6152 *Macromolecules* **2010**, *43*, 6152–6155
DOI: 10.1021/ma100750e

Macromolecules
ARTICLE

Designing Nanofibers via Electrospinning from Aqueous Colloidal Dispersions: Effect of Cross-Linking and Template Polymer

Evgueni Klimov,* Vijay Raman, Rajan Venkatesh, Walter Heckmann, and Ruediger Stark

BASF SE, Polymer Research Division, Carl-Bosch-Strasse 38, D-67056 Ludwigshafen, Germany

Received April 7, 2010; Revised Manuscript Received May 28, 2010

ABSTRACT: Nano- and mesofibers were prepared via electrospinning of dispersions of styrene−acrylate copolymers from an aqueous environment. The synthetic versatility of emulsion polymerization technique allowed us to incorporate cross-linking strategies to improve the thermal and mechanical stability of fibers. In general, a water-soluble template-polymer (<10 wt %) had to be added to the polymer dispersion to provide the viscoelasticity required for electrospinning. The molecular weight of the template polymer used had a significant influence on the electrospinnable composition of the mixture (ratio wt % polymer particle: wt % template polymer), and in general the higher the molecular weight of the template polymer the lower the mass required to obtain the nanofibers.

Introduction

Electrospinning was rediscovered several years ago and has become a common method to fabricate polymer and inorganic nanofibers for filtration, textile and biomedical applications.[1] In this technique, the fibers are obtained using strong electrical field that creates an electrostatically driven jet from a polymer solution or melt. Although the conditions are mild the choice of the solvent is essential as in many cases flammable, toxic, or corrosive solvent have to be used. In general, environmentally friendly solvent like water can be used for water-soluble polymer but the resulting electrospun fibers are water-soluble and/or hygroscopic unless they are post-cross-linked via UV or high temperature treatments. However, water stability of nanofiber nonwovens is important for numerous applications. A possible alternative to organic solvent-based electrospinning has been recently found by electrospinning aqueous dispersions of water insoluble polymers.[2] In this technique, the fibers were fabricated using a formulation of polystyrene particles and a 10−20 wt % of a water-soluble template polymer to provide viscoelasticity to the solution, necessary for jet and subsequent fiber formation. However, polystyrene fibers were characterized by poor mechanical integrity due to its high T_g and resulting poor interdiffusion of polymer between particles. In the subsequent work,[3] we used the ability of polymer colloids having minimum film formation temperature (MFFT) below room temperature to obtain homogeneous nanofibers with improved dimensional stability. MFFT of dispersed polymer (polymer particles) is usually related to its T_g. Although on one hand reducing the MFFT/T_g helps to improve interdigitation between polymer particles and to obtain homogeneous fibers on the other hand gives nanofibers that are not stable at higher temperatures (>100 °C). Thus, in order to enhance the thermal stability and in addition mechanical stability of nanofibers obtained from polymer dispersions, cross-linking was introduced within the particle (intraparticle) and between particles (interparticle). Furthermore, we demonstrate that nanoindentation could be used to investigate the mechanical properties of nanofibers and to investigate the effects of different cross-linking strategies (intra/interparticle) employed.

Table 1. Parameters of Aqueous Polymer Dispersions Used for Electrospinning

	composition, wt %				
sample	*n*-butyl acrylate	styrene	cross-linker	particle size, nm	T_g, °C
SBa (standard)	50	50	-	137	27.2
SBaIntra	49.5	50	0.5 AMA[a]	109	28.3
SBaInter	48	48	4 DAAM[b]	111	30.1

[a] AMA: allyl methacrylate. [b] DAAM: diacetone acrylamide.

The impact of the template polymer properties on electrospinnability was investigated. Using the template polymer with higher molecular weight, its percentage could be significantly reduced to ~2 wt % related to polymer particle concentration.

Experimental Section

Materials. Aqueous poly(styrene-*co*-n-butyl acrylate) (SBa), poly(styrene-*co*-n-butyl acrylate-*co*-allymethacrylate) (SBaIntra) and poly(styrene-*co*-n-butyl acrylate-*co*-diaceton acrylamide) (SBaInter) dispersions were prepared using emulsion polymerization at BASF SE. The T_g (DSC) and averaged particle sizes (HDF) are summarized in Table 1.

Poly(vinyl alcohol) (PVA) (MOWIOL 28−99, $M_w = 145$ kg/mol, 99% hydrolyzed) was purchased from Kuraray Specialties Europe KSE GmbH. The polymer was used without further purification. A series of poly(vinyl formamides) (PVFA) with different molecular weight were obtained from BASF SE as solutions in water and their properties are listed in Table 2.

