

Scalable Process for the Spinning of PVA–Carbon Nanotube Composite Fibers

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ABSTRACT: We report a water-based spinning process to produce polyvinyl alcohol (PVA)–carbon nanotube composite fibers that contain a large fraction of nanotubes. The process differs from previous methods to achieve related materials because the spinning solution is injected in a static coagulation bath instead of being circulated in coflowing streams. The resultant wet spinning process is reminiscent of processes industrially developed for neat PVA fibers. Considering its robustness, the process is therefore expected to be easily scalable for greater production. The present method is based on the stabilization of nanotubes by appropriate surfactant molecules that allow the nanotubes to remain homogeneously dispersed in

aqueous solutions of PVA. The obtained fibers are homogeneous, uniform in diameter, and can be spun indefinitely. They are electrically conductive and potentially useful for conducting textile applications. The present process being based on the colloidal stability of the particles in PVA solutions, it is believed that it could be extended to several other types of composite PVA fibers provided that the particles are stabilized by similar surfactants. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E191–E196, 2012

Key words: fibers; polymer nanocomposites; carbon nanotubes; coagulation; polyvinyl alcohol; fiber wet spinning

INTRODUCTION

Carbon nanotubes (CNTs) can be used as fillers in polymer fibers to improve mechanical properties or provide new functionalities such as electrical conductivity and piezoresistivity. Melt fiber spinning is a common approach that consists in extruding a polymer melt filled with CNTs.^{1–11} Unfortunately, this approach is not well suited to make fibers with a large fraction of CNTs. Indeed, the presence of CNTs, even at weight fraction below 10 wt %, results in a strong increase in the viscosity of the polymer. This increase makes polymer extrusion and fiber spinning particularly difficult. In contrast, wet spinning approaches that consist in making fibers from polymer solutions allow the inclusion of greater fractions of CNTs, provided that the nanotubes are homogeneously dispersed in the polymer solution. Polyvinyl alcohol (PVA) is among the main polymer that is industrially spun via wet or gel spinning approaches.¹² This polymer combines good mechanical properties and chemical stability. It is

used in a large variety of applications.¹² In addition, PVA can be spun from aqueous solutions; this is a significant advantage in terms of production cost and environmental impact. It is known that PVA strongly interacts with nanotubes in aqueous solutions and cause their coagulation.^{13,14} The aggregation of the nanotubes in the presence of PVA results from the adsorption of polymer chains onto two or more CNTs; this mechanism is known as bridging coagulation. Adsorption of the polymer chains can occur even if the nanotubes are covalently functionalized¹⁵ or if surfactants are weakly adsorbed at their interface. PVA indeed interacts sufficiently strongly with the nanotubes to displace weakly adsorbed surfactant molecules. This phenomenon was previously used on purpose to spin PVA–CNT fibers with large fractions of CNTs, that is, above 10 wt %.^{13,14} This process consisted in injecting a CNT dispersion in the coflowing stream of a PVA solution. This led to fibers with large energy to failure,^{16,17} novel shape memory capabilities,¹⁸ high electrical conductivity, and piezoresistivity potentially useful for sensing applications.¹⁹ The injection of solutions in coflowing configurations can be easily achieved on a laboratory scale using devices with rotating bath or coaxial pipes. Unfortunately, controlling coflowing streams on large scale and in multifilament configurations, as needed for most applications, is particularly challenging. Fiber spinning in

