Associative Polymer Facilitated Electrospinning of Nanofibers

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ABSTRACT: Electrospun nanofibers present an exciting avenue for development of novel materials with well-defined functionalities; however, broadening the scope of electrospinning to a diverse range of polymers remains a major challenge. In particular, a recurring issue in this field is the inability to spin polymers at lower concentrations in order to achieve smaller fiber diameters. This work explores the use of associative polymers as a means to overcome this limiting factor that prevents the electrospinnning of nanofibers from low-concentration polymer solutions. Hydrophobically modified alkali-soluble emulsion (HASE) polymers are comblike associative polymers with pendant hydrophobes that form a network in aqueous media consisting of both intra- and intermolecular hydrophobic junctions. Rheological measurements reveal that addition of HASE polymers in small amounts to poly(ethylene oxide) solutions leads to considerable increase in viscosity as well as dynamic moduli of the system. More importantly, these rheological changes are translated into significant changes in fiber morphology, from beaded to uniform nanofibers, as well as reduction in fiber diameter. The concept of using rheology modifiers is further extended to another associative polymer, guar galactomannan, which associates through a different mechanism. Similar improvements in fiber formation are observed, thereby lending credence to the universality of this approach.

Introduction

Compared to conventional fiber spinning techniques such as melt or solution spinning, the size of fibers produced via electrospinning is at least an order of magnitude lower.[1] Owing to their small diameter, the resulting nonwoven fiber mats possess a high specific surface area, a large degree of porosity, and ample flexibility in tailoring the properties of these fibers to specific applications such as protective clothing,[2] wound dressing,[3] filtration devices, membranes, electronic devices, and reinforced composites.[4,5]

The process of electrospinning is relatively easy to implement, and a large number of studies have been published dealing with electrospinning different polymer systems — either individually or in conjunction with a second polymer — as well as in examining the role of various process and solution parameters on the electrospinning process.[6,7] Nonetheless, there are issues related to poor spinnability or lack of spinnability of polymer solutions at dilute concentrations. In such cases, the formation of beads or beads-on-string morphology dominates rather than the desired uniform bead-free fibers.[8–11] In this study, we examine the scope of incorporating small amounts of associative polymers in such systems to facilitate nanofiber formation. We exploit the ability of associative polymers to act as rheology modifiers and generalize the concept using polymers having different mechanisms of association.

McKee et al.[12] have shown that the morphology of fibers produced through electrospinning is a strong function of the polymer concentration. One can go from producing polymer droplets to beaded nanofibers to defect-free nanofibers by increasing the concentration of the polymer in the precursor solution. The minimum concentration at which the polymer can be spun into uniform fibers is limited by the entanglement density of the polymer solution, as given by critical entanglement concentration (C_e). The critical concentration is the boundary between the semidilute unentangled and the semidilute entangled regimes and represents the onset of the regime where significant overlap between the polymer chains topologically constrains the chain motion.[13] On the basis of their observations, the authors concluded that C_e was the minimum concentration required to obtain beaded nanofibers and that uniform bead-free fibers were obtained at 2−2.5 times C_e. They argued that the presence of entanglements prevents the breakup of the charged fluid into droplets, resulting in the formation of uniform fibers. The role of entanglements in electrospinning has been further validated in several other publications.[14,15] In another study by the same authors on poly(methyl methacrylate-*co*-methacrylic acid) copolymers containing self-complementary quadruple hydrogen-bonding groups in the molecule,[16] the electrospinning behavior was found to be similar to polymers with higher molecular weight. This behavior was attributed to the presence of extensive hydrogen bonding between the molecules which essentially act as chain entanglements, hence reducing the C_e of the system. In a similar vein, lecithin, a low-molecular-weight amphiphile which forms cylindrical wormlike micelles in solution above a certain concentration, was electrospun from a chloroform/DMF solution.[17] In this case, at high enough concentrations, the wormlike micelles form physical entanglements in solution which effectively substitute for chain entanglements in polymer systems in the semidilute entangled regime.

The occurrence of beads during electrospinning is a result of the interplay between three factors, namely surface tension, charge density, and the viscoelastic forces. Surface tension tends to minimize surface area of the electrified jet, hence favoring the formation of beads, while net charge density and viscoelastic forces favor the formation of fibers. Therefore, additives like cationic surfactants have been shown to reduce bead density during the electrospinning of polystyrene fibers.[18] The improvement in fiber formation is brought about by an increase in charge density as well as simultaneous decrease in surface tension.

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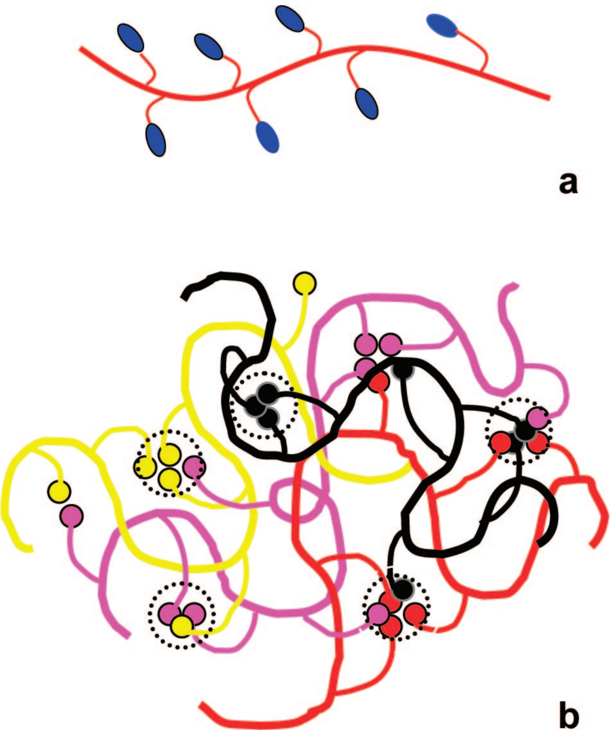


Figure 1. Schematic representation of HASE associative polymer. (a) A polymer molecule by itself consisting of hydrophobes shown as the tip of the pendant groups. (b) HASE polymer in aqueous solution showing inter- and intramolecular association of the hydrophobes.

