

Blending cellulose with polyethylene-co-acrylic acid in alkaline water suspension

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Abstract Alkaline solutions of cellulose and polyethylene-co-acrylic acid (PE-co-AA) were mixed in order to prepare homogeneous cellulose/PE-co-AA blends. Different mixing methods were tested and the evolution of solutions was characterized by rheological methods and optical microscopy. In addition to the solution stage studies, the precipitated dry blends were characterized by Differential Scanning Calorimetry, Scanning Electron Microscopy, Fourier Transform Infrared and Dynamic Mechanical Analysis. Mixing the solutions led to the formation of a suspension, consisting of PE-co-AA particles dispersed evenly throughout the cellulose solution. Based on the conducted studies, it became clear that a uniform quality and the best mixing were attained with a method in which the suspension was frozen and melted between the mixing. In dry blends the polymers were found to be mixed on 1 μm scale, and the crystallization temperature of the PE-co-AA phase was increased $\sim 6^\circ\text{C}$ due to the nucleation ability of the cellulose phase.

Keywords Polymer Blend · Cellulose · Rheology · Nucleation

Introduction

When looking at alternative materials for petroleum based polymers, polymers from renewable resources raise a great deal of interest due to their eco-friendly characteristics. For this purpose, cellulose and cellulose-based materials are one of the key bio-based substances offering numerous new possibilities for polymeric materials, having an important role as a raw material for future plastic materials (Simon et al. 1998).

Even though cellulose is the most common natural polymer, its usage has been effectively limited by the strong hydrogen bonding between cellulose fibers. These bonds result in a tightly packed crystalline material, which is insoluble in nearly all solvents. In addition, these strong intermolecular interactions are the main reason why cellulose degrades rather than becomes molten when heated. Because of these disadvantages, the processing of cellulose has been limited to viscose process, thermoformable cellulose derivatives, and to regenerated cellulose grades which are dissolvable in alkaline water solutions or in special solvent systems (Simon et al. 1998; Zhou and Zhang 2001; Yan et al. 2009).

Cellulose can be dissolved in aqueous solvent such as NaOH in water (Isogai and Atalla 1998; Roy et al.

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2001; Roy et al. 2003; Egal et al. 2007; Moigne and Navard 2010) in a narrow range of temperatures and concentrations (from 7 to 10 wt% NaOH in water at -4 to -8 °C). First dissolutions in NaOH were already done in 1939 by Sobue et al. In addition, various aqueous alkaline solvent systems, such as aqueous NaOH/urea, NaOH/thiourea, NaOH/urea/thiourea (Zhou and Zhang 2001; Ruan et al. 2004; Cai and Zhang 2005, 2006; Cai et al. 2007; Yan et al. 2007; Qi et al. 2008; Zhang et al. 2010) LiOH/urea (Cai and Zhang 2005) and NaOH/ZnO (Vehviläinen et al. 2008; Liu et al. 2011) can dissolve cellulose completely, even cellulose grades with relatively high DP (DP = 500–900) (Ruan et al. 2004; Cai and Zhang 2005; Qi et al. 2008, 2011). The addition of substances such like urea, thiourea or zinc oxide are reported to be helping cellulose dissolution and work as a solution stabilizer against gelation. Furthermore, aqueous solvent systems, like N-methylmorpholine-N-oxide/H₂O (Bang et al. 1999; Biganska et al. 2002; Liu et al. 2007) have been developed to dissolve cellulose.

Blending cellulose with synthetic polymers is an important process to prepare functional polymeric materials. Conventionally all polymer blends are prepared in a melt extruder, and this is also the case if thermoplastic cellulose derivatives are blended e.g. with polyethylvinylacetate (Girija et al. 2010). Likewise, regenerated cellulose grades are blended with synthetic polymers in solutions using new kinds of non-aqueous solvent systems, like N-methyl-2-pyrrolidinone/Lithium chloride (Schartel et al. 1996) or N,N-dimethylacetamide/Lithium chloride (Nishio and Manley 1988; Nishio et al. 1989) for blending cellulose with polyvinylalcohol, and dimethyl sulfoxide/para-formaldehyde for blending cellulose with poly-vinylpyrrolidone (Masson and Manley 1991a), poly-4-vinylpyridine (Masson and Manley 1991b), or polyacrylonitrile (He et al. 2002).