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static media would be more suitable. Indeed, coagulation of a polymer in a static bath would be reminiscent of conventional industrial wet spinning processes²⁰ and therefore easily scalable. Successful efforts to directly spin fibers from mixture of PVA and CNTs in static coagulating baths have been recently reported in the literature. Homogeneous fibers with excellent mechanical properties could be produced from dispersions made of nanotubes, PVA, DMSO, and water.^{21–23} However, the nanotubes were not specifically stabilized against aggregation and were used at low concentration. The solutions were injected into a methanol bath at low temperature, thus forming a gel fiber. The final amount of CNT in the composite fibers was between 0.3 and 3 wt %, which is insufficient to achieve a significant electrical conductivity. Xue et al.²⁴ proposed an alternative method to spin electrically conductive yarns made of PVA and CNTs. In their previous approach, CNTs were directly mixed with PVA in aqueous media with a weight ratio of CNT to PVA up to 40%. However, in such conditions, the nanotubes form aggregates and the dispersions are inhomogeneous. Nevertheless, these dispersions could still be injected in a static coagulation bath made of an aqueous solution of sodium sulfate salt. This is a typical medium for the coagulation of PVA fibers.¹² The achieved fibers had an average diameter of 500 μm and exhibited nonuniform properties and structure because of the presence of aggregates in the spinning dispersions. They were conductive and showed an average resistivity on the order of several tens of $\text{k}\Omega/\text{cm}$. However, such fibers are fragile and their conductivity varies along the filament. Therefore, it appears that despite the above progresses, methods reminiscent of conventional PVA fiber technologies could not yet be used to achieve homogeneous and uniform PVA fibers loaded with a large fraction of CNTs.

We propose such a method in this work. The main challenges consist in stabilizing CNTs in aqueous solutions of PVA to prevent the formation of aggregates before fiber spinning. The spinning solutions have to contain a large ratio of CNT to PVA and to be sufficiently concentrated. In addition, the stabilization should be achieved by modifying the nanotubes without completely screening or downgrading their properties. We found that all these requirements can be met by using polyoxoethylene glycol octadecyl ether, a nonionic surfactant additive that coats the nanotubes and that prevents the PVA chains from adsorbing at the interface of the nanotubes. This surfactant has been selected among others after different tests. The selected surfactant avoids bridging coagulation and destabilization of the dispersion. The choice of the appropriate surfactant is particularly delicate because the surfactant

has to be strongly adsorbed onto the nanotubes via a large hydrophobic group and to still be water soluble. The fibers are spun by the injection of the PVA–CNT dispersion in a static bath of an aqueous solution of sodium sulfate salt. The coagulated fibers are continuously circulated in a bath of water to be washed and are then dried using infrared (IR) heating before being wound up. All these stages match the basic phenomena used in the continuous spinning of industrial PVA fibers. The proposed approach allows the spinning of fibers that contain a ratio of CNT to PVA above 10 wt % and that are electrically conductive. Their structure, electrical, and mechanical properties are described.

EXPERIMENTAL SECTION

Two different types of CNTs are used: purified Elicarb single-walled CNTs (SWCNTs) purchased from Thomas Swan (Consett, UK) and multiwalled CNTs (MWCNTs) provided by Arkema (Colombes, France) Graphistrength C100 (Batch 6078). Both types of CNTs are grown by catalyzed chemical vapor deposition. SWCNTs are used as received. MWCNTs are purified in H_2SO_4 acid. This purification allows iron catalysts and catalyst supports to be removed. The nanotubes are washed several times with distilled water to fully remove the remaining acid. After purification, the tubes contain a fraction of residual iron catalysts of about 3 wt % and no other forms of impurities.

Different aqueous dispersions are made by dispersing 0.5 wt % SWCNTs using the following water-soluble surfactant molecules at a concentration of 1 wt %: polyoxoethylene glycol octadecyl ether (commercial name Brij® 78, $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$); polyoxoethylene glycol dodecyl ether (commercial name Brij® 35, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$); and sodium dodecyl sulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$).

The two tested Brij® surfactants exhibit a similar nonionic structure and approximately the same molecular weight. However, they differ by the size of their hydrophobic and hydrophilic groups. In particular, Brij® 78 has a greater hydrophobic chain than Brij® 35.

MWCNTs are dispersed at a concentration of 0.9 wt % with 1.2 wt % of the above surfactants as stabilizing agents. The dispersions are homogenized by sonication using a Branson Sonifier 205A (Danbury, Connecticut) equipped with a horn. Each CNT dispersion is mixed at a 50 wt %/50 wt % ratio with an aqueous solution of PVA. The polymer solution contains 8 wt % of PVA. The used PVA was purchased from Seppic (Putteaux, France) and has a molecular weight of $M_w = 195 \text{ kg/mol}$ and a hydrolysis ratio of 98%.