Final formulations for electrospinning were prepared by mixing certain amount of an aqueous latex dispersion with water-soluble template polymer (PVA and PVFA) at room temperature. The amounts were calculated as wt % of the entire solids (polymer particle + template polymer) in the formulation. And usually formulation of 20−25 wt % solids was electrospun.

Electrospinning of Dispersions. The syringe electrospinning setup has been described previously.[4] A 0.3 mm diameter needle was used as an upper electrode where positive potential was provided by a high voltage power supply (0 to 30 kV). A flat counter-electrode was positioned 20 cm below the upper electrode and was connected to the high voltage power supply. A piece of aluminum foil or a metal net placed on the counter electrode was used as collecting substrates. The flow rate of

---

*To whom correspondence should be addressed. E-mail: evgueni.klimov@basf.com.

Table 2. Properties of Poly(vinylformamide) (PVFA) Used as Water-Soluble Template Polymer

sample	solid content, wt %	M_w, kg/mol
PVFA-1	36.5	64
PVFA-2	12.7	390
PVFA-3	4.9	770
PVFA-4	5.1	960
PVFA-5	2.5	1110

dispersions was about 0.7 mL/h. The applied voltage has been varied between 15 and 60 kV.

Morphology of fibers was observed with a scanning electron microscope (SEM, model Zeiss Ultra 55 with accelerating voltage of 3 and 5 kV). The averaged fiber diameter was estimated from at least 20 single fibers.

Mechanical Tests on Fibers and Films. To characterize the material properties of the fibers, nanoindentation measurements have been performed on the fiber mat of cross-linked and noncross-linked fibers. During the measurement, the sample surface is indented with a diamond tip at increasing load for 30 s up to a specific maximum load; the load is held for 10 s, and again released over a time of 30 s.

E-modulus, hardness, and creep at the sample surface can be calculated from the recoded load vs depth curve using the Oliver–Pharr model.[5] It is based on the relationships of Sneddon, but includes the increase of the contact area during the indentation.

For known tip geometry, the hardness is given by the maximum penetration depth at maximum load

$$H = \frac{p_{\max}}{A(h_c)} \tag{1}$$

with $A(h_{max})$ as contact area at highest depth.

The E-modulus is calculated from the slope of the tangent line to the unloading curve at the maximum loading point. At this point, the response of the sample is fully elastic (Figure 1). With a stiffness of $S = pd/dh$, the reduced E-modulus is given by

$$E_r = \frac{S \cdot \sqrt{A(h_{\max})}}{2\sqrt{\pi}} \tag{2}$$

Using eq 2, the E-modulus of the sample can be calculated for known Poisson ratios of sample and tip and E-modulus of the tip.

The creep is given by the distance the tip penetrates into the material during the holding period of the indentation.

In the case of the fiber mats, the samples are not completely solid, but have large voids in between the fibers. Also the fibers themselves can slide on each other and the structure of the fiber mat is not fixed. This will lead to much too small E-modulus and hardness values and too large creep values compared to a bulk reference material. However, assuming the "porosity" of two fire mats is comparable, it should still be possible to measure relative differences of the material properties of the fibers.

To test the fiber mats, small loads of 0.2–0.5 mN have been used. A Berkovich tip (three sided pyramid with a tip angle of 142.3°) with a tip radius of 50 nm was used. Around 10 measurements were averaged to obtain statistically significant E-values.

Results and Discussion

Effect of Cross-Linking of Dispersions on Fibers. As it was shown previously, best dimensional integrity and mechanical stability was achieved by using polymer dispersions, where the polymer in the particle had a minimum film formation temperature close to the value, at which electrospinning is performed. Under this condition polymer chains within the particles have enough mobility to interdiffuse and interdigitate with polymer chains between particles to form a continuous medium. Styrene–acrylate copolymers, which fulfill the above condition, can be prepared by increasing the amount of acrylate monomer. On the other hand, these copolymers will be characterized by low mechanical stability at elevated temperatures.

