Polymer Bulletin 55, 209–215 (2005)
DOI 10.1007/s00289-005-0421-2

Polymer Bulletin

Nanofibers from recycle waste expanded polystyrene using natural solvent

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Received: 7 March 2005 / Revised version: 20 June 2005 / Accepted: 23 June 2005
Published online: 19 July 2005 –

Summary

A new recycling technique has been developed. In this method, EPS (expanded polystyrene), generally called Styrofoam, is dissolved with natural solvent, *d*-limonene and electrospun. This method can economically produce the nanofibers. The electrospinning process produces a nonwoven mat of long polymer fibers with diameters in the range of 10-500 nm and high surface areas per unit mass. PS (Polystyrene) polymer dissolved in different solvents such as THF (Tetrahydrofuran), DMF (Dimethylformaide), and DMAc (Dimethylacetamide) etc. may all be electrospun into nanofibers. These solvents cause environmental problem and difficulty of process handling. Natural solvent, *d*-limonene is used for dissolving PS. PS nanofibers are produced with PS solution using *d*-Limonene. This paper describes the use of polystyrene (PS) nanofibers electrospun from recycled EPS solution dissolved in *d*-limonene. The electrospun polystyrene nanofiber diameters vary from 300 to 900 nm, with an average diameter of about 700 nm.

Introduction

Environmental and economic concerns have caused much interest in developing new technique to solve the plastic waste problem [1,2]. The disposal of waste plastic or polymer poses a serious problem, because plastics are not usually biodegradable. Landfill and incineration of plastics waste are reasonable cheap method, but environmental consideration give rise to many major problems. Therefore, alternative methods for plastic and polymer waste recycling will be required. For this reason, various techniques for recycling waste plastics effectively by chemical, thermal recycle and material recycle have been actively developed. Material recycle among them is thought to be the most recommended one, when taking account of waste's energy and natural resources and environmental pollution.

Expanded polystyrene (EPS) is commonly used for insulation and packing materials. EPS is manufactured in the form of very small beads of polystyrene with a molecular weight between 160,000 and 260,000 and contains 4 to 7% blowing agent, usually pentane or butane. Many industries use EPS because of its versatility, dimensional stability, cleanliness, and low cost. However, EPS is one of the least economical polymer products to recycle because it contains so much air, making the bulk volume uneconomical to transport to recycle facilities. As a result, EPS usually ends up in land fills or is incinerated. Conventional recycling process such as thermal, chemical and material recycle required high energy consumption. Nanofibers using natural solvent will not only allow one to meet increasingly strict regulations but also have a positive impact on production quality. If EPS can be recycled into a useful nanofiber for which large lengths are produced per mass of polymer then the economics may be more favorable. Industrial application of nanofibers is growing.

This recycling system should have several advantages over the convention recycling system. These advantages include the decrease of environmental problem using the safe, high effective and biodegradable natural solvent. The new method can help to simplify the ventilation system and recovery system for toxic gas and improved working conditions. This electrospinning recycle method does not require a separation process. The solvent for producing PS nanofibers is used without any further treatment. The direct connection from collecting place to facilities such as filter company etc. will reduce not only recycling cost but also time. Conventional processes require a separation step to separate the PS solution in d-limonene into PS and d-limonene liquid. However this method can reduce the separation in the recovery process flow. This will enhance the economics.

Shin et al. (2004) recycled waste EPS polymer into a useful nanofiber for which large lengths are produced per mass of polymer and used in a coalescence filtration application. Polystyrene nanofibers with diameters of around 600 nm were produced by the electrospinning method. The addition of the nanofibers to conventional micron sized fibrous filter media improves the separation efficiency of the filter media from 68 to 88 % [3].

The electrospinning process is a method to produce polymer fibers from polymer solutions, with diameters in the range of 10-500 nm and high surface areas per unit mass. Nanofibers, due to their high ratio of surface area to mass and extraordinary small diameters around 100 nm, have received much attention for a wide variety of applications such as biomedical applications, sensors, and filtration [9-13].