Similarly, addition of other ionic additives such as salts[19–21] and polyelectrolytes[22] has also been found to improve fiber formation by increasing solution conductivity.

At low concentrations, however, even the presence of ionic additives in the polymer solution proves ineffective in eliminating beads.[8] This is likely due to insufficient viscoelastic forces. Yu et al.,[23] in their work on electrospinning of Boger fluids, have demonstrated the requirement of sufficient fluid elasticity to obtain uniform fibers. In this work, we investigate the efficacy of using associative polymers to improve fiber formation from dilute polymer solutions that lack spinnability or produce beaded fibers. An obvious advantage of spinning at low concentrations is derived from the proportional relationship between fiber diameter and polymer concentration. Keeping other parameters constant, an increase in polymer concentration results in an increase of the fiber's diameter.[12,24]

Hydrophobically modified associative polymers are water-soluble polymers with hydrophobic groups either attached to their ends or spread throughout the backbone in a comblike manner.[25–29] Hydrophobically modified alkali-soluble emulsion (HASE) polymers are a class of comblike associative polymers with pendant hydrophobes that form a transient network in an alkaline solution consisting of both intra- and intermolecular hydrophobic junctions.[30–37] A schematic of a HASE polymer molecule and its interactions in an aqueous solution is shown in Figure 1. The presence of these hydrophobic junctions, even at small concentrations, leads to a significant increase in viscosity as well as in the viscoelastic properties of the polymer solution. Because of their unique thickening mechanism and ability to act as rheology modifiers, these water-soluble polymers find applications in paint formulations, paper coatings, and oil drilling fluids.[38–41] To the best of our knowledge, no attempt has been made to assess the utility of these associative polymers as an electrospinning aid for polymer systems that lack spinnability.

As such, this study is the first successful attempt of using associative polymers as an electrospinning aid for spinning polymer solutions that lack spinnability at low concentrations. We investigate the effect of addition of HASE associative polymers on the properties of the precursor solution as well as on the electrospinnability of these dilute systems. Subsequently, we discuss the various factors that can possibly influence the bead formation in these systems. Finally, we extend the concept of using HASE associative polymers to improve spinnability, to other nonhydrophobic associative polymers, thereby lending credence to the universality of this approach.

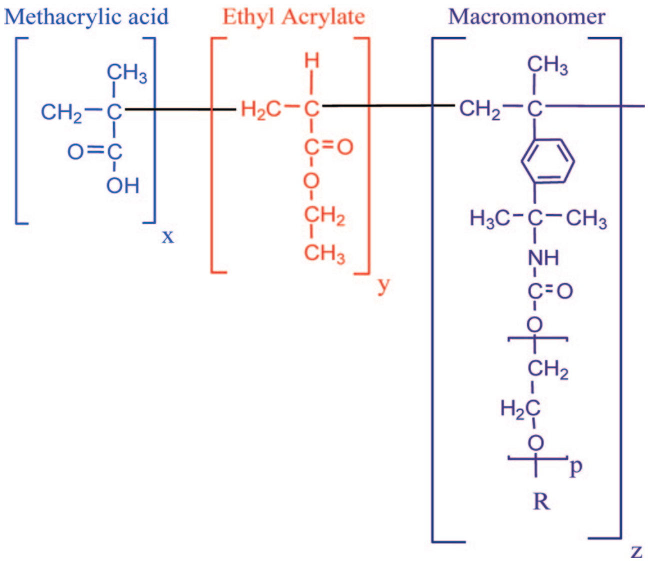
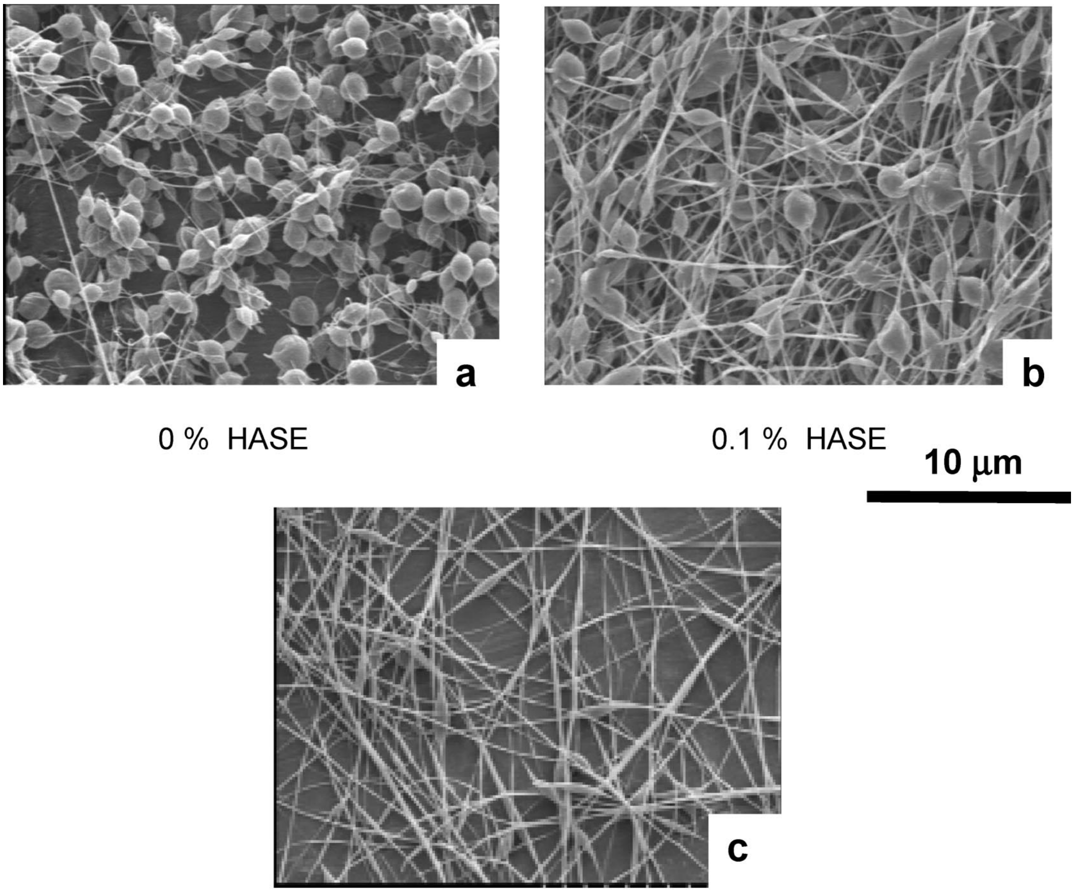


Figure 2. Molecular structure of the model HASE polymer. R = C22 alkyl chain polymer hydrophobe; P = 40 EO poly(ethylene oxide) spacer; *x*/*y*/*z* = 43.57/56.21/0.22.

