Effect of Hyperbranched Poly(ester amine) Additive on Electrospinning of Low Concentration Poly(methyl methacrylate) Solutions

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ABSTRACT: Electrospinning of low concentration polymer solutions has the advantage of producing fibers with small diameters, but unfortunately beaded fibers are often observed. This article reports the use of hyperbranched poly-(ester amine) (PEA) as an additive for low concentration polymer solutions to eliminate beads and improve the fiber uniformity. Electrospinning of low concentration poly(methyl methacrylate) solutions was investigated. With only 1 wt % hyperbranched PEA, the fiber uniformity was significantly improved. The principle of improvement was investigated by measuring the solution properties, and it is inferred that the improvement is attributed to the significant increase in solution conductivity. The solution viscosity and surface tension only change slightly. The versatility of this approach was demonstrated by electrospinning low concentration solutions of two other polymers: polystyrene and polyoxymethylene. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3687–3696, 2010

Key words: additives; fibers; hyperbranched; electrospinning; bead-free

INTRODUCTION

Electrospinning has been gaining more attention in recent years as a simple and effective processing technique for producing nano to micro-scale fibers, which are one to several orders of magnitude thinner than those fabricated by conventional melt or solution spinning. Owing to a number of characteristics such as high specific surface area, high aspect ratio, and high porosity, the electrospun fiber mats are expected to have a wide range of applications such as optoelectronics, sensor technology, catalysis, filtration, and medicine.[1,2]

The solution concentration is one of the most important parameters in controlling the electrospinning process of polymer solutions. A minimum concentration is needed to ensure sufficient chain entanglement for successful electrospinning. When the solution concentration is low, beads, beaded fibers, or beads-on-string structure are often obtained. There are some work[3–7] dealing with the minimum concentrations for obtaining beaded fibers and uniform bead-free fibers, and some empirical rules were reported. Mckee et al.,[3] investigated a series of linear and branched poly(ethylene terephthalate-*co*-ethylene isophthalate) copolyesters and pointed out that the entanglement concentration (C_e) is the minimum concentration required for obtaining beaded fibers, and that 2–2.5 C_e is the minimum concentration required for producing uniform fibers. Other researches[4,5] showed that the onset of fiber formation and the minimum concentration for uniform fiber formation vary with the type, molecular weight (MW) and molecular weight distribution (MWD) of polymers. Koski et al.,[6] used Berry number $[\eta]C$ to discuss the minimum concentration for obtaining fibrous structure. For aqueous poly(vinyl alcohol) (PVA) solutions investigated in their work, the minimum concentration corresponds to Berry number $[\eta]C \sim 5$. Shenoy et al.,[7] established a correlation between chain entanglements and fiber formation based on experimental data obtained from electrospinning of several polymer/solvent systems. For initiation of fibers, the number of entanglements $(n_e)_{soln} = 2$, and $\phi_p M_w = 2M_e$; whereas for complete fiber formation, $(n_e)_{soln} \geq 3.5$ i.e., $\phi_p M_w \geq 3.5M_e$ (Here, M_e and M_w are the entanglement and weight-average MW, ϕ_p is the volume fraction of polymer). This allows prediction of polymer concentration (ϕ_p) for successful electrospinning.

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The interest in electrospinning of low concentration solutions is to obtain fibers with small diameters, as the fiber diameter usually increases almost linearly with the increase in solution concentration.[8] A few attempts[9–14] have been made to eliminate beads and shown success by incorporating a small amount of additives (typically 1 wt % to polymer) to low concentration electrospinning solutions. The principle is to modify one or two of the three solution properties: conductivity, solution viscosity, and surface tension. Ionic additives such as salts,[9] cationic surfactants,[10] and polyelectrolytes[11] have been proved to be useful in electrospinning of low concentration solutions by increasing the solution conductivity. Lin et al.,[10] added a small amount (10^{-6} mol/L) of tetrabutylammonium chloride or dodecyltrimethylammonium bromide to a low concentration polystyrene (PS) solution in N, N-dimethylformamide (DMF)/tetrahydrofuran (THF) (1 : 1), and they discovered that the beads were completely eliminated. Son et al.,[11] reported that the addition of 2 wt % poly(allylamine hydrochloride) or poly(acrylic acid sodium salt) into aqueous polyethylene oxide (PEO) solutions can lower the minimum concentration for electrospinning. The usefulness of viscosity modifiers in electrospinning of low concentration solutions was also reported. Lin et al.,[12] used chitosan, a commonly used food thickener, for elctrospinning of low concentration PVA solutions. The presence of 1 wt % chitosan (to PVA) can considerably improve the fiber uniformity. The improvement may be attributed to the increase in both solution viscosity and conductivity. Talwar et al.,[13] explored the use of associative polymers in improving fiber formation of low concentration PEO solutions, which gave mostly beaded fibers. With only 0.2 wt % of the associative polymer, the solution viscosity increased considerably and almost uniform fibers were obtained. Hunley et al.,[14] used hyperbranched surface-migrating additive to eliminate beads of poly(methyl methacrylate) (PMMA) fibers obtained from electrospinning of low concentration solutions by mediating surface tension of the solutions. With only 1 wt % partially perfluorinated hyperbranched polyethyleneimine additive, uniform fibers were obtained even at concentrations below C_e.

In this article, another type of hyperbranched polymer, poly(ester amine) (PEA), which does not have the ability of surface migration, is used for electrospinning of low concentration PMMA solutions to eliminate beads. The principle of this approach was investigated by measuring the solution properties. The idea was extended to other polymer/solvent systems, PS/DMF : CHCl$_3$[15], and polyoxymethylene (POM)/1,1,1,3,3,3-hexafluoroisopropanol (HFIP)[16] to show versatility of this approach.