The properties of cellulose and polyolefins are totally different and therefore it is of interest to combine these properties via blending technique. However, due to the disadvantages of cellulose and the different natures of these polymers (hydrophilic vs. hydrophobic) the preparation of well mixed blends is extremely demanding. The homogeneous morphology in the polymer/polymer blends is still the main requirement when the properties of the polymers are to be combined. One convenient way to prepare a cellulose/polyolefin blend could be to use ethylene/

acrylic acid copolymer as the polyolefin. These both polymers are soluble in alkaline water phase and they precipitate simultaneously by acidic treatment. Although this type of cellulose based blend has not been studied in the past, starch-based plastic materials have been in focus of scientific research for decades. Thermoplastic blends of starch and poly(ethylene-co-acrylic acid) were studied for agricultural purposes for a number of years starting at the end of the seventies. (Otey et al. 1977; Gould et al. 1990; Fanta et al. 1992; Swanson et al. 1993).

In this study the blends of cellulose and poly(ethylene-co-acrylic acid) (PE-co-AA) were prepared by mixing their alkaline water solutions. As a result, a suspension is formed. To characterize suspension mixing, studies were carried out by rotational rheometry and optical microscopy. The final dry blends were characterized by Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR).

Experimental

Materials and methods

Alkaline cellulose water solution (3 wt% cellulose, 6.5 wt% NaOH, 1.3 wt% ZnO) was received from the Tampere University of Technology. The enzyme treated softwood pulp from Domsjö Fabriker AB (intrinsic viscosity 520 ml/g) was dissolved into NaOH/ZnO as published previously by Vehviläinen et al. 2008. The preparation of this solution is described in the patent application of Vehviläinen et al. (2009). After preparation the cellulose solution was kept frozen in freezer (-20 °C). Alkaline (pH ~ 10) polyethylene-co-acrylic acid water solution (20 wt% of PE-co-AA) was obtained from BIM Finland Oy and it was stored in refrigerator ($+5$ °C). The both solutions were allowed to warm up just prior the use. All the preparation steps were made at 23 °C unless otherwise mentioned.

Mixing of the abovementioned solutions was done in a 100 ml glass vessel under vigorous magnetic stirring. Dosages of PE-co-AA solution were done with a syringe by feeding it slowly to the vortex of cellulose solution (cellulose batch ~ 30 – 35 ml). The formed suspension was mixed directly for 24 or 48 h, or so that after 24 h of mixing it was frozen, thawed,

and stirred for another 24 h. This freeze-melting method between mixing was done in order to dissolve any cellulose which may have gelled during mixing. The polymer compositions of the suspensions are presented in Table 1.

After the mixing step, the alkaline polymer suspension was moved in acidic solution (20 wt% H_2SO_4) to precipitate the polymer blend. After precipitation, the blend was washed several times (until neutral) and dried in vacuum oven at 40 °C overnight.

The film samples (for ATR and SEM) were prepared as such: a drop of the suspension was flattened between silica layers where the polymer blend was regenerated by immersing the layers in acidic solution (20 wt% H_2SO_4). After complete regeneration (~ 1 h), the silica layers were removed and the sample was washed carefully with water until neutral. The wet film sample was placed back on a silica layer and allowed to dry (and stick to the layer) at room temperature overnight. The final drying was then performed in vacuum oven over night. The thickness of the film was ~ 20 – 40 μm .