Materials and Methods

The model HASE polymer used in this study was obtained from UCAR Emulsion Systems (Dow Chemicals, Cary, NC). Figure 2 shows a schematic of the chemical structure of HASE polymer. It is a copolymer of methacrylic acid, ethyl acrylate, and macromonomer, their molar ratio being 43.57/56.21/0.22, respectively. The macromonomer is composed of a poly(ethylene oxide) (PEO) spacer with an average number of EO groups equal to 40 mol and a C_{22} alkyl group linked to the backbone via a urethane linkage. Because of the association of HASE polymer in dilute solutions, it is difficult to determine its absolute molecular weight (MW). The MW of HASE polymers with similar structure to the one used in this study have been found to be in the range 100−200 kDa.[25] The HASE polymer was supplied in the form of an aqueous latex at a solid concentration of ~26 wt %. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulosic membrane (cutoff MW = 10 000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under a vacuum of 100 mTorr to obtain the HASE polymer in a powdered form. The pH of the subsequent prepared HASE solutions was adjusted between 7 and 7.5 by adding 0.1 M NaOH. Details of this procedure are provided in previous publications.[32,33,35]

PEO (MW 600 kDa) was purchased from PolySciences Inc., Warrington, PA. Commercial PEO usually contains about 2−3 wt % inorganic fillers in the form of calcium carbonate and silica. As the presence of these fillers can influence the molecular interactions in solution, we first purify the PEO in order to truly assess the effect of HASE on solution rheology of PEO as well as the final fiber formation. CO_2 was bubbled through a solution of 3 wt % PEO in acetonitrile for 1 h with constant stirring in order to facilitate the precipitation of filler particles. The solution was then centrifuged for 30 min at 4000 rpm. The supernatant from the centrifuged solution was poured into glass dishes, and purified PEO was obtained after the solvent evaporated. Purified PEO was used for



0 % HASE

0.1 % HASE

0.2 % HASE

Figure 3. SEM images of electrospun fibers obtained from 3 wt % PEO solution with different associative polymer (HASE) concentrations.

all the experiments in this work unless otherwise noted. Guar gum (MW 2000 kDa) was purchased from Sigma-Aldrich, and the sample impurities were removed using a purification procedure as reported elsewhere.[42]

The polymer solutions were placed in a water bath overnight at 40 °C to remove entrained air and left in the bath for 48 h prior to rheological measurements. All rheological experiments were performed at 25 °C in a TA Instruments AR-2000 stress controlled rheometer using cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, and dynamic frequency sweep tests were run within this range. All rheological measurements were performed at least twice to ensure reproducibility within ±5%.

The electrospinning setup consisted of an aluminum collector plate, a precision syringe pump (Harvard Apparatus, Holliston, MA), and a high-voltage power supply (Gamma High Voltage Research, model D-ES30 PN/M692 with a positive polarity). The syringe pump controlled the flow of polymer solution to a metallic needle which was connected to the positive electrode of the power supply. The collector plate was grounded, and the fibers were collected on an aluminum foil wrapped on the collector plate. The tip-to-collector distance and solution flow rate were fixed at 15 cm and 1 mL/h, respectively, and the applied voltage ranged between 7 and 13 kV. The electrospun fibers obtained were gold-sputtered, and SEM measurements were obtained on a Hitachi S-3200 scanning electron microscope. The average fiber diameter was determined by measuring fiber diameters of individual fibers from multiple SEM images using Image J software. The statistical significance of the difference in fiber diameter from different samples was established by performing *t* test using Excel.

Results and Discussion

Electrospinning of Low-Concentration Solutions of PEO Using HASE Associative Polymer. As a first step in determining the feasibility of using HASE associative polymers as an electrospinning aid for water-soluble polymers, we selected poly(ethylene oxide) (PEO) as our model polymer system. Electrospinning of PEO having different molecular weights (MWs) has been extensively studied in the literature.[43–47] For our purpose, though, we selected a PEO concentration which does not electrospin into uniform fibers and instead forms mostly beaded fibers. A 3 wt % PEO solution satisfies this criteria as is evident from the mostly beaded fiber SEM images observed in Figure 3a. Attempts to improve fiber formation from the 3 wt % PEO solution by varying process parameters such as voltage and tip to target distance were also unsuccessful, in agreement with existing published literature.