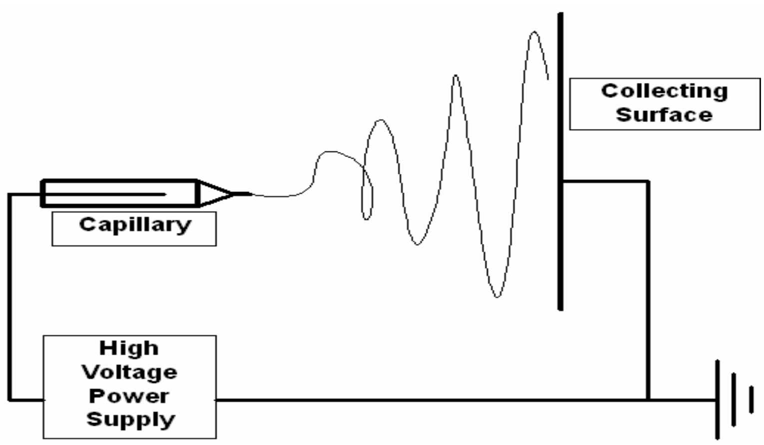

Figure 1. Electrospinning process

Figure 1 shows a schematic diagram of the apparatus used for electrospinning. The polymer solution is loaded into the syringe. A tube from the syringe connects to a needle and the needle is charged. The electrospinning process is driven by the electrical forces on free charges on the surface or inside a polymer solution. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of a cone protruding from a liquid drop of the polymer. As the jet stretches and elongates in the air, the solvent evaporates, leaving behind a charged polymer fiber that lays itself randomly on a collecting metal screen. Thus, continuous fibers are produced to form a non-woven fabric. Various parameters such as surface tension, viscoelastic properties of the polymer solution, conductivity, etc. affect the electrospinning process [11,14,15]. The relationship of polymer concentration and fiber was studied. The main factors of formation of the beaded nanofiber are solution viscosity, net charge density carried by the electrospinning jet and surface tension of the solution [11,16,17]. Changing the polymer concentration can vary the solution viscosity. Increasing the polymer concentration makes the solution viscosity higher. This effect favors the formation of smooth filaments [11]. Yarin [18] and Entov and Shmaryan [19] studied about instability of the jet of polymer solution and developed a mathematical model for the break-up jets of polymer liquids.

Electrospinning is conducted at room temperature with atmosphere conditions. Before the solution jet reaches the collecting screen, the solvent is evaporated. Most polymers are dissolved in some solvents before electrospinning. The polymer solution is introduced into the capillary tube for electrospinning. Some solvents may emit unpleasant smell or toxic gas, so the processes should have a ventilation system and recovery system. An extra cleaning process or time for evaporating solvent will be required to remove the residue of solvent on the fiber.

An aromatic hydrocarbon, toluene, chlorinated aliphatic hydrocarbon, methyl ethyl ketone, ethyl acetate and a cyclic hydrocarbon are well known PS solvents. Usually solvents such as DMF, THF, toluene and DMAc etc. are used and PS dissolved in these solvents have been successfully electrospun into PS nanofibers. Noguchi et al. developed a method to shrink EPS using *d*-limonene. The volume of EPS can be reduce 1/20th using *d*-limonene. Recycled EPS has no molecular weight degradation and has original mechanical properties [2].

d-Limonene is a natural oil from the rind of citrus fruits. After the juicing process, the oil was extracted from peel. *d*-Limonene uses are versatile such as cleaner (household/institutional, adhesives, and paint), pesticide/herbicide/biocide, heat transfer fluid, and solvent. As a solvent, d-Limonene can replace a wide variety of products, including mineral spirits, methyl ethyl ketone, acetone, toluene, glycol ethers, and fluorinated and chlorinated organic solvents. *d*-Limonene is highly effective, safe, biodegradable and occurs in nature as the main component of the citrus peel oil. *d*-Limonene has high solubility of PS (40%), is safe and has good compatibility with various materials such as aluminum, stainless steel, ceramic, epoxy, PET, Nylon etc. In general, polyethylene and polypropylene should be avoided.

In this paper, the electrospun PS nanofiber from EPS solution dissolved in natural solvent, *d*-Limonene solvent will be studied and compared with PS nanofiber from PS solution dissolved in DMAc, THF, and DMF.

Experimental

EPS, from packaging of a chemical bottle from Aldrich was used without further purification. Two solutions were prepared in this study. First, EPS was dissolved in *d*-limonene to make solutions with concentrations up to 35 wt%. Second, polystyrene solution was prepared by dissolving 10 wt% waste EPS in 90 wt% DMAc and 20 wt% waste EPS in 80 wt% DMAc. The solutions were prepared at room temperature, and gently stirred. Solutions were spun from a glass pipette with tip opening range 1mm. A Gamma High Voltage Research, ES30P power supply was used to produce voltage about 20kV. A flat piece of aluminum foil, placed 20 cm below the tip of pipette, served as the grounded collector surface. A 10 ml quantity of EPS/*d*-limonene or EPS/DMAc solution was placed in a glass pipette. The pipette was clamped to a ringstand that 20 cm above the grounded aluminum foil. The ES30P power supply was connected to the copper wire which dipped in the polymer solution. The morphology of the electrospun nanofibers was observed with a Scanning Electron Microscope (Model No. JSM-5310).