EXPERIMENTAL

Materials

PMMA and PS were purchased from Mitsubishi chemical corp. and Formosa Plastics Group, respectively. GPC analysis (Viscotek Trisec Model 302) revealed $M_w = 110$ kg/mol, $M_w/M_n = 1.6$ for PMMA and $M_w = 280$ kg/mol, $M_w/M_n = 5.0$ for PS. POM was a commercial grade powder (M90) without any additives and supplied by Yunnan Yuntianhua Co. Ltd, China. It is a copolymer type with a melt flow index of 9.0 g/10 min and M_w of 68,000. HFIP, chloroform, and DMF were used as solvents without further purification. The hyperbranched polymer, PEA, was synthesized as previously reported by Gao et al.,[17] from 1-(2-aminoethyl)piperazine and poly(ethylene glycol) diacrylate (PEODA; $CH_2=CHCOO(CH_2-CH_2O)_3OCCH=CH_2$), which were purchased from Fluka and Aldrich respectively, and used as received.

Electrospinning

For PMMA and PS, 1 : 1 (v : v) DMF : CHCl$_3$ mixture was used as the solvent, and the hyperbranched PEA solution in CHCl$_3$ obtained as the product of the synthesis was used without any further treatment. For POM, HFIP was used as the solvent, the hyperbranched PEA solution in CHCl$_3$ was poured into 300 mL diethyl ether, and the precipitate was washed and collected. Electrospinning solutions were prepared at the desired concentrations and stirred for 24 h before electrospinning. Electrospinning was conducted under ambient conditions. The solution was placed into a 10 mL glass syringe capped with a 9-gauge blunt end needle. The positive lead from a high voltage supply was connected via an alligator clip to the external surface of needle. A rectangular (15 × 15 cm) aluminum foil was placed 20 cm from the tip of the needle as the collector. The voltage was kept at 20 kV.

Characterization of the electrospun fiber mats

The morphology of the fibers was examined using a JSM-7401 field emission gun scanning electron microscope (FESEM) at an accelerating voltage of 1 kV. TEM (JEM 2010 operated at 120 kV) was used to investigate the dispersion of PEA additive in the electrospun fibers. Cetyltrimethylammonium bromide (CTAB, 0.5 wt %) was added to the electrospinning solution to make thinner fibers for TEM observation. The fibers were directly electrospun onto Cu grids covered with an ultra-thin carbon layer, and stained with RuO$_4$ for 15 min. The surface tension of solutions was measured with a tensiometer (DCAT 21, Dataphysics). The solution viscosity was
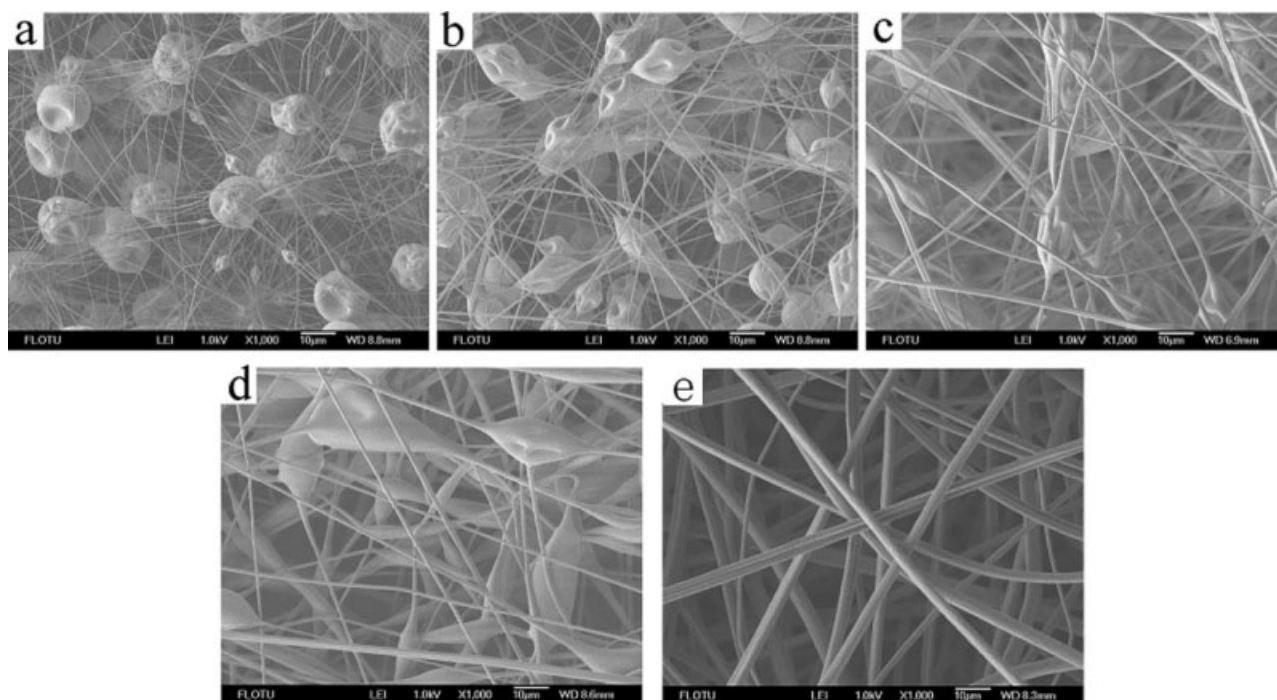
Figure 1 FESEM images of PMMA fibers obtained with different solution concentrations: (a) 17 wt %, (b) 19 wt %, (c) 20 wt %, (d) 21 wt %, and (e) 22.5 wt %.