Solutions of 3 wt % PEO with different concentrations of HASE were prepared to examine the effect of HASE on the rheological properties of the precursor solution as well as on the morphology of the electrospun fibers. No phase separation was observed in the aqueous solutions of HASE−PEO mixtures within the concentration range studied. Owing to their ability to form intra- and intermolecular hydrophobic junctions, addition of HASE can considerably affect the rheology of PEO solutions. Figure 4a illustrates the effect of HASE addition on steady shear viscosity. The addition of HASE to the PEO solutions, even in small amounts, is found to significantly increase the viscosity of the system. For example, the shear viscosity of the solution in the presence of 0.2 wt % HASE is more than an order of magnitude higher than that of a 3 wt % PEO solution without any HASE. Moreover, the viscosity profile progressively shows

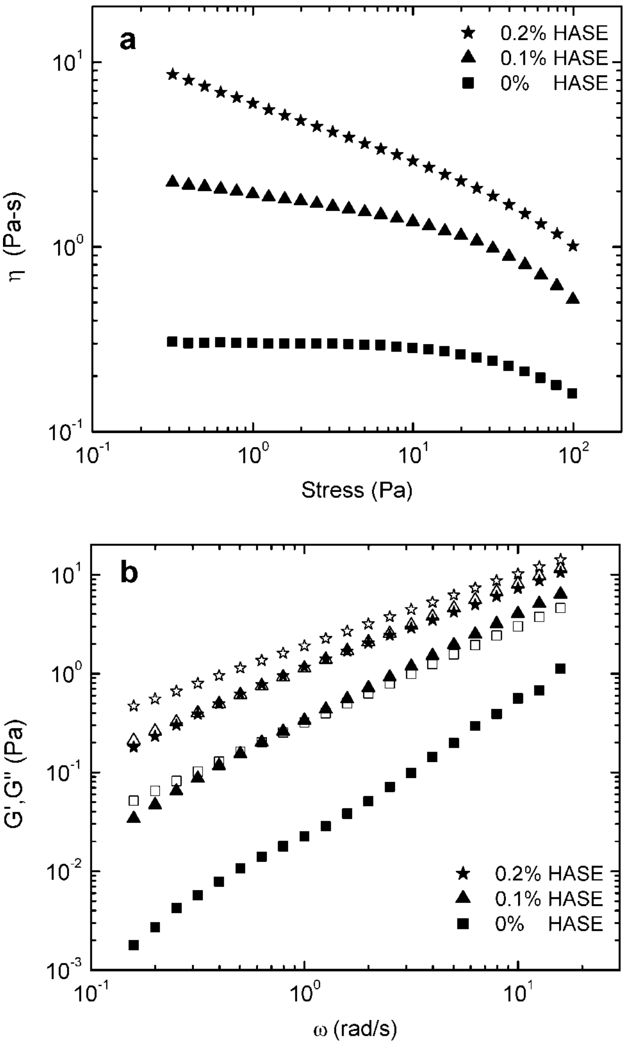


Figure 4. Steady shear viscosity (a) and dynamic frequency spectrum of the elastic (*G'*, closed symbols) and viscous (*G''* open symbols) moduli (b), shown for 3 wt % (600K MW) PEO with different HASE concentrations.

more dependence on shear stress upon HASE addition and an absence of a Newtonian region. Both the increase in viscosity and the nonlinear steady shear response upon addition of HASE indicate the formation of a network structure presumably due to the associative nature of HASE polymer, which is known to form hydrophobic junctions in solution. The above hypothesis of evolution of a polymer network in the presence of HASE is reinforced by the frequency spectra of elastic and loss moduli of the solutions as denoted by G' and G'', respectively (Figure 4b). The values of both the dynamic moduli progressively increase with the addition of HASE and become less frequency dependent. Although we do not observe a crossover of the dynamic moduli in the frequency range studied, it appears to shift toward lower frequencies with increasing HASE concentration, signifying an increase in the characteristic relaxation time of the polymer system.[25,32,36] These results are characteristic of the formation and strengthening of the polymer network in the presence of HASE. These changes in the solution rheology of the 3 wt % PEO solution, which otherwise would result in mostly beaded fibers, translate into uniform fibers as can be seen from the SEM images in Figure 3. The bead density reduces at 0.1 wt % HASE concentration, and uniform, defect-free fibers are obtained on further increasing the HASE concentration to 0.2 wt %.

On the basis of the above results, we believe that the improvement in fiber morphology is primarily a consequence of the formation of a physical interaction comprising of hydrophobic junctions in solution. The C_e of purified PEO is 1.4 wt % as obtained from the transition in the change in slope of specific viscosity (not shown here). The 3 wt % PEO is above its C_e, and hence there are sufficient entanglements in solution to form beaded fibers but not enough to obtain bead-free fibers. Upon the addition of HASE, the ensuing network of hydrophobic associations effectively substitutes for additional entanglements required to facilitate the development of uniform fibers. We refrain from delving further into this issue of "entanglement" modification as it is beyond the scope of this study.

In a related work on the effect of chitosan – a linear polysaccharide which is commonly used as a food thickener—on electrospinning of poly(vinyl alcohol) (PVA), Lin et al.[8] showed that the addition of chitosan improved the uniformity of fibers. However, the improvement in fiber formation was not very significant considering that even in the absence of chitosan, the minimum concentration of PVA that they explored was high enough to form beads-on-string morphology instead of predominantly beaded fibers as is usually the case when spinning from dilute concentrations. The effect of chitosan on lower PVA concentrations, which would otherwise result in mostly beads, was not reported. Moreover, as discussed by the authors, the conductivity of the solutions increased significantly on chitosan addition due to the presence of ammonium cationic ions present in the chitin molecule, which also positively influenced the reduction in bead density.

Suppressing the Polyelectrolyte Effect of HASE. From a practical standpoint, it is important to minimize the amount of associative polymer added to aid electrospinning because the presence of a second polymer can affect the properties of the resulting PEO fibers. A simple approach in this regard would be to suppress the polyelectrolyte effect of HASE polymers. Apart from increasing the solution conductivity which favors jet stretching, the presence of polyelectrolytes in an electrospinning solution also leads to jet instabilities caused by the lower mobility of the polyions and poor fiber morphology. Son et al.[48] studied the influence of solution pH on the electrospinning of poly(vinyl alchohol) (PVA) solutions. They reported that electrospinning of PVA under acidic pH resulted in the formation of beaded fibers which was attributed to the protonation of the hydroxyl groups on PVA, thereby rendering it a polyelectrolyte nature. According to the authors, the low mobility of protonated PVA led to local variations in charge density which inhibited a stable jet formation. McKee et al.,[49] in their work on electrospinning of cationic polyelectrolytes, also reported difficulties in electrospinning at lower concentrations. Unlike neutral polymers which form uniform fibers at 2–2.5 times C_e, concentrations well above C_e ($\sim 8C_e$) were required to obtain fibers for their system. They added NaCl salts to their system to shield the electrostatic charges present on the polymer backbone and found that the minimum concentration to obtain fibers decreased as the concentration of salt increased. The authors attributed this observation to the screening of repulsive charges which in turn helped to stabilize the jet.

