of the fibers increased as the concentration of the polymer increased. The average diameter of fibers for precursor solutions of 15, 20, 25, 30, and 35 wt.% were 1.85, 2.09, 2.66, 3.59, and 7.38 μm, respectively. When d-limonene was used as the solvent, there was an observable change in the morphology from particles, beaded fibers and up to beads-free fibers as the concentration of polymer increased. At a concentration of 15 wt.%, the particles were not uniform with an average diameter of 9.61 μm. When the concentration was increased to 20 %, beaded fibers were formed with an average diameter of fibers 0.92 μm and once the concentration was increased further to 25 wt.%, fewer beads were formed with an average diameter of fibers of 1.52 μm. The beads were totally disappeared for the concentrations of 30 and 35 wt.% with the average diameters of 1.59 and 2.86 μm, respectively. When mixed solvents of DMF/d-limonene were used, the higher volume ratio of DMF reduced the number of beads and increased the diameter of fibers. For the concentration of the mixture solvent of d-limonene / DMF at 75:25, 50:50 and 25:75, the average diameters of fibers were, respectively, 1.06, 1.73, and 1.86 μm. (c) Lastly, the addition of acetone was found to be able to decrease the diameter of the produced fibers. However, too much addition of acetone caused the fibers to be wet. For the additions of acetone of 0, 10, 20, and 30 %, the obtained average diameters of fibers were 12.01, 9.08, 5.09, and 8.89 μm, respectively.

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