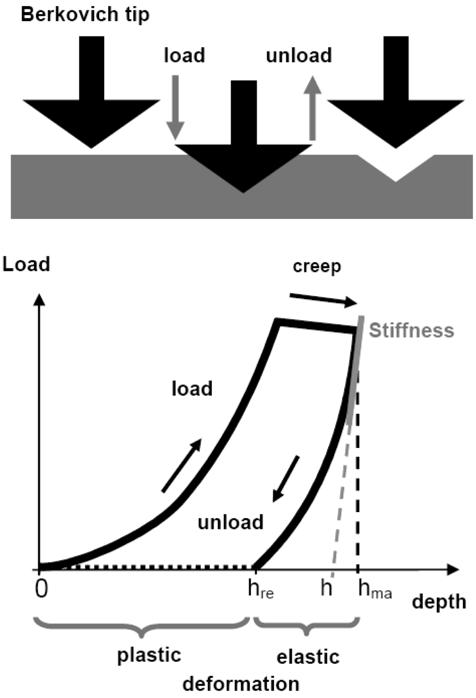
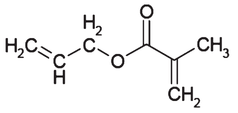


Figure 1. Principle of nanoindentation measurements of elastic modulus.



allylmethacrylate

Figure 2. Intraparticle cross-linker used in polymer dispersion to improve the stability of nanofibers.

One of the effective ways to keep materials integrity at elevated temperature is to introduce cross-links to obtain a 3-dimensional structure. There are multiple approaches to produce cross-linked network structures. Since one of the goals of our nanofiber fabrication technology is to avoid post treatments, two strategies were applied, which are already known for emulsion polymerization and do not require any additional radiative or thermal treatment.

Strategy 1 utilizes allyl methacrylate as comonomer, which is added during the polymerization reaction. Its chemical structure is shown in Figure 2.

Because of existence of two polymerizable vinyl and methacrylate groups, it is able to cross-link and form 3-D network. The T_g of polymer is only slightly increased — its film formation temperature is still in the range of $T_{\text{process}} \pm 15$, as was shown in a previous study.[3] Since this method works only within of each polymer particle, it is called intraparticle cross-linking.

Strategy 2 was used to improve cross-linking between particles. Diacetone acrylamide, which has an acrylate unit, was copolymerized with styrene and n-butyl acrylate. Adipinic acid dihydrazide (ADDH) is postadded and is found in the water phase. Upon water evaporation, condensation reaction

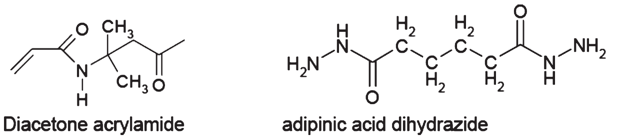


Figure 3. Interparticle cross-linkers used in polymer dispersion to improve stability of nanofibers.

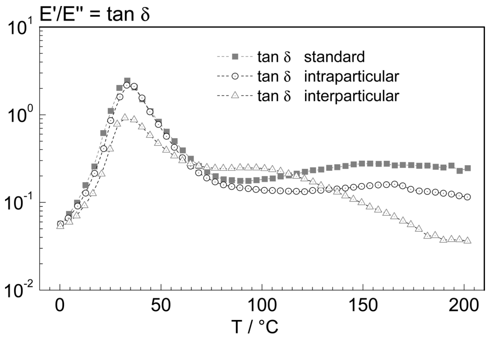


Figure 4. Tan δ vs temperature of films cast from dispersions without and with cross-linkers.

takes place between NH_2 groups of ADDH and carbonyl units which are present in the particle surface (Figure 3).

In the resulting fiber, the polymer particles are cross-linked with each other. This method we call interparticular cross-linking. It is important to note that this reaction occurs at normal ambient drying conditions and requires no additional radiative or thermal treatment.

The impact of cross-linkers can be demonstrated by dynamic-mechanical analysis (DMA) data of films made from non-cross-linked and cross-linked dispersions. Figure 4 shows the tan δ, which is a ratio of the loss to storage modulus, as a function of temperature for samples with intraparticle, interparticle and no cross-linkers.

Obviously, a network formation after cross-linking has a positive influence on the elasticity of materials. The sample with interparticular cross-linking demonstrates the lowest tan δ value at temperatures above 120 °C. It indicates that elastic behavior of this material still dominates the viscose term at elevated temperature.

Fiber mats with few tens of μm thickness were prepared from polymer dispersions with and without cross-linker and mechanical data were obtained via indentation technique. The averaged diameter of fibers varied in the range of 260−500 nm (380 ± 120 nm for standard and 350 ± 60 nm for cross-linked polymers).

The trends of the elastic moduli obtained by indentation of fibers (Figure 5) show good agreement with DMA data measured on films. A small increase of the E-modulus from intraparticular to interparticular cross-linker (Figure 5) and a decrease to noncross-linked fibers is observed. Although the error bars are of the order of 2.5 MPa, the change from cross-linked to noncross-linked mats is significant.