measured with a rotating viscometer (Model NDJ-8S, Shanghai Rex Instruments). The solution conductivity was tested with a conductivity instrument (Model DDSNDJ-307, Shanghai Rex Instruments). X-ray photoelectron spectroscopy (XPS) data were

obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV. The water contact angles of the
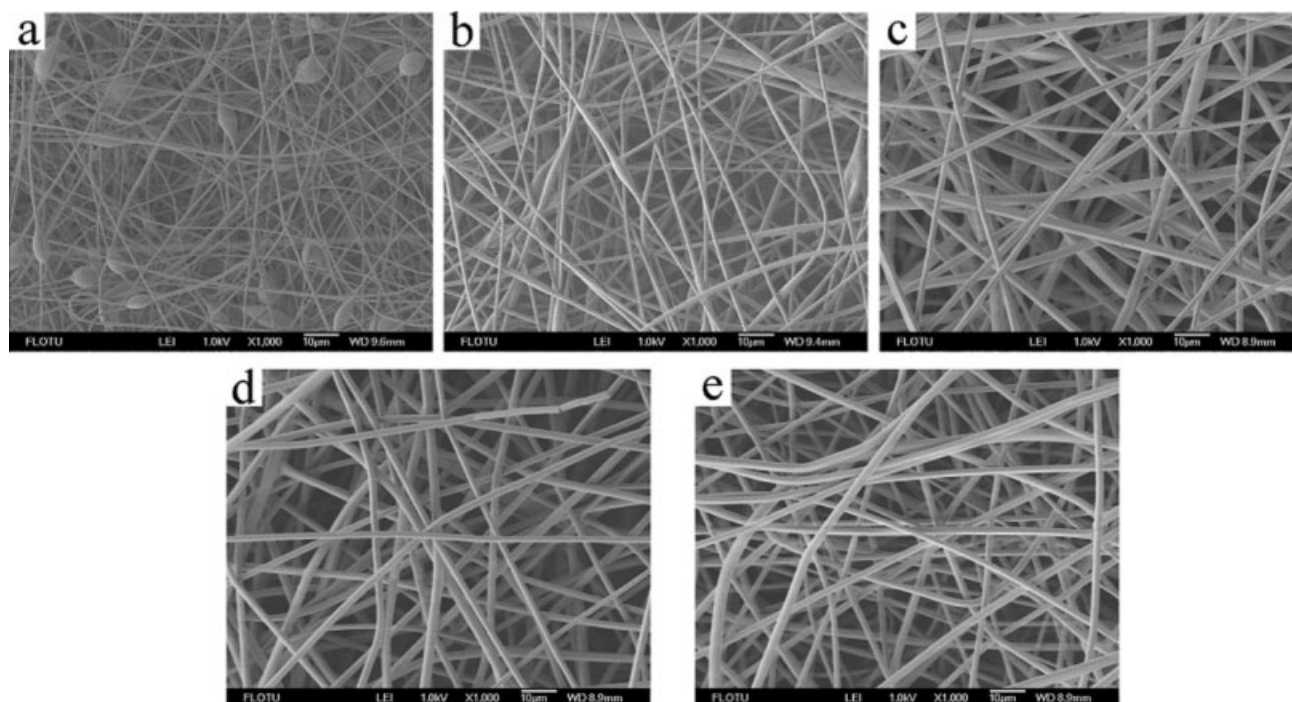

Figure 2 FESEM images of PMMA fibers obtained from solutions containing 1 wt % hyperbranched PEA at concentrations of (a) 17 wt %, (b) 19 wt %, (c) 20 wt %, (d) 21 wt %, and (e) 22.5 wt %.
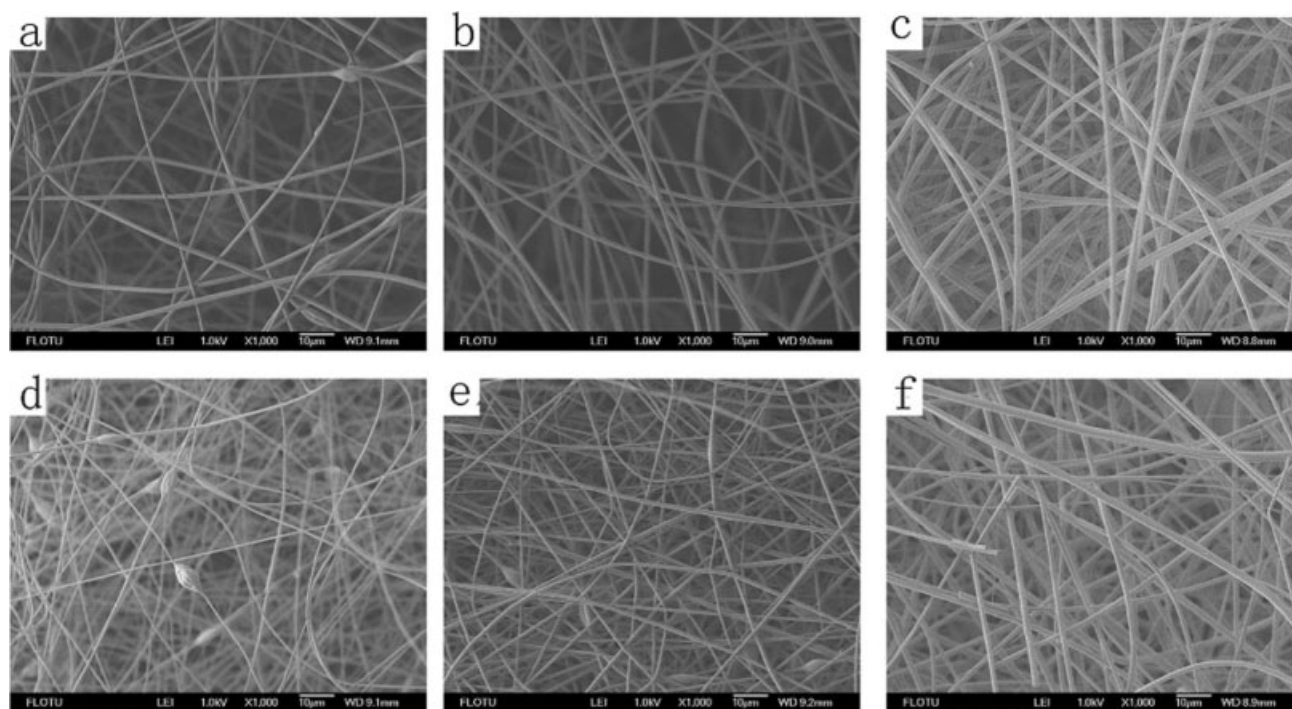
Figure 3 FESEM images of PMMA fibers obtained at different solution concentrations: (a–c) 19 wt %, (d–f) 17 wt %, with different amounts of hyperbranched PEA: (a) 2 wt %, (b) 3 wt %, (c) 5 wt %, (d) 2 wt %, (e) 3 wt %, and (f) 5 wt %.