The stability of the mixture is assessed by macroscopic observations and optical microscopy, as

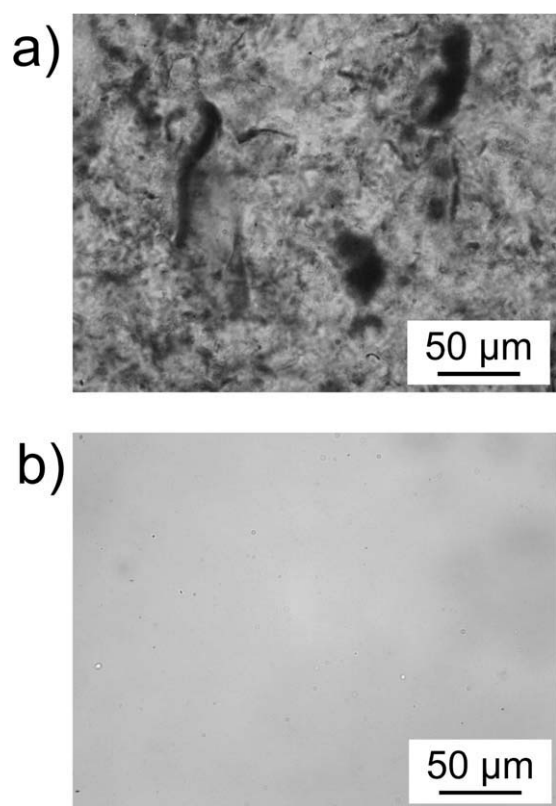


Figure 1 Optical micrographs of nanotube dispersions. (a) A dispersion of single-walled nanotubes initially stabilized by SDS surfactant is destabilized on the addition of PVA. Large aggregates are formed. This dispersion is not suitable for fiber spinning. The same behavior is observed when the nanotubes are stabilized by the Brij® 35 surfactant. (b) A dispersion of nanotubes stabilized by Brij® 78 remains stable after the addition of PVA as shown in the micrograph. The uniform texture reflects the absence of aggregates typically greater than 1 μm . Scale bar = 50 μm .

shown in Figure 1. Dispersions that contain aggregates are discarded, whereas dispersions that are found to be stable are used for fiber spinning.

Fiber spinning is achieved by the continuous injection of stable dispersions in a static coagulation medium made of an aqueous saturated solution of sodium sulfate at 40°C. Saturation of the coagulating solution is achieved at 40°C for a concentration of 320 g/L of sodium sulfate. The injection is controlled by a Teledyne ISCO (Lincoln, Nebraska) dosing piston pump. The dope is injected at 1 m/min through three to five conical spinnerets, which have a diameter of 300 μm at their tip. The three to five coagulated filaments stick to each other to form a single fiber. The latter is then taken up and drawn into a water bath to be washed, dried by IR heating, and lastly collected onto a winder. The washing bath allows salt and water-soluble surfactants to be removed from the fibers. Nevertheless, it is likely that a certain fraction of surfactant remains in the final fibers. The fibers experience a continuous drawing during their formation

along the line. The total draw ratio depends on the injection rate of the dispersion, residence times in the coagulation and washing media, and final winding rate. The typical diameters of the presently investigated fibers are in the range of 15–60 μm depending on the spinning conditions. The properties of fibers with a total draw ratio of 4 are studied in this work. The winding rate can be raised up to 10 m/min. The typical residence times in the coagulation and washing bath do not exceed a minute. The line used for such a spinning is sketched in Figure 2.

After winding, some SWCNT fibers are drawn at 140°C at different strain rates, from 75 to 200%, using an oven coupled to a tensile load instrument Zwick Z2.5/TN1S (Ulm, Germany). Drawing is performed at a strain rate of 3%/min. The temperature of 140°C lies in between the glass transition and melting temperatures of the neat PVA.

Different structural and property characterizations of the fibers are performed. Thermogravimetric analysis (TGA) is used to determine the amount of PVA in the composite fibers. The experiments are performed using a Setaram (Caluire, France) TAG 16 instrument. The dispersion of the nanotubes within the fibers is qualitatively assessed from scanning electron microscopy (SEM) observations performed with a JEOL JSM-840A SEM (Tokyo, Japan). The fibers are frozen in liquid nitrogen and fractured perpendicular to their long axis to achieve observations of their cross section.