Thus, in order to further reduce the concentration of HASE required to electrospin PEO into uniform fibers, we resorted to the use of salts that could suppress the polyelectrolyte effect of HASE by shielding the charges present on the HASE backbone. Figure 5 shows the SEM images of fibers spun from solutions of 3 wt % PEO with different HASE concentrations in the presence of 0.005 M NaCl. Also shown is the image of fibers spun from 4 wt % PEO in the absence of HASE. In the presence of NaCl, we are able to obtain uniform, bead-free fibers with 0.1 wt % HASE as opposed to 0.2 wt % HASE in the absence

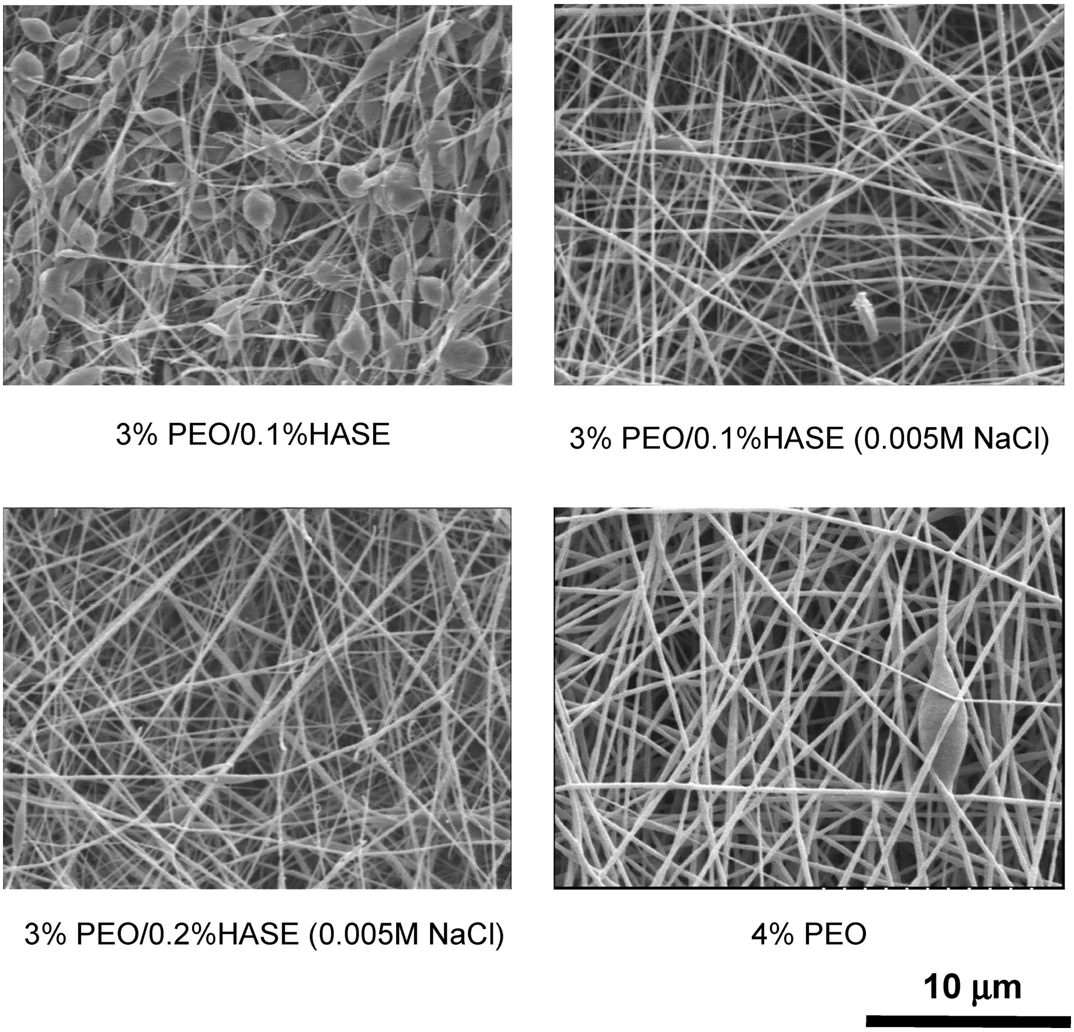


Figure 5. SEM images of electrospun nanofibers obtained from 3 wt % PEO solution with different HASE concentrations in the presence of salt as well as from 4 wt % PEO.

of any salt (cf. Figure 3c). Reducing the polyelectrolyte effect by adding salts thus helps to improve the electrospinnability. A notable observation in Figure 6 is the similarity between the rheological behavior of a 3% PEO/0.1% HASE/NaCl solution and that of 4 wt % PEO solution, which by itself is readily electrospinnable. We observe that both viscosity and the dynamic moduli of 3% PEO increase and become similar to that of 4% PEO upon the addition of HASE. The electrospun fibers in turn become more defect free and uniform. In essence, we are able to replicate the rheology of the 3% PEO to that of the 4% PEO system by incorporating HASE. This observation underlines the importance of rheological modification in the fiber spinning process. The overlapping of the curves in Figure 6 in this particular case may be fortuitous. Nonetheless, the overarching observation is that the rheological properties of 3 wt % PEO approach those of 4 wt % PEO, thereby implying a change in molecular interactions in the system. For instance, in the absence of salt, the addition of HASE improves fiber formation wherein the rheological properties of 3 wt % PEO/0.1 wt % HASE and that of 4 wt % PEO are similar, albeit not overlapping. These results are further validated in the next section where we report the use of another associative polymer instead of HASE.