electrospun fiber mats containing different amounts of hyperbranched PEA were measured using a contact angle analyzer (Dataphysics oca20).

RESULTS AND DISCUSSION

Electrospinning of PMMA solutions with and without hyperbranched PEA additive

Electrospinning of PMMA over a wide range of concentrations has been well investigated in various solvents or solvent mixtures.[4,5,14,18,19] The minimum concentration for forming beaded fibers is found around C_e and that for obtaining uniform fibers is 1.2–3.4 C_e, depending on MW and MWD of PMMA.[4,5] In this work, PMMA solutions with different concentrations in 1 : 1 DMF : CHCl$_3$ were prepared and electrospun. Figure 1 shows FESEM images of the electrospun fibers. When the concentration was relatively low (17–21 wt %), beads-on-string structure was observed. The shape of the beads changed from quasi-spherical to spindle-like

TABLE I
The Fiber Morphology and Average Fiber Diameters of PMMA Fibers

| Entry	PMMA Concentration (wt %)	PEA Content (wt %)	Fiber morphology	Average fiber diameter (μm)
1	17	0	Beaded	0.54 ± 0.08
2	19	0	Beaded	0.76 ± 0.11
3	20	0	Beaded	0.99 ± 0.16
4	21	0	Beaded	1.24 ± 0.18
5	22.5	0	Bead-free	2.24 ± 0.26
6	17	1	Beaded	0.90 ± 0.12
7	19	1	Beaded	1.25 ± 0.15
8	20	1	Bead-free	1.82 ± 0.38
9	21	1	Bead-free	2.17 ± 0.28
10	22.5	1	Bead-free	2.33 ± 0.24
11	17	2	Beaded	0.90 ± 0.11
12	17	3	Beaded	1.14 ± 0.18
13	17	5	Bead-free	1.74 ± 0.35
14	19	2	Beaded	1.41 ± 0.23
15	19	3	Bead-free	1.42 ± 0.18
16	19	5	Bead-free	1.87 ± 0.35
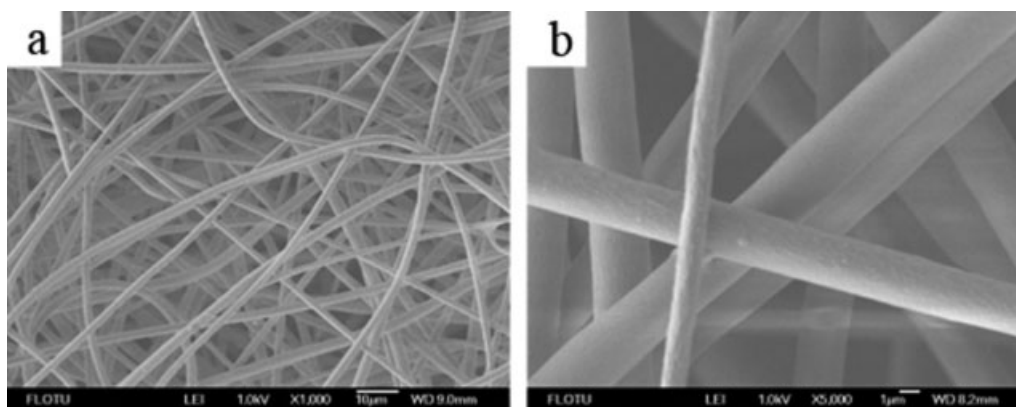
Figure 4 FESEM images of PMMA fiber mat containing 1 wt % hyperbranched PEA after soaking in water for 2 days.

as the concentration increased from 17 to 21 wt %. When the solution concentration increased to 22.5 wt %, uniform bead-free fibers were observed. The C_e of the PMMA is 16 wt % as obtained from viscosity measurement. Thus, beaded fibers were obtained above C_e and the minimum concentration for obtaining uniform fibers is 1.4 C_e, being in agreement with the results reported by Mckee et al.,[4] who were work-

ing on PMMA with a slightly higher MW in the same type of solvent mixture with similar composition.