The mechanical properties of the fibers are characterized under tensile load using a Zwick Z2.5/TN1S instrument. The gauge length of the samples is about 2 cm. Their resistivity is measured by a two-probe DC method with a Keithley 2000 multimeter (Cleveland, Ohio).

RESULTS AND DISCUSSION

The three selected surfactants allow a good dispersion of the nanotubes in water. No aggregates can be

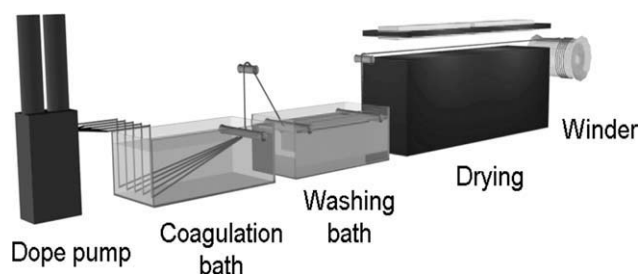


Figure 2 Sketch of the spinning line used to produce CNT-PVA composite fibers. A dispersion of CNT in a PVA solution is injected through spinnerets in a coagulation bath. They are taken up and circulated through a washing bath before being dried by IR heating and wound onto a roll.

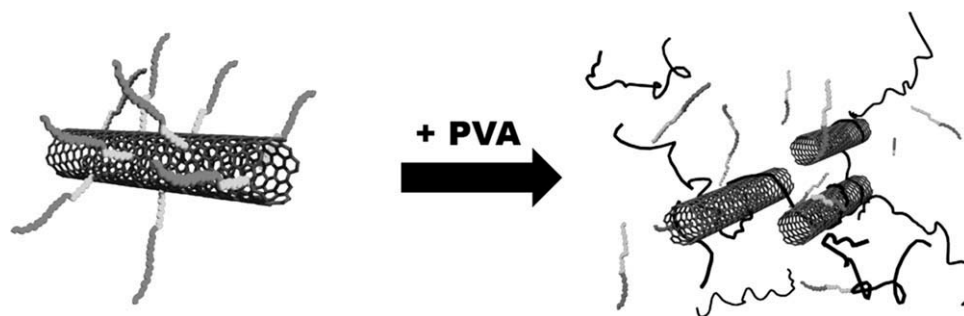


Figure 3 Sketch of the behavior of the Brij® 35 or SDS surfactant before and after the addition of the PVA solution to the CNT dispersion. The surfactant molecules are displaced by the PVA chains. This mechanism leads to the aggregation of the nanotubes. The surfactant molecules are represented by the bicolor chains, whereas the PVA polymer is schematized as long black chains.

observed after sonication at the optical resolution of optical microscopy. This confirms the absence of aggregates typically greater than 1 μm . However, some dispersions are readily destabilized when the PVA solution is added to the system. This is shown in the optical micrographs of Figure 1. As indicated in the Introduction section, this phenomenon was already reported in previous studies and even the basis of a spinning process in coflowing streams. Fast nanotube aggregation is observed for both SWCNTs and MWCNTs, which are dispersed with Brij® 35 and SDS. The aggregation of the nanotubes is explained by the competitive adsorption of surfactant and polymer at the surface of the nanotubes. Both SDS and Brij® 35 have small hydrophobic chains that are not strongly anchored at the surface of the nanotubes and, as sketched in Figure 3, can be displaced by the PVA chains. Consequently, polymer bridging can induce the aggregation of the nanotubes.

In contrast, CNT dispersions remain stable when a surfactant with a greater hydrophobic chain, but still water soluble such as Brij® 78, is used. This can be understood by the greater energy of adsorption of the surfactant that can better resist against the displacement by PVA chains. In addition, this surfactant molecule is not too large and, as shown further, does not screen the properties of the CNTs.

Considering the above observations, attempts to spin CNT–PVA fibers were performed only with dispersions stabilized by the Brij® 78 surfactant. It is observed for both SWCNT and MWCNT materials that coagulation takes place as quickly as the dispersion is injected in the sodium sulfate solution. The coagulated fiber is already strong enough to be taken up and transported along the spinning line through the washing bath and IR heating oven. The process can be run continuously and leads to the formation of indefinitely long and uniform single filament. An example of a kilometer long filament on a wheel is shown in Figure 4.