Assuming the same porosity of cross-linked and noncross-linked mats, this can have two reasons. One reason being, that fibers slide across each other much easier for non-cross-linked fibers, and the mats are therefore deforming at lower forces. The other reason would be a reduction of the E-modulus of the fibers themselves. In the first case, the surface and frictional forces would govern the E-modulus, in the second case, only the stiffness of the fibers will be measured. In our case, we generally assume that both effects play a role.

The changes from the interparticle and intraparticle cross-linking should also affect the surface and the friction of the fibers, but apparently this does not influence the E-modulus significantly. Therefore, we believe that the decrease results mainly from the stiffness of the fibers.

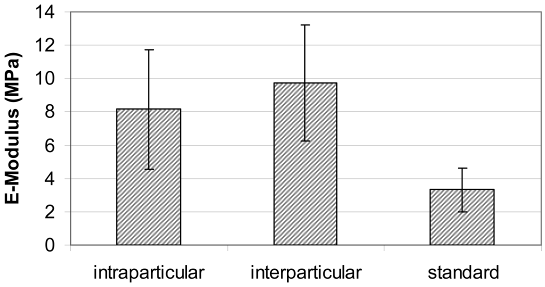


Figure 5. Elastic modulus (E) of nanofibers obtained by electrospinning of polymer dispersions with intraparticle, interparticle and no cross-linker.

It should be mentioned, at this point, that the fiber structure of the mat has not been accounted for in the calculation of the E-modulus, resulting in too small absolute values.

The integrity of fibers is observed upon temperature treatment. Figure 6 shows electron micrographs of nanofibers obtained without cross-linkers (top) and with interparticle cross-linkers (bottom) before (left) and after (right) short-time (max 5 min) thermal treatment above 150 °C.

The nanofibers obtained by electrospinning polymer dispersion with interparticle cross-linkers are more thermally stable as the morphology does not change significantly their shape at elevated temperature. These data correspond well with DMA results above 120 °C, where elastic part is more pronounced.

Effect of Template Polymer on Electrospinnability of Polymer Dispersions. For many potential applications of nanofibers spun from polymer dispersions, the template polymer can negatively influence their desired properties, e.g., water sensitivity of fibers. Once involved in the film formation of colloidal particles during water evaporation in electrospinning, template polymers cannot be removed completely from the fibers. A suitable approach to eliminate template polymer impact on fiber properties is to minimize the content. We made use of increasing viscosity with increasing molecular weight of the template polymer in aqueous solution to tune the electrospinnability of dispersions.

In the case of the homogeneous polymer solution, the minimum concentration, at which the polymer can be spun into uniform fibers, was roughly determined and is plotted vs molecular weight for several poly(vinyl formamide) samples in Figure 7.

Obviously, this concentration is limited by the entanglement density of the polymer solution, as given by critical entanglement concentration (C_e). C_e depends directly on the molecular weight of the polymer. It is observed in Figure 7 that the polymer with highest molecular weight of more than one million g/mol requires smallest concentration in water solution to obtain fibers using electrospinning. Accordingly, during the electrospinning of dispersions the molecular weight of the template polymer used to increase the viscosity and viscoelasticity of the water phase is expected to have a significant impact on the electrospinnable composition of the mixture (wt % of polymer particle: wt % of template polymer). Table 3 shows three formulations containing template polymers PVFA-5 and 4 (1110 and 960 kg/mol) and PVA (145 kg/mol) that were investigated.

Using PVFA-5 with the highest molecular weight of 1110 kg/mol we could obtain an electrospinnable mixture