Results and discussion

The morphology of fibers produced by the electrospinning process are compared. Figure 2 shows the PS nanofibers from EPS/DMAc solution. Figure 3 shows the PS nanofibers from EPS dissolved in *d*-limonene. Physical properties of d-limonene are presented in Table 1.

Table 1. Physical properties of *d*-limonene

Specific Gravity (25°C)	0.838 - 0.843
Flashpoint	> 43°C
Boiling Point	176°C
Evaporation Rate	0.2 (BuAc=1)
Water Solubility	Insoluble
Vapor Pressure (20°C)	<2mmHg
Melting Point	-96 °C

The concentration of EPS in the solution affects the electrospinning. If the concentration of polymer is too dilute the polymer jet may spray small drops instead of a continuous fiber jet, or it may spin out fibers that have beads of polymer (Figure 2(a) and Figure 3(a)). If the solution is too concentrated the electrical forces may not be strong enough to form the jet. At intermediate concentrations continuous fibers are formed. A 10 wt% solution of EPS in DMAc forms beaded fibers (Figure 2 (a)) whereas a 20 wt% solution forms smooth nanofibers (Figure 2(b), 2(c) and 2(d)). Figure 2(b)-(d) shows the SEM photographs of EPS nanofiber with 20 wt% concentration in different solvents. The EPS is completely dissolved in a proper amount of these three solvents, THF, DMF, and DMAc. EPS is dissolved in three solvents before electrospinning, as the processing condition is same except solvents. It was observed that the diameter of EPS nanofibers from EPS/THF, EPS/DMF and EPS/DMAc are from 200 nm to 500 nm. The average diameter and morphology of nanofibers from various solutions are different respectively. Solution properties such as viscosity, elasticity, conductivity and surface tension can influence the transformation of polymer solution into nanofibers. A similar trend was observed in PS nanofibers from EPS/*d*-limonene solution. Polystyrene was dissolved in d-limonene to form solutions that contained various amounts of polystyrene. The electrospinning jet stability of polystyrene is poor at low concentration (below 10 wt%) compared to other solvents such as THF, DMF, and DMAc. After polystyrene polymer jet initiation, the jet broke up to droplets at low concentration. Therefore it is difficult to collect continuous nanofibers.