When 1 wt % hyperbranched PEA was added to the aforementioned electrospinning solutions (Fig. 2), the size and density of the beads were considerably smaller at relatively low concentrations (17 and 19 wt %), and the beads completely disappeared at higher concentrations (20 and 21 wt %).
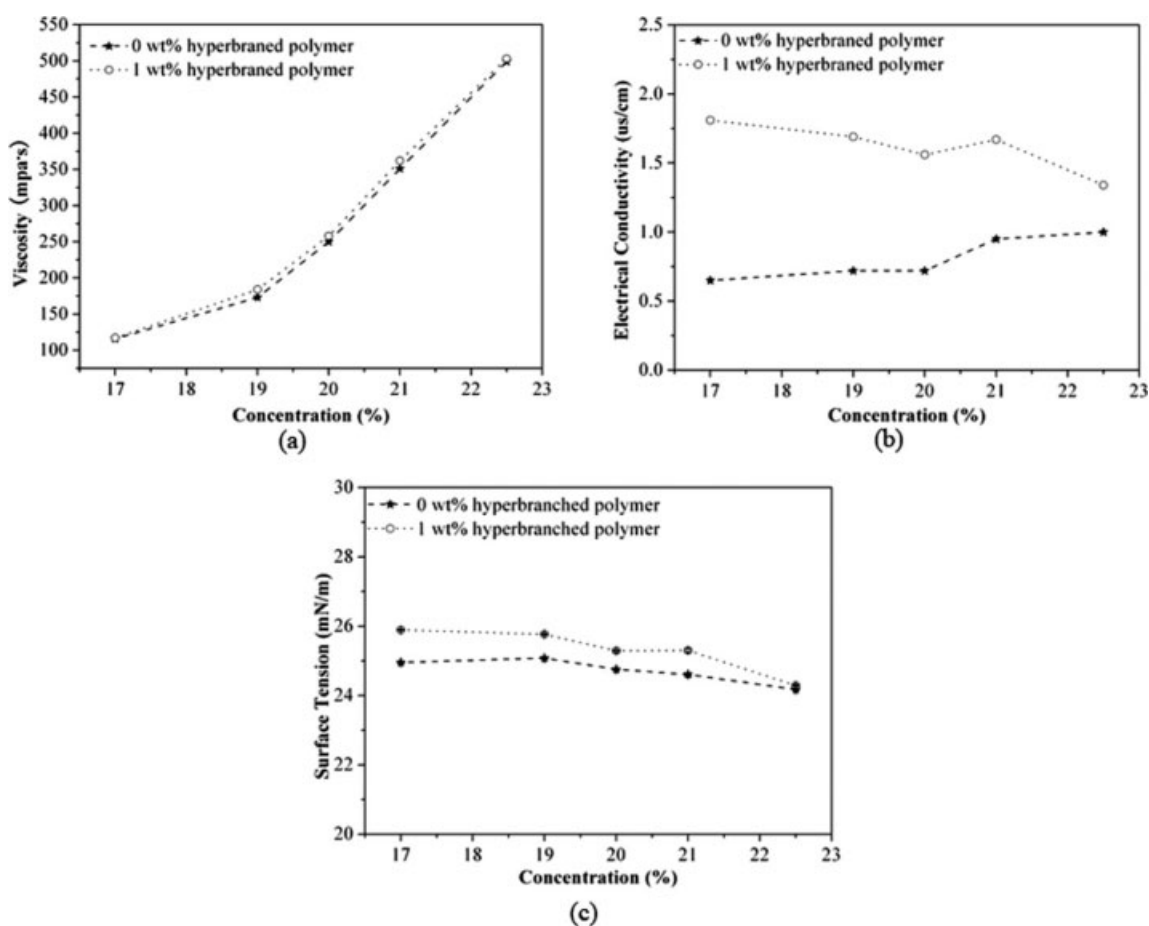

Figure 5 The viscosity (a), conductivity (b) and surface tension (c) of PMMA solutions at different concentrations with and without 1 wt % hyperbranched PEA.
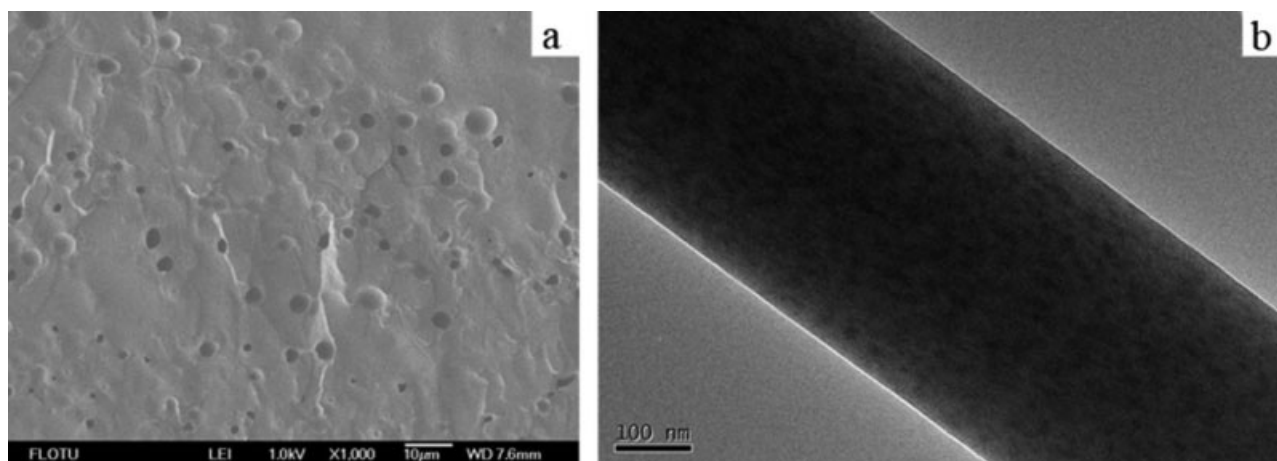
Figure 6 (a) FESEM image of a solution cast film and (b) TEM image of an electrospun fiber.

To know whether the beads could be completely eliminated at low concentrations (17 and 19 wt %) where the beads still remained with the addition of 1 wt % PEA, more PEA was added to the electrospinning solutions. As shown in Figure 3, uniform bead-free fibers were observed when 3 and 5 wt % PEA were used for solution concentrations of 19 and 17 wt %, respectively. The above observations reveal the effectiveness of hyperbranched PEA in eliminating beads and improving the electrospinnability of low concentration PMMA solutions.