Structural characterizations

As shown in the SEM micrographs of Figure 5, the nanotube–PVA composite fibers exhibit a uniform surface texture and diameter. The bright dots homogeneously distributed throughout the fiber cross



Figure 4 Picture of a several hundred meters long PVA–CNT composite filament on a wheel.

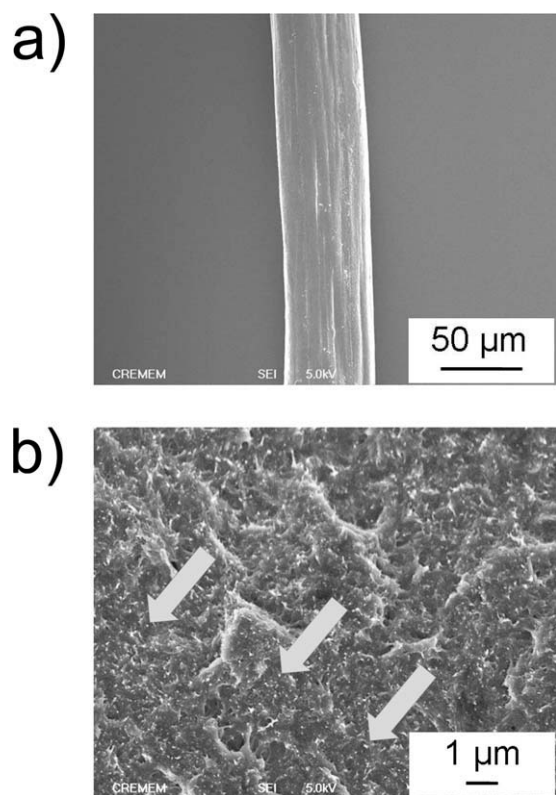


Figure 5 Scanning electron micrographs of a MWCNT-PVA fiber. (a) External texture of the fiber. Scale bar = 50 μm . (b) Fiber cross section. The nanotubes that appear as white dots are homogeneously distributed in the cross section. Some of them are marked by white arrows pointing toward them. Scale bar = 1 μm .

section reflect the presence of the nanotubes. Some of these dots are marked by white arrows.

The nanotube weight fraction in the fibers as determined by TGA is about 12 and 17 wt % for the fibers spun with SWCNTs and MWCNTs, respectively.

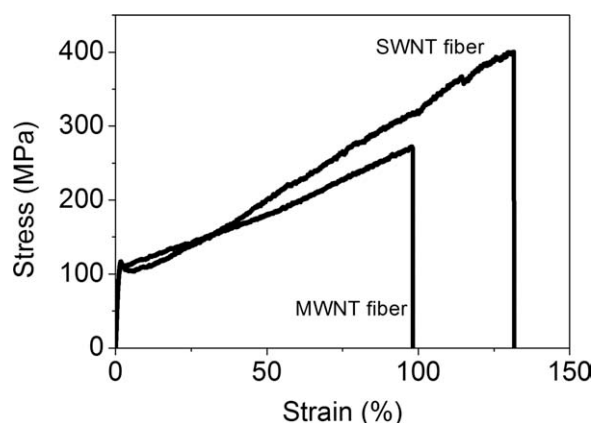


Figure 6 Stress versus strain curves of carbon nanotube-PVA composite fibers. It is observed that SWCNT-PVA fibers exhibit better mechanical properties than MWCNT-PVA fibers.

Mechanical properties

Typical stress-strain curves for SWCNT and MWCNT fibers are shown in Figure 6. The Young's modulus, strength to failure, and energy to failure are of 12 GPa, 400 MPa, and 230 J/g, respectively, for SWCNT-PVA fibers. The values for MWCNT-PVA fibers spun in similar conditions, with a total draw ratio of 4, are slightly lower. The Young's modulus, strength to failure, and energy to failure are 10 GPa, 270 MPa, and about 130 J/g, respectively, for these fibers. Unfortunately, a direct comparison with neat PVA fibers is not straightforward because we could not spin pure PVA fibers in exactly similar conditions. In particular, the total draw ratio had to be above 4 to successfully spin neat PVA fibers. This results in an improvement of the PVA chains alignment and to a greater Young's modulus regardless the presence of the fillers.