Characterization

All the analyses were performed at 23 °C unless otherwise mentioned. The rheological characterization of the solutions and suspensions were done using a Physica MCR 301 rotational rheometer (Anton Paar GmbH, Austria) equipped with DIN concentric cylinders geometry with bob and metal cup diameters of 26.665 mm and 28.918 mm, respectively (CC 27). In order to estimate the changes in suspension structure during mixing, a series of measurements were done. First a frequency sweep measurement with frequency

ranging from 0.1 to 50 rad/s at strain of 0.2% in linear viscoelastic region was performed, with the exception of the neat cellulose solution that was measured with 5% strain due to the low viscosity. Next, rotational measurement of steady shear flow (0.01–1,000 l/s) was performed for all of the suspensions and solutions. In addition, a 10 min recovery time was used before the steady shear flow test.

To clarify the rheological results, changes in the suspension structure were also estimated with centrifugation (Hereus Multifuge 3 s, 4,000 rpm) and Olympus BH-2 optical microscopy equipped with a digital camera. A drop of the suspension was placed between microscope glass plates and the pictures were taken with 100 \times and 200 \times magnification.

The thermal behavior of the dry blends was measured with a Mettler Toledo DSC 821e under a nitrogen atmosphere. The thermal history of the blend was destroyed by heating the sample to 150 °C at 20 °C/min. The crystallization behavior was then determined from the peak area and the peak temperature of the crystallization exotherm (T_C), which was obtained at a cooling rate of 10 °C/min (from 150 °C to -30 °C). After the cooling step, the melting endotherms (ΔH) and the peak melting temperatures (T_m) were measured by reheating the sample at 10 °C/min. The weight of the samples varied between 10 and 20 mg depending on the PE-co-AA concentration in the blend (PE-co-AA amount in the sample 5 mg).

To analyze the amount of free/unbound PE-co-AA in the blend (in the powder form) it was leached in hot toluene (70 °C, 30 min) in which the pure PE-co-AA was found to be soluble. The sample was weighed before and after the leaching procedure.

Table 1 The polymer compositions of the suspensions

Suspension ID	Cell./PE-co-AA solutions volume ratio	Polymer concent. (wt%)	Cellulose (wt%)	PE-co-AA (wt%)	Mixing (h)	Freeze-melted
Cell-75-24 h	100/5 = 20	3.8	75	25	24	–
Cell-75 f-m	100/5 = 20	3.8	75	25	48	Yes
Cell-50-15 min	100/15 = 6.7	5.2	50	50	0.25	–
Cell-50-3 h	100/15 = 6.7	5.2	50	50	3	–
Cell-50-24 h	100/15 = 6.7	5.2	50	50	24	–
Cell-50-48 h	100/15 = 6.7	5.2	50	50	48	–
Cell-50-f-m	100/15 = 6.7	5.2	50	50	48	Yes

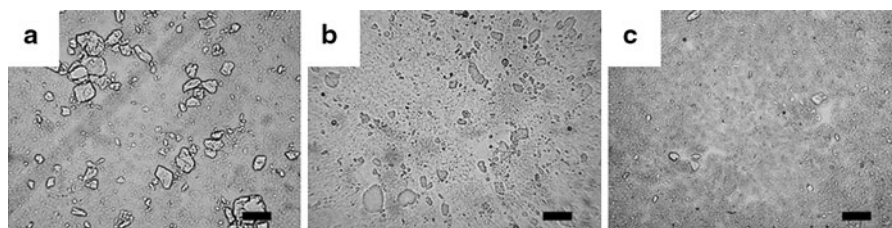


Fig. 1 Optical microscopy pictures of the cellulose/PE-co-AA suspension (Cell-50) after mixed for **a** 15 min, **b** 3 h, or **c** 24 h. The size of the scale bar is 100 μm

The morphology of the blend was analyzed with Hitachi TM-1000 field emission SEM using an acceleration voltage of 15 kV. The SEM-micrographs were taken from the film sample (on a silica carrier) before and after the sample was leached with hot toluene (70 $^{\circ}\text{C}$, 3 h) to remove free/unbound PE-co-AA phase. Before analysis the samples were sputter-coated with gold.

Fourier transform infrared attenuated total reflection (FTIR-ATR) spectra of the samples were recorded on a PIKE GladiATR diamond crystal installed to MATTSON 3000 FTIR spectrometer. The spectrum was recorded from the film sample (on a silica carrier) before and after the sample was leached with hot toluene.

Mechanical properties of the film samples (thickness $\sim 30\ \mu\text{m}$) were analyzed with DMA (TA instruments Q800) at 23 $^{\circ}\text{C}$ using a film/tension measuring head. Stress sweeps of the samples were done from 0 to 30 MPa or until they broke down.

Results and discussion

The effect of mixing procedure

The basic idea of blending cellulose and PE-co-AA relies on the fact that both of the polymers are soluble in alkaline water phase, where they were expected to form a uniform quality blend, and that both of the polymers regenerate fast and simultaneously via acidic treatment, where the homogeneous morphology of the blend should be maintained (i.e. diminished phase separation during regeneration). In practice, however, the preparation of the cellulose/PE-co-AA blend via solution mixing was not so straightforward. The main drawback was that the PE-co-AA solution started to form gel particles (Fig. 1a) when it was

added in cellulose solution. It became obvious that the PE-co-AA was soluble only in modestly alkaline solution (pH 10) whereas at higher pH's (cellulose solution pH 14) the solubility was diminished. In order to clarify the structural changes in the cellulose/PE-co-AA suspensions during the mixing, microscopy pictures from the solutions were taken after 15 min, 3 and 24 h of mixing (Fig. 1a, 1b, and 1c, respectively). As the pictures show, large particles of PE-co-AA were seen after 15 min, but when mixing was continued, the particles and aggregates started to decay. When the mixing was continued to 24 h, most of the remaining aggregates were broken-down and spread evenly throughout the suspension.

An improvement in the uniformity of suspension was also seen when the suspensions were centrifuged after the mixing step (Fig. 2). After 15 min of mixing

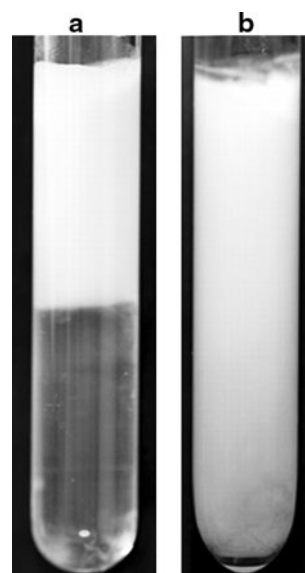


Fig. 2 Centrifuged Cell-75 suspension samples. Before centrifugation the suspension was mixed for **a** 15 min or, **b** 24 h

the suspensions were phase separated into a lighter part on the top, consisting relatively big particles of PE-co-AA, while the mixed part of the suspension, consisting mostly of the cellulose, was on the bottom. After 24 h of mixing, no more phase separation was observed in centrifugation, since the suspensions were clearly more uniform. This correlated with the optical microscopy results.

In addition to PE-co-AA aggregation, it was also expected to see the gelling of cellulose during the mixing procedure. The gelation behavior of cellulose, dissolved in NaOH based systems, is reported to take place via several factors (Roy et al. 2003; Ruan et al. 2008; Cai and Zhang 2006). On average, the used neat cellulose solution has been known to lose its stability if stored at RT for prolonged times (>24 h). Also, drop-wise addition of the PE-co-AA locally reduced the pH in the cellulose solution for a while, which may have triggered the cellulose gel formation. To get more information of the solution stage properties the produced suspensions were also subjected to dynamic oscillation frequency sweep tests with rheometry. These results clearly showed how the complex viscosity of the suspension increased in parallel of mixing time (Fig. 3). This evolution was the sum of several different phenomenon, i.e. the solubility levels (soluble vs. gel vs. aggregate) of cellulose and PE-co-AA as well the size and amount of these different phases during the mixing. Therefore it was difficult to find any direct correlation between the rheological result and the miscibility of the polymers.

In order to remove the effect of cellulose gel formation on the rheological properties of the

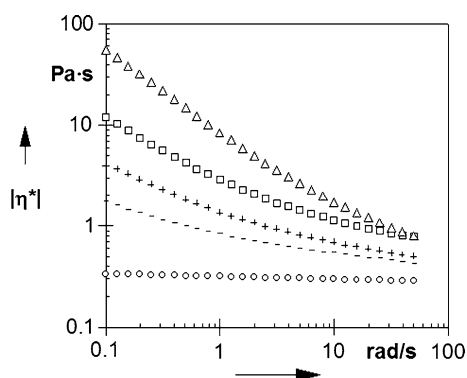


Fig. 3 Complex viscosities of neat cellulose solution (open circle), Cell-50-15 min (—), Cell-50-3 h (+), Cell-50-24 h (open square) and Cell-50-48 h (open triangle)

suspension, a freeze-melting procedure was performed after 24 h mixing. This freezing-melting was expected to dissolve any gelled cellulose phase. Figures 4a, b shows the storage and loss modulus of Cell-50 and Cell-75 suspensions as function of different mixing procedures. These results clearly showed that if the suspension was mixed for 48 h straight without freezing and melting, the gel like behavior was seen as a rise of G' (Fig. 4a). However, when the freezing-melting procedure was performed after 24 h mixing, the G' and G'' levels remained, or even reduced during the following 24 h mixing procedure (Fig. 4a, b).

The influence of the freeze-melting procedure was found also in the flow properties of the suspensions (Fig. 5). All the suspensions seemed to form a kind of structure which required sufficient high shear force to break down before the suspension started to flow. The required shear force was, however, clearly lower in freeze-melted samples. It was quite obvious that during longer mixing procedures the freezing-melting step was required to reduce the gelation of cellulose.

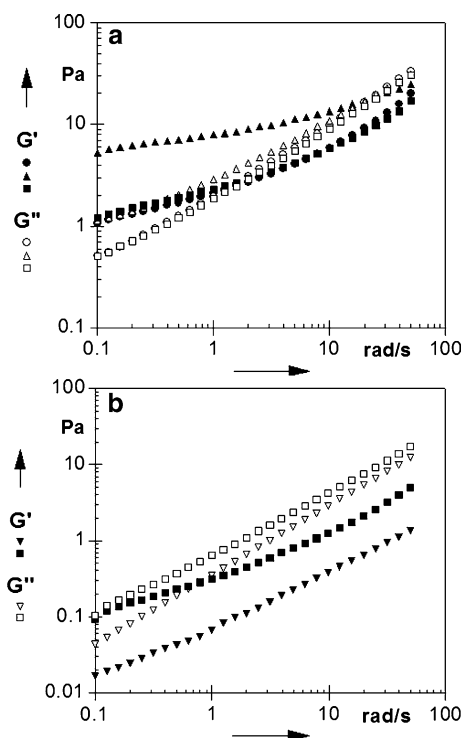


Fig. 4 Frequency sweeps of **a** Cell-50-24 h (filled square), Cell-50-48 h (filled triangle), Cell-50-fm (filled circle), and **b** Cell-75-24 h (filled square) and Cell-75-fm (filled inverted triangle) suspensions. Storage modulus G' (filled symbols) and loss modulus G'' (open symbols)

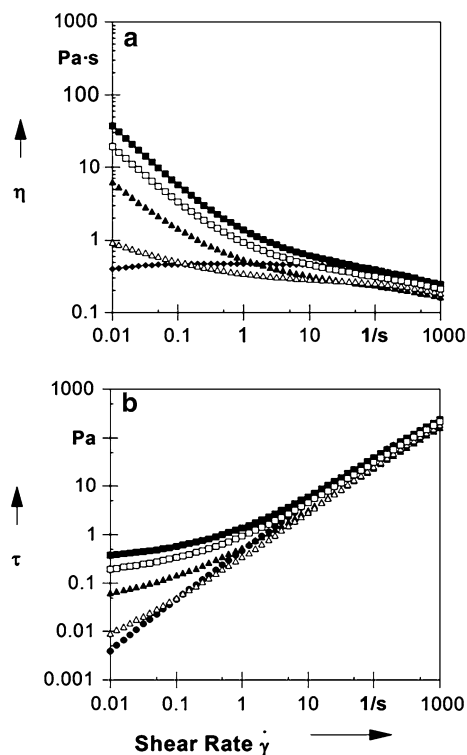


Fig. 5 **a** Viscosities, and **b** shear stresses of the cellulose (filled circle), Cell-75-fm (open triangle), Cell-75-24 h (filled triangle), Cell-50-fm (open square), and Cell-50-24 h (filled square) suspensions as a function of shear rate

Morphology of the cellulose/PE-co-AA blends

After the synthesized cellulose/PE-co-AA blends (Cell-50-fm and Cell-75-fm identified as Cell-50 and Cell-75 hereafter) were dried and their morphology was studied in more detail using SEM. A thin layer (20–40 μm) of the blend was prepared on a smooth silica surface, whereafter the free/unbound PE-co-AA phase was removed from the film by leaching in toluene (70 $^{\circ}\text{C}$, 3 h). The SEM pictures of the selected samples, before and after leaching, are presented in Fig. 6. The neat cellulose film was even and smooth, and no clear microstructure was observed (Fig. 6a). In the blend samples, however, small $\sim 1\ \mu\text{m}$ size flakes were seen at the surface of the film (Fig. 6b, c). These flakes were most likely from the unbound PE-co-AA phase, as none were present in the leached samples (Fig. 6d). In addition, small holes ($<1\ \mu\text{m}$)

were seen in leached samples indicating the past location of the unbound PE-co-AA phase.

Before the SEM analysis, these film samples were also characterized with FTIR-ATR (Fig. 7a–d). The resolution of the IR analysis is not very high but, as can be seen, it was enough to show the difference between the samples Cell-50 and Cell-75 when the characteristic vibrations of PE-co-AA and cellulose phases were observed (1,701 cm^{-1} and $\sim 1,050\ \text{cm}^{-1}$, respectively). Finally, when the unleached Cell-50 and the leached Cell-50 samples were compared (Fig. 7c vs. d) no clear difference in the amounts of the PE-co-AA phases could be drawn. It seemed that, for some reason most of the PE-co-AA phase was out of reach of toluene leaching.

In addition to studying the leaching of the film samples, the leaching procedure was performed also for the blend in powder form. As a result, only 5% of the PE-co-AA phase was removed via toluene leaching. This promoted the IR-results which indicated that only a small fraction of the PE-co-AA was dissolved in hot toluene.

It is also noteworthy to note that preliminary stress–strain measurements performed in DMA for film samples showed that the neat cellulose film was more brittle than corresponding blend film samples.

Finally, the thermal behavior of the blends was analyzed with DSC. Over the measured temperature range there was no indication of thermal transition points of cellulose phase, but the thermal transitions of PE-co-AA phase were clearly observed. These transitions were not influenced, except the crystallization temperature, which was clearly higher in blend samples than in neat PE-co-AA (Fig. 8a $T_{\text{C}} = 65, 7\ ^{\circ}\text{C}$ vs. 8b–c $T_{\text{C}} = 71\text{--}72\ ^{\circ}\text{C}$). The increase in crystallization temperature clearly indicated that the rigid/solid cellulose acted as a strong nucleation agent for the molten PE-co-AA phase. This was a slightly unexpected result as strong nucleation efficiency is normally seen in polypropylene rather than in the polyethylene-based matrix (Dikobe and Luyt 2010; Lipponen et al. 2009). In addition, the nucleation efficiency is usually even weaker in low density polyethylene, which resembles PE-co-AA, than in high density polyethylene (Bouafif et al. 2009; Lipponen and Seppälä 2005; Huang et al. 2007). One explanation for this strong nucleation effect in