The fiber morphology and average fiber diameters are listed in Table I. After the addition of 1 wt % PEA, the fibers become larger due to elimination of large beads. The average fiber diameter of the bead-free fibers obtained from 22.5 wt % PMMA solution has practically no change, indicating that the effect of the increase in solution viscosity is balanced with that in solution conductivity. As seen from Entry 15 and 16, when PEA mass fraction increases from 3 to 5 wt %, the average fiber diameter increases slightly due to the increase in solution viscosity, which shows more influence than the increase in solution conductivity. The size distribution of the fibers in all cases does not change obviously.

For comparison, linear PEA was synthesized from the same monomers using a method described in the literature.[20] In contrast to the hyperbranched PEA, the linear analogue is not soluble in common organic solvents such as DMF, $CHCl_3$, and THF, and thus not suitable for use in electrospinning of PMMA from 1 : 1 DMF : $CHCl_3$. The advantage of hyperbranched polymer in solubility gives the possibility to hyperbranched PEA in use for improving the electrospinnability of low concentration PMMA solutions.

It should be noted that the hyperbranched PEA is also soluble in water. This property allows its removal from the electrospun fibers by washing with

water. We examined this possibility by soaking a PMMA fiber mat containing 1 wt % PEA in water for 2 days, and no N was detected by XPS (the surface N content is 1.41% before soaking in water). Figure 4 shows the FESEM micrographs of the fibers after soaking in water. It could be seen that the fiber morphology was not altered by water treatment. The average fiber diameter has no obvious change after water treatment (1.74 µm as compared to 1.82 µm), and the fiber surface seems to be smooth [Fig. 4(b)].

PMMA solution properties with and without hyperbranched PEA

The electrospinnability of polymer solution and the fiber morphology are related to the solution properties when all other conditions are kept constant. To find out the principle of improvement in electrospinnability of low concentration PMMA solutions in the presence of hyperbranched PEA additive, the
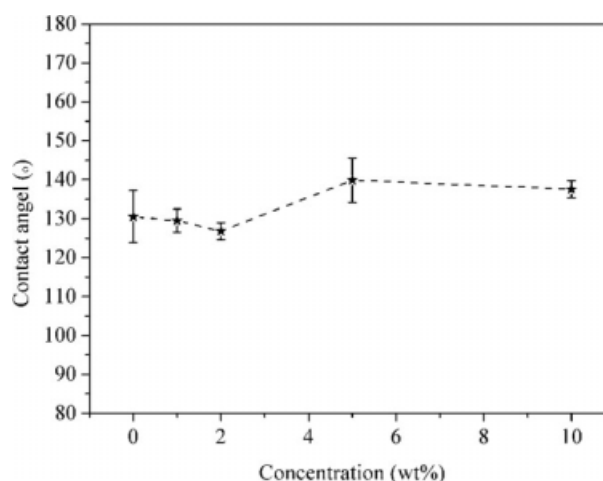

Figure 7 The water contact angles of the electrospun fiber mats containing different amounts of hyperbranched PEA.
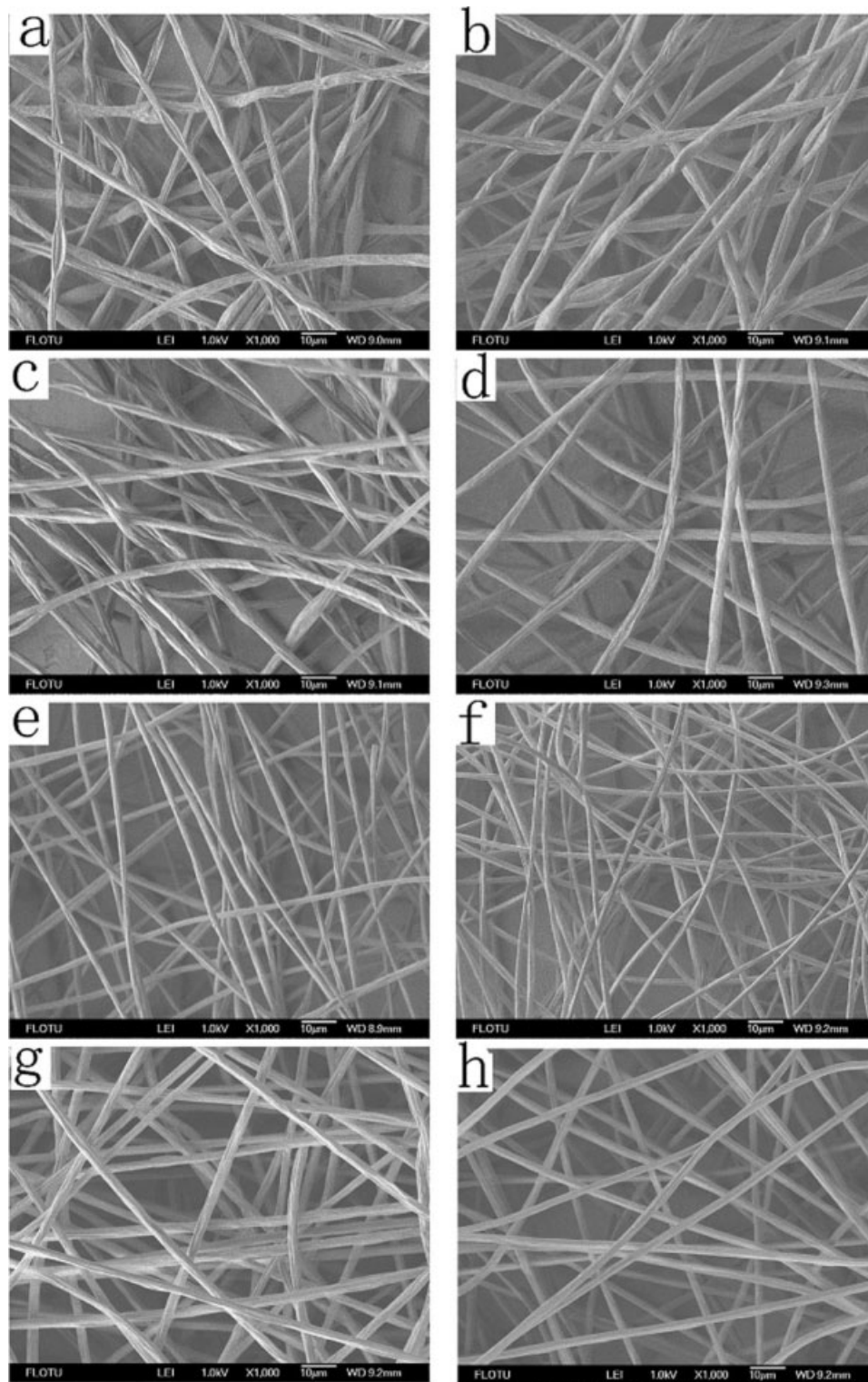
Figure 8 FESEM images of PS fibers electrospun from solutions at concentrations of (a) 6 wt %, (b) 7.5 wt %, (c) 9 wt %, (d) 11 wt % without hyperbranched PEA, and (e) 6 wt %, (f) 7.5 wt %, (g) 9 wt %, (h) 11 wt % with 1 wt % hyperbranched PEA.