It was shown that hot-drawing can strongly affect the mechanical properties of CNT-PVA fibers and increase in particular their Young's modulus.¹⁷ Hot-drawing improves the orientation of both the polymer chains and nanotubes. In addition, it increases the polymer crystallinity and thereby enhances the stress transfer between nanotubes and PVA in the composite fibers. The mechanical properties of fibers that have experienced hot-drawing at different strain rates are shown in Figure 7. As expected, hot-drawing yields a large increase of the Young's modulus from 12 GPa for a raw fiber up to 38 GPa for a fiber stretched by 200% at 140°C. This treatment also yields a large increase of the tensile strength: from 400 MPa to 1.1 GPa.

Electrical properties of the fibers

SWCNT-PVA fibers were found to be poorly conductive despite the large fraction of CNTs they

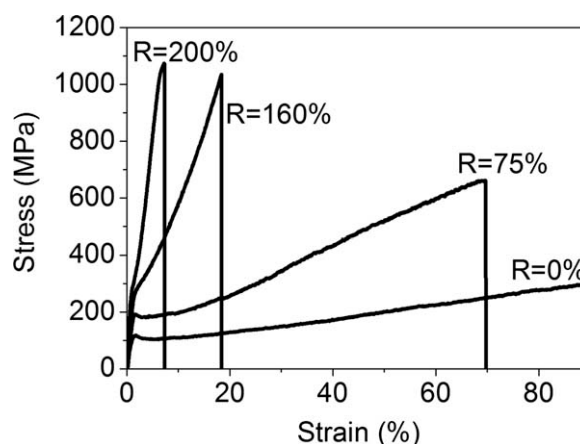


Figure 7 Stress versus strain curves of SWCNT-PVA composite fibers that have been drawn at 140°C and different draw ratios specified by R .

contain. This results presumably from highly resistive intertube contacts. Indeed, SWCNT have a small diameter and therefore a small surface area at their contact points. In addition, a large fraction of SWCNTs is semiconducting. In contrast, MWCNTs are all metallic. MWCNT–PVA fibers also contain a greater fraction of nanotubes and larger particles. They are consequently found to be more conductive. The resistivity of the composite MWCNT–PVA fibers at room temperature is about 35 k Ω /cm and uniform along the filament. This value compares well with the resistivity found by Xue et al.²⁴ Nevertheless, the resistivity of the present fibers is greater than that of PVA–CNT fibers obtained by coagulation in coflowing streams.¹³ The difference can arise from the presence of remaining surfactants at the surface of the nanotubes in the present fibers. It can also be due to the lower fraction of CNTs achieved with the present method. However, the resistivity can be decreased by annealing the fibers at high temperature.²⁵ Raw MWCNT–PVA fibers were placed in an oven at 180°C for 1 h. After being cooled down, the resistivity of the fibers was found to be about 300 Ω /cm. The observed improvement, by two orders of magnitude, is ascribed to the relaxation of mechanical stress that allows better intertube contacts.

CONCLUSION

The possibility to spin continuous and homogenous CNT–PVA fibers with a large fraction of CNTs was demonstrated. The process is based on the stabilization of the CNTs in the spinning solution with appropriate surfactants that resist against the adsorption of the polymer chains. The present method is reminiscent of processes industrially developed for neat PVA fibers. It is therefore expected that it could be easily scaled up for greater production. In terms of properties, it was observed that fibers spun with MWCNTs exhibit good electrical conductivity. In contrast with other conducting textile fibers coated with conducting particles, the CNTs are embedded in the core of the fibers and not simply deposited at the surface of the fibers. This distinctive structure is expected to provide a better resistance against friction, wear, and washing. The resistivity of annealed MWCNT–PVA is about 300 Ω /cm. This value is far from the intrinsic conductivity of individual nanotubes but already sufficient for applications such as heating, sensing, or antistatic textiles. In addition to these potential applications, it is believed that the present process could be extended to organic or inorganic particles other than CNTs to spin a variety of composite fibers with a PVA matrix. The main conditions for such extensions remain based on the stabilization of the particles with appropriate surfactants that are

not displaced by PVA and that do not prevent the PVA to coagulate in conventional media such as sodium sulfate solutions.

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