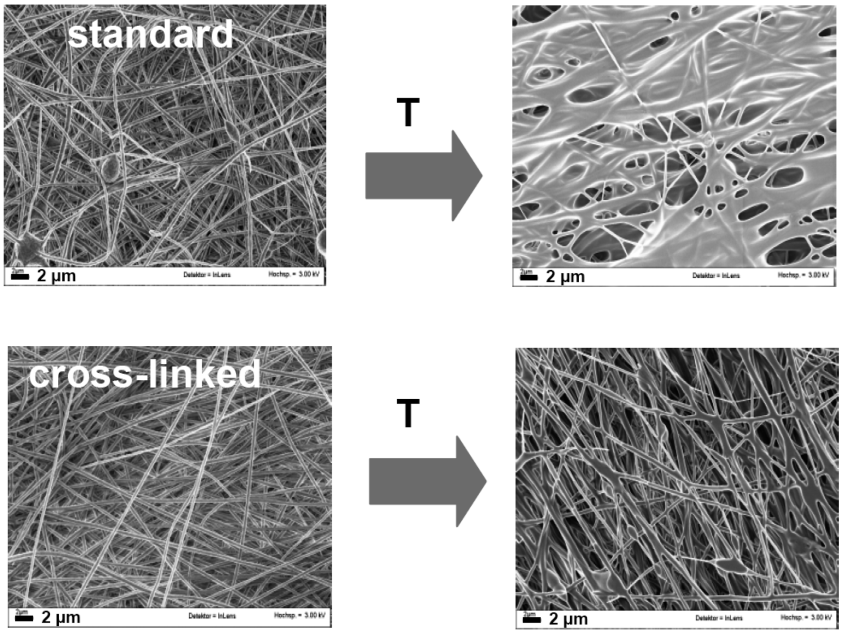


Figure 6. Electron micrographs of nanofibers obtained by electrospinning of dispersion with no cross-linker (top) and with interparticle cross-linker (bottom) before (left) and after (right) thermal treatment above 150 °C. The scale bar is 2 μm.

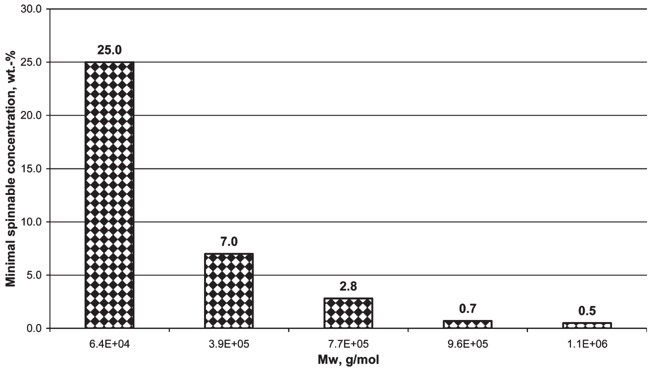


Figure 7. Minimal spinnable concentration vs M_w of poly(vinylformamide).

Table 3. Electrospinnable Composition versus Molecular Weight of the Template Polymer

template polymer	molecular weight (kg/mol)	electrospinnable composition (wt % polymer particle: wt % template polymer)
PVFA-5	1110	98:2
PVFA-4	960	96:4
PVA (MOWIOL 28−99)	145	93:7

with the lowest amount of template polymer. In this case the nanofibers could be obtained with 98 wt % of polymer particle and only 2 wt % of the template polymer as compared to 96:4 for PVFA-4 with 960 kg/mol and 93:7 for PVA (MOWIOL 28−99) with 145 kg/mol. The averaged diameter of electrospun fibers for three formulations shown in Table 3 has varied in the range 400−700 nm due to viscosity variations. Thus, higher molecular weight of the template polymer decreases its amount required to obtain the fibrous structure from polymer dispersions.

Conclusions

It was shown that mechanical strength of nanofibers prepared from polymer dispersions could be improved using intraparticle and interparticle cross-linkers. Accordingly, the nanofibers obtained using interparticle cross-linkers were more thermally stable than the fibers without any cross-linking.

In general, the molecular weight of the template polymer used to electrospin polymer dispersions has a significant influence on the electrospinnable composition of mixture (ratio of wt % polymer particle to wt % template polymer), and in general, the higher the molecular weight of the template polymer the lower the amount required to obtain the nanofiber morphology.

Acknowledgment. We thank Prof. A. Greiner and T. Röcker (University of Marburg, Germany) for experimental support and discussions, Joachim Haehnle (BASF SE) for providing PVFA samples.

References and Notes

(1) Greiner, A.; Wendorff, J. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5670.
(2) Stoiljkovic, A.; Ishaque, M.; Justus, U.; Hamel, L.; Klimov, E.; Heckmann, W.; Eckhardt, B.; Wendorff, J. H.; Greiner, A. *Polymer* **2007**, *48*, 3974.
(3) Stoiljkovic, A.; Venkatesh, R.; Klimov, E.; Raman, V.; Wendorff, J.; Greiner, A. *Macromolecules* **2009**, *42*, 6147–6151.
(4) Bognitzki, M.; Hou, H.; Ishaque, M.; Frese, T.; Hellwig, M.; Schwarte, C.; Scharper, A.; Wendorff, J. H.; Greiner, A. *Adv. Mater.* **2000**, *12*, 637.
(5) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564.