solution properties, viz. solution viscosity, conductivity, and surface tension, were measured with and without the presence of 1 wt % PEA. The results are shown in Figure 5.

The solution viscosity is almost unchanged after the addition of 1 wt % PEA at the same PMMA concentration, while the surface tension has a slight increase. However, the conductivity increases

TABLE II
The Fiber Morphology and Average Fiber Diameters of PS and POM Fibers

Entry	Polymer/Concentration (wt %)	PEA content (wt%)	Fiber morphology	Average fiber diameter (μm)
17	PS/6	0	Beaded	2.65 ± 0.30
18	7.5	0	Beaded	2.78 ± 0.46
19	9	0	Beaded	2.96 ± 0.58
20	11	0	Bead-free	3.07 ± 0.30
21	6	1	Bead-free	1.84 ± 0.19
22	7.5	1	Bead-free	1.79 ± 0.22
23	9	1	Bead-free	2.75 ± 0.29
24	11	1	Bead-free	2.81 ± 0.27
25	POM/2	0	Beaded	0.39 ± 0.06
26	3	0	Beaded	0.70 ± 0.12
27	4	0	Bead-free	0.94 ± 0.13
28	2	1	Bead-free	0.25 ± 0.04
29	3	1	Bead-free	0.27 ± 0.04
30	4	1	Bead-free	0.29 ± 0.07

significantly with the addition of 1 wt % PEA at all the concentrations, since the conductivity of PEA is much higher than that of PMMA due to the existence of polar groups in the structure. For example, the conductivity of 20 wt % solution changes from 0.7 to 1.5 μs/cm, an increase of 100%. According to Lin et al.,[10] the increase in solution conductivity suggests the increase in net charge density of the jet, and, thus, the whipping instability is enhanced and the jet is stretched under stronger force, resulting in bead-free fibers. Therefore, the improved electrospinnability in this case can be attributed to the increase in solution conductivity.

When more hyperbranched PEA is added to a solution with fixed PMMA concentration, the conductivity increases sharply and almost linearly with the increase in PEA content while the viscosity only increases slightly. For example, when PEA content increases to 3 and 5 wt %, the conductivity of 19 wt % solution increases 3.2 and 4.6 times, respectively, while the viscosity only increases to about 220 mPa s, a value which cannot produce uniform fibers according to Figure 5(a). Therefore, the improvement in electrospinnability with more PEA is also resulted from the increase in solution conductivity.

Location of hyperbranched PEA in the fibers

Different from hyperbranched PFA used in the work of Hunley et al.,[14] hyperbranched PEA does not have the ability of surface-migration. When a 20 wt % PMMA solution containing 10 wt % (to PMMA) PEA was cast into film at room temperature, phase separation occurred. Sea-island structure was observed [Fig. 6(a)]. The phase morphology of the electrospun fibers were investigated by TEM. RuO_4 staining was used to selectively stain PEA. As the fiber diameters are larger than 1 μm, it is hard to see

the phase morphology under TEM, therefore, a small amount of ammonium salt CTAB (0.5 wt % to PMMA) was used to make thinner fibers to facilitate TEM observation. Figure 6(b) shows TEM image of PMMA fibers containing 5 wt % PEA. Similar to the cast film, sea-island structure was observed with PEA as the dispersed phase and PMMA as the continuous phase. This type of fiber morphology was previously observed for poly(L-lactide-co-ε-caprolactone)/collagen electrospun fibers.[21]

XPS analysis of the electrospun fiber mat obtained from a 20 wt % PMMA solution containing 10 wt % PEA gave N/C ratio of 0.04, which is much smaller than the calculated value for pure PEA (0.17). This indicates that the surface is not covered with pure PEA, supporting the sea-island fiber morphology.

Contact angle measurements of a series of the electrospun fibers containing different amounts (0, 1, 3, 5, 10 wt %) of PEA reveal that the contact angle with water does not decrease with more addition of PEA (Fig. 7). This indicates that the addition of PEA additive has no influence on wettability of PMMA fiber mats.

Generalization of the approach

In most work found in the literature, the effectiveness of the additive for improvement of fiber morphology was only demonstrated with one model polymer/solvent system. To show the versatility of hyperbranched PEA in eliminating beads, other polymer/solvent systems (PS/1 : 1 DMF : $CHCl_3$ and POM/HFIP), were also investigated.

Figure 8 shows the morphology of the electrospun fibers obtained from PS solutions in 1 : 1 DMF : $CHCl_3$ with and without 1 wt % hyperbranched PEA. The beads in 6, 7.5, and 9 wt % solutions are completely eliminated with the use of 1 wt % PEA.
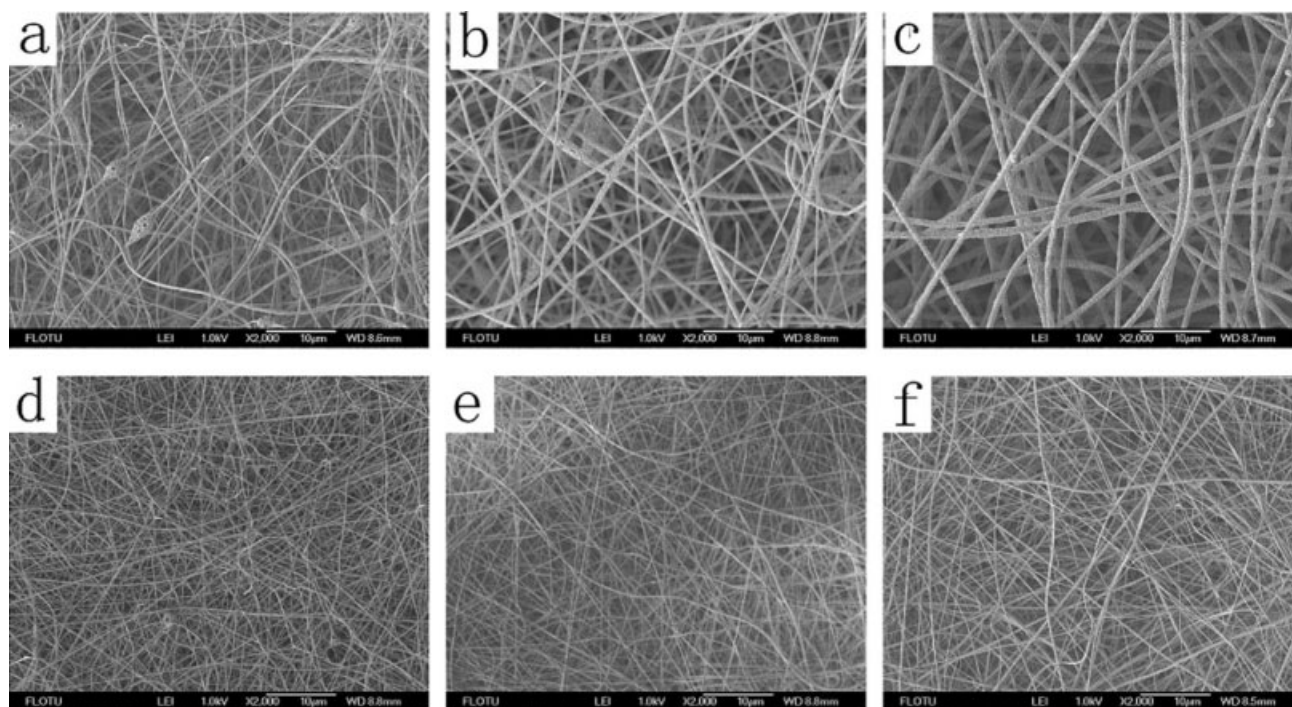
Figure 9 FESEM images of POM fibers electrospun from solutions at concentrations of (a) 2 wt %, (b) 3 wt %, (c) 4 wt % without hyperbranched PEA, and (d) 2 wt %, (e) 3 wt %, (f) 4 wt % with 1 wt % hyperbranched PEA.

To verify the principle of improvement in fiber morphology, the solution properties of 7.5 wt % PS solutions with and without 1 wt % PEA were measured. The viscosity and surface tension have a slight increase from 25 to 29 mpa s, and from 23.2 to 31.1 mN/m, respectively, while the conductivity increases by 1.4 times from 0.89 to 2.15 µs/cm. Therefore, it can be concluded that the improvement in fiber morphology is due to the conductivity increase, similar to the case of PMMA discussed earlier. The fiber morphology and average fiber diameters are listed in Table II. After the addition of 1 wt % PEA, the fiber diameters decrease, being different from the case of PMMA. This is because the beads in PS fibers are much smaller than those in PMMA fibers (as seen from Fig. 8), and the increase in solution conductivity causes the decrease in fiber diameter.

Figure 9 shows the morphology of the electrospun fibers obtained from POM solutions in HFIP with and without 1 wt % hyperbranched PEA. The beads in 2 and 3 wt % solutions are completely eliminated with the use of 1 wt % PEA. The conductivities of 2 wt % POM solutions with and without 1 wt % PEA were measured, and an increase of 8.6 times from 1.2 to 11.5 µs/cm was found when 1 wt % PEA was added. Therefore, similar to the cases of PMMA and PS discussed above, the improvement in fiber morphology is due to the conductivity increase. As seen from Table II, the average fiber diameters decrease after the addition of 1 wt % PEA due to the significant increase in solution conductivity.

CONCLUSIONS

Hyperbranched PEA is an effective and versatile additive for electrospinning of low concentration polymer solutions to improve the fiber uniformity, as demonstrated by electrospinning of low concentration solutions of PMMA, PS, and POM in different types of solvents. For solutions with concentrations slightly lower than the minimum concentration for obtaining uniform bead-free fibers, the beads can be completely eliminated by adding only 1 wt % hyperbranched PEA, while for solutions with much lower concentrations (near C_e), the beads can be eliminated with more addition of hyperbranched PEA. The principle of improvement in fiber uniformity can be attributed to the increase in solution conductivity. The ability to electrospin low concentration polymer solutions would allow production of thinner fibers.

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