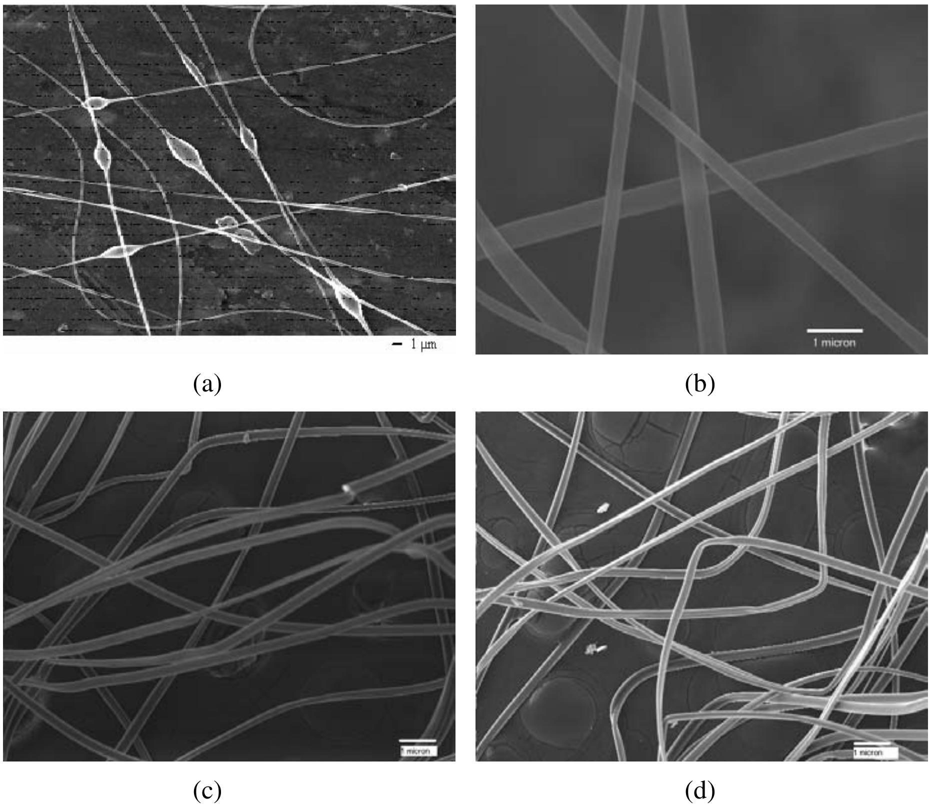

Figure 2. SEM image PS nanofibers (a) 10 wt% solution EPS in DMAc, (b) 20 wt% solution EPS in DMAc, (c) 20 wt% solution EPS in DMF, (d) 20 wt% solution EPS in THF

Various EPS/d-limonene concentration solutions were tested (Figure 3). Successfully EPS was recycled into the polymer nanofibers. The electrospun polystyrene nanofiber diameters vary from 300 to 900 nm, with an average diameter of about 700 nm at 30 wt% concentration. Changing the polymer concentration can vary the solution viscosity. At low concentrations below 15 wt%, electrospinning process produced a polymer nanofibers and droplets. As higher concentration, the quantity of droplets is decreased. However higher concentration above 50 wt% is difficult to overcome the surface tension between pipette and polymer solution. At the higher concentrations, nanofibers are more uniform in diameter and thinker than lower concentration.

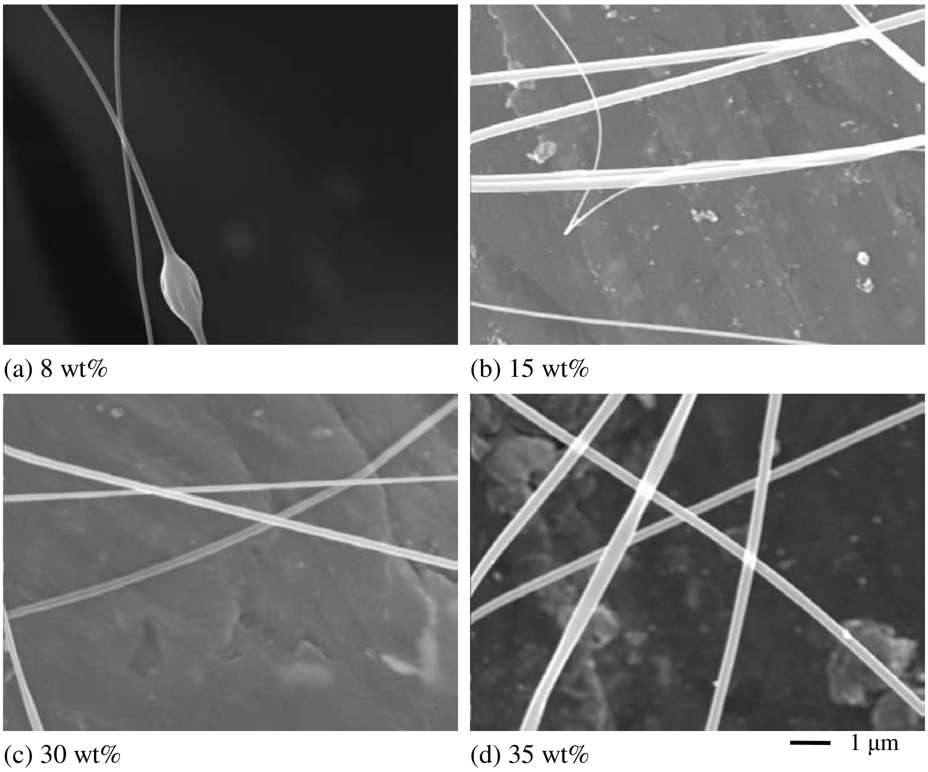

Figure 3. The morphology of beaded fibers verses solution concentration. Voltage is 20 kV, the tip-to-target distance is 20 cm. SEM images of EPS nanofibers (8 to 35 wt% solution EPS in *d*-limonene)