One caveat that can possibly be associated with the above results is that reduction in bead density could be a consequence of increased conductivity upon addition of HASE. Increasing the net charge density of a precursor solution increases charge repulsion along the jet leading to stronger elongational forces which favor the formation of fibers instead of beads. This phenomenon of reduction in bead density in the presence of ionic additives such as inorganic salts has been amply reported in literature.[19–21] Since HASE polymer acts as a polyelectrolyte owing to its anionic backbone of carboxylate groups, the addition of HASE increases the conductivity of 3 wt % PEO solution from 90 μS/cm in the absence of HASE to around 1.44 mS/cm at 0.1 wt % HASE (0.005 M NaCl) concentration. Hence the formation of uniform fibers upon HASE addition may also be attributed to the increase in conductivity.

To address this issue and to establish that the improvement in the spinnability is predominantly derived from an increase in molecular associations in the presence of HASE and not due to an increase in conductivity, we prepared a 3.2 wt % PEO solution with conductivity similar to that of the 3 wt % PEO/0.1 wt % HASE (0.005 M NaCl) solution by adding NaCl salt to the PEO-only solution. A 3.2 wt % PEO was selected for this purpose as it represents a conservative limit when comparing fibers from both samples: one with a higher concentration (3% PEO/0.2% HASE) and the other with a higher conductivity (3% PEO/0.1% HASE with salts) as both these factors are expected to improve fiber morphology. As seen from Figure 7, increasing the conductivity of a 3.2 wt % PEO solution does not result in improvement in fiber formation as mostly beaded fibers are obtained. These results affirm that the improvement in the

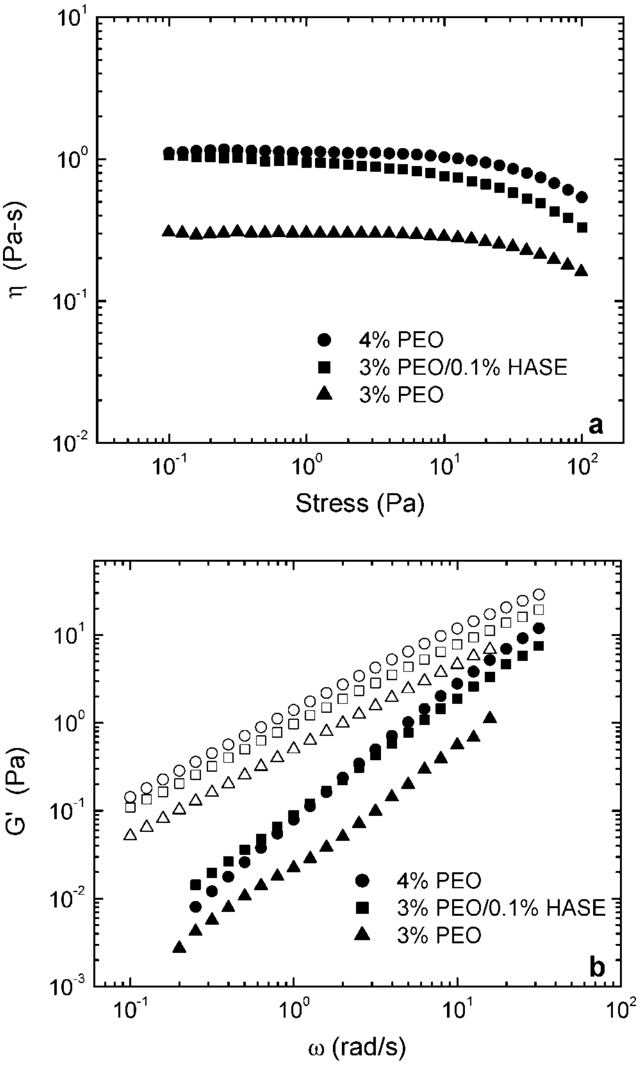


Figure 6. Steady shear viscosity (a) and dynamic frequency spectrum of the elastic (G' closed symbol) and viscous (G'' open symbol) moduli (b), shown for 3 wt % (600K MW) PEO with and without 0.1 wt % HASE (0.005 M NaCl). Also shown are the profiles for 4 wt % PEO. The figure shows how addition of HASE to 3 wt % PEO replicates the rheology of 4 wt % PEO.

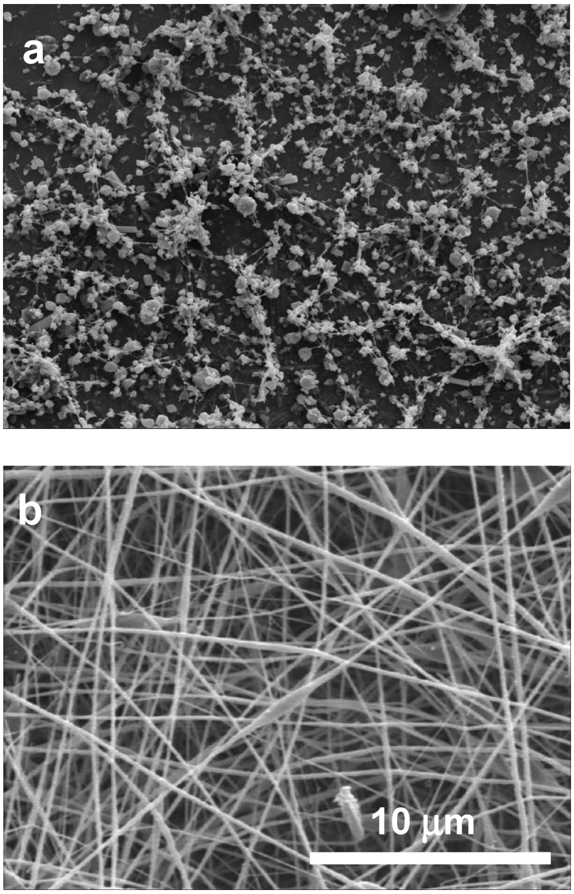


Figure 7. SEM images of electrospun nanofibers obtained from (a) 3.2 wt % PEO solution and (b) 3 wt % PEO/ 0.1% HASE (0.005 M NaCl) with similar solution conductivities. Both images have the same 5000× magnification.

Table 1. Average Fiber Diameter of Electrospun Fibers Obtained from Various Polymer Systems

sample	av fiber diameter (nm)	standard deviation (nm)
4% PEO	230	56
3% PEO/0.2% HASE	180	64
3% PEO/0.1% HASE (with NaCl)	120	44
3% PEO/0.2% guar	170	30

morphology of the resulting fibers is primarily derived from increase in associations in solution.

The obvious advantage of spinning at lower concentrations lies in reduction in fiber diameters from spinning at lower concentrations. Compared to the average fiber diameter of ~230 nm obtained from 4 wt % PEO, the fiber diameters in case of 3 wt % PEO (otherwise not electrospinnable into uniform fibers by itself) in the presence 0.2 wt % HASE and 0.1 wt % HASE with salt are ~180 and ~120 nm, respectively (Table 1). This reduction in fiber diameter at overall lower polymer concentrations is statistically significant in both cases at the $\alpha = 0.05$ level.

Electrospinning of PEO Solutions Using Guar Galactomannan. The concept of using hydrophobically modified associative polymers as an electrospinning aid can be applied to other associative polymers which can modulate solution rheology. To validate this hypothesis, we used guar galactomannan, a water-soluble associative polymer which is a non-polyelectrolyte and affects solution rheology via hydrogen bonding instead of forming hydrophobic associations. Guar galactomannan is a low-cost, naturally abundant polysaccharide consisting of β-1,4-linked mannose units as its backbone with randomly attached α-1,6-linked galactose side chains.[50–54] The ratio of mannose to galactose units is roughly 2:1. Guar forms extensive hydrogen-bonding network in an aqueous solution and is therefore used as industrial thickener in several applications including food, oil recovery, drug delivery, and personal and health-care products.[53,55] The effect of adding guar on the steady-state viscosity profile of a 3 wt % PEO solution is shown in Figure 8. It is to be noted that no phase separation was observed in the solutions of guar−PEO mixtures within the examined concentration range. Similar to the data obtained for HASE polymers, the presence of guar causes an increase in the PEO solution viscosity. However, the magnitude of change in viscosity is less than that compared to the effect of HASE (cf. Figure 4a). This observation is not unexpected as hydrophobic associations are much stronger than those through the formation of hydrogen bonds. The difference in their association mechanism is also reflected in dissimilarity in their viscosity profiles. Unlike HASE, which shows a nonlinear steady shear response, PEO solutions in the presence of guar exhibit Newtonian behavior at low stresses. More importantly, though, addition of guar does not lead to any change in solution conductivity; as such any changes in

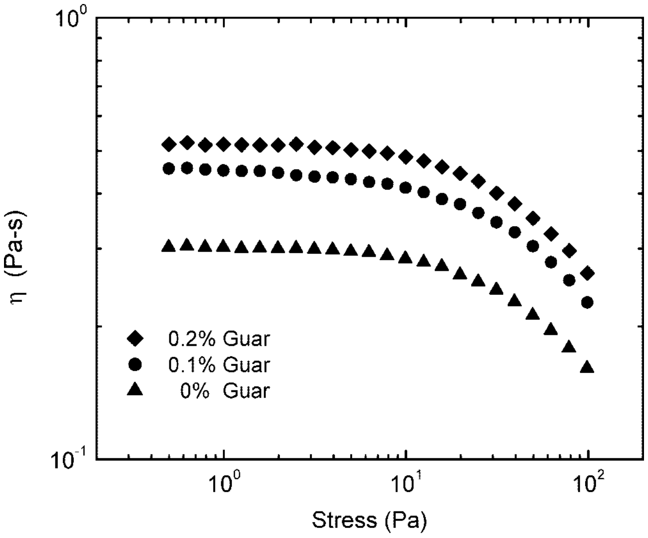


Figure 8. Steady-state viscosity profile of 3 wt % (600K MW) PEO with different guar concentrations.

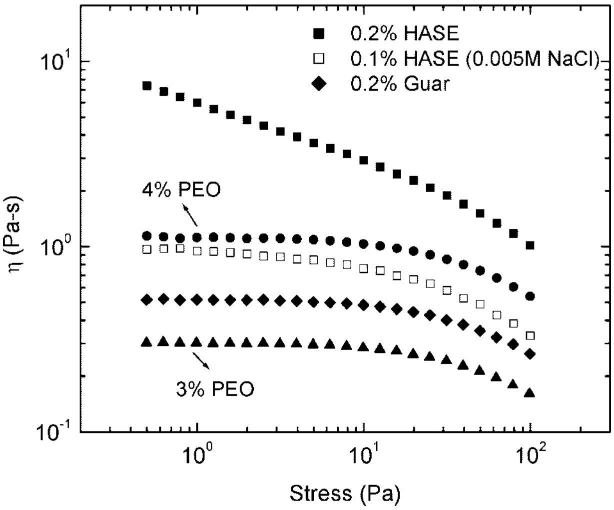


Figure 10. Steady-state viscosity profiles of 3 wt % PEO solution with and without different associative polymer systems. Also shown is the viscosity of a 4 wt % PEO solution.

nanofiber properties for the PEO−guar system can be readily attributed to entanglement effects. Figure 9 shows the images of electrospun fibers obtained from 3% PEO solution with increasing guar concentration. We find that a systematic increase in the concentration of guar improves the morphology of final fibers. The bead density decreases as guar content in solution is increased from 0.05 to 0.1 wt %, and at 0.2 wt % guar, we observe uniform, bead-free PEO fibers similar to those obtained using HASE. Here again we observe smaller fibers in the presence of 0.2 wt % guar (average fiber diameter ~170 nm) as compared to ~230 nm for 4 wt % PEO. These results further validate our hypothesis that associative polymers can be used

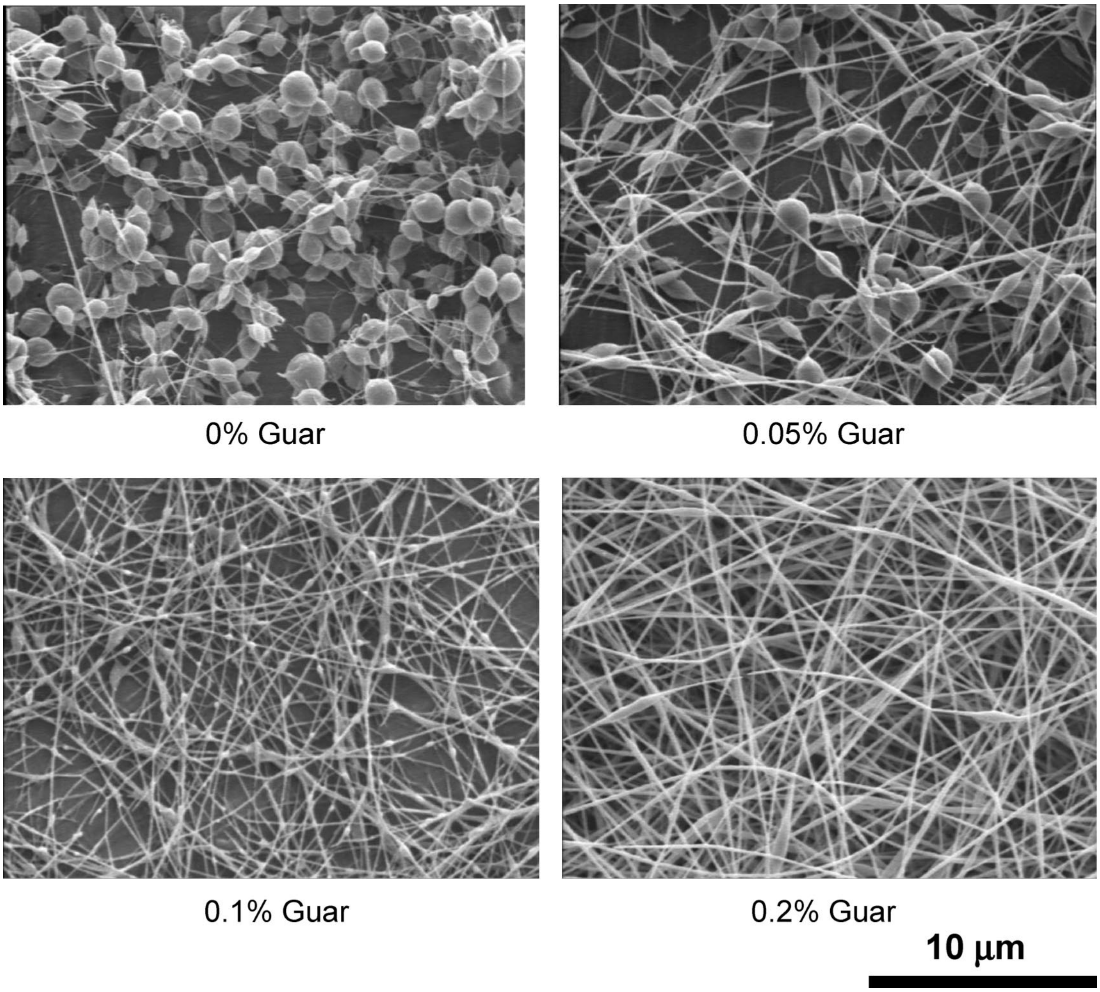


Figure 9. SEM images of fibers from 3% PEO with different guar concentrations.

effectively as an aid in electrospinning of polymers that lack spinnability, by tailoring their solution rheology.

In Figure 10, we juxtapose the viscosity profile of different associative polymer systems discussed so far, guar and HASE with and without salt, together with that of 3 and 4 wt % PEO solutions, to bring together a coherent picture on the overall role of rheology on nanofiber formation. The concentrations of associative polymers in the figure correspond to the minimum concentrations at which uniform fibers were obtained. While the lowest viscosity curve of 3% PEO corresponds to a sample that is not electrospinnable, all other viscosity data correspond to spinnable formulations. Several other features are notable. First, both the addition of either 0.2% guar or 0.2% HASE produces nanofibers with very similar average diameters (170 nm vs 180 nm; Table 1). This is consistent with the fact that the total polymer concentration is the same in both and the role the associative polymer primarily being that of increasing the chain "entanglements" or interactions. However, the viscosity of the HASE sample is substantially higher because the association mechanism in HASE is much more potent than that of guar. Incorporating associative polymers in precursor solutions thus enables us to isolate the effect of viscosity on fiber diameter and highlights the dominance of concentration over viscosity in determining the final fiber size. Second, we observe that 0.2% HASE is needed to achieve electrospinnability vs 0.1% HASE with salt. This behavior is in accordance with the polyelectrolyte nature of HASE, wherein a higher concentration of the polymer is required to impart jet stability. Finally, the 4% pure PEO sample and the 3% PEO containing 0.1% HASE with salt show similar viscosity, but the latter when electrospun produces a smaller fiber diameter (120 nm vs 230 nm). This behavior is in agreement with the fact that a lower total polymer concentration in the precursor solutions manifest in smaller diameter of the electrospun nanofibers.[11,56]

Summary

In this contribution, we have demonstrated the utility of associative polymers in improving fiber formation of poorly electrospinnable polymer systems. We established that the addition of hydrophobically modified associative polymers (HASE) in small amounts to PEO solutions leads to significant changes in solution rheology and considerable improvement in the morphology of the resulting electrospun fibers. In addition, we demonstrated that the concentration of HASE required to improve the quality of fibers can be further lowered by suppressing the polyelectrolyte effect of HASE using salts. Similar changes in rheology and fiber formation were observed upon using guar associative polymer that interacts via hydrogen bonding. In both cases, hydrophobic associations or hydrogen bonding effectively substitutes for additional entanglements required to facilitate the development of uniform fibers. Our results highlight the dominance of overall polymer concentration over solution viscosity in determining the final fiber size. The use of associative polymers enables us to alter the solution viscosity without substantially changing the concentration, thereby isolating the two effects. The reported findings also have another important implication as they elucidate the role of associative polymers in controlling hydrophobic and hydrogen-bonding interactions in dilute polymer solutions, hence adding a new degree of freedom for the production of submicron fibers via electrospinning.

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