The electrospun beaded fibers are related to the capillary instability of the jet of polymer solution, surface tension of the solution, and viscoelastic properties of the polymer solution [18]. There are many parameters that can effect the transformation of polymer solutions into nanofiber through electrospinning process. Many researchers have studied processing parameters such as viscosity of polymer solution, voltage, tip-to-target distance, and surface tension [9-11, 15-17]. The effect of polymer solution concentration of electrospinning process has been studied [11, 15, 20]. Fong et al. [11] studied the formation of the beaded nanofibers. They found the polymer concentration affects the formation of the beads. The higher concentration of polymer solution less is likely to form beads and beaded fiber. The surface tension and viscoeleastic properties of the polymer solution are the main parameters for the formation of beaded nanofibers. Zong et al. [20] found that with 1wt% salt addition, the resulting of polymer nanofibers were bead free. The addition of salts improves the charge density on the surface of the solution, bringing more electric charges to the polymer jet during the electrospinning. Deitzel et al.[15] have found that solution concentration affects fiber size, with fiber diameter increasing with increasing solution concentration according to a power law relationship.

The experimental result shows the alternative method for waste EPS recycling using natural solvent, *d*-limonene. The electrospun PS nanofibers from EPS solution dissolved in natural solvent, *d*-limonene have similar diameters compared with PS nanofiber dissolved in DMAc, THF, and DMF.

Conclusions

Various EPS/d-limonene concentration solutions were tested. The EPS is completely dissolved in a proper amount of these three solvents, THF, DMF, and DMAc. It was observed that the diameter of EPS nanofibers from EPS/THF, EPS/DMF and EPS/DMAc is from 200 nm to 500 nm. Successfully EPS was recycled into the polymer nanofibers from EPS/d-limonene solution. The electrospun polystyrene nanofiber diameters vary from 300 to 900 nm, with an average diameter of about 700 nm at 30 wt% concentration. The average diameter and morphology of nanofibers from various solutions are different respectively because solution properties such as viscosity, elasticity, conductivity and surface tension can influence the transformation of polymer solution into nanofibers. *d*-limonene is a good solvent for polystyrene. However the electrospinning jet stability of polystyrene is poor at low concentration (below 10 wt%) compared to other solvents such as THF, DMF, and DMAc.

Acknowledgements. This work was supported by Ahlstrom Paper Group, Donaldson Company, Fleetguard, Hollingsworth and Vose, Parker Hannifin and the Produced Water Seminar. This work was also supported by the National Science Foundation grant CTS-0310429 and DMI-0403835.

References

1. Bajdur W, Pajaczkowska J, Makarucha B, Sulkowska A, and Sulkowski WW (2002) European Polymer J 38:299.
2. Noguchi T, Inagaki Y, Miyashita M, Watanabe H (1998) Packaging Tech and Sci 11:19.
3. Tacuchi Y, Tanaka M (2001) J of Appl. Polym Sci 80:2662.
4. Taguchi, Y, Tanaka, M. (2003) J Appl. Polymer Sci. 88:483.
5. Guoxi, X, Rui, L, Qinhu, T, Jinghua, L (1999) J Appl Polymer Sci. 73:1139.
6. Huang F-C, Ke C-H, Kao C-Y, Lee W-C (2001) J Appl Polym Sci. 80:39.
7. Karaduman A, Şimşek EH, Çiçek B, Bilgesü AY (2002) J. Analy. Appl. Pyrolsis 62:273.
8. Shin C, Chase GG, Reneker DH (2004) 9th World Filtration Congress 18, New Orleans, Louisiana paper 4 session 236.
9. Reneker DH, Chun I (1996) Nanotechnology 7:216.
10. Doshi J, Reneker DH (1995) J of Electrostatics, 35:151.
11. Fong H, Chun I, Reneker DH (1999) Polymer 40: 4585.
12. Reneker DH, Yarin AL, Fong H, Koombhongse S (2000) J Appl. Phys 87:4531.
13. Shin C, Chase GG, Reneker DH (2004) 9th World Filtration Congress 18, New Orleans, Louisiana paper 4 session 236.
14. Frenot A, Chronakis LS (2003) Current Opinion in Colloids and Interface Sci 8:64.
15. Deitzel, JM, Kleinmeyer J, Harris NC, Beck Tan NC (2001) Polymer 42:261.
16. Jaeger R, Schonherr H, Vancso J (1996) Macromolecules 29:7634.
17. Jaeger R, Bergshoef M, Batlle C, Schonherr H, Vancso J (1998) Macromolecular Symposium 127:141.
18. Yarin AL (1993) Free liquid jets and films: hydrodynamics and rheology, New York: Wiley.
19. Entov VM, Shmaryan LE (1997) Fluid Dynamics 32:696.
20. Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B (2002) Polymer 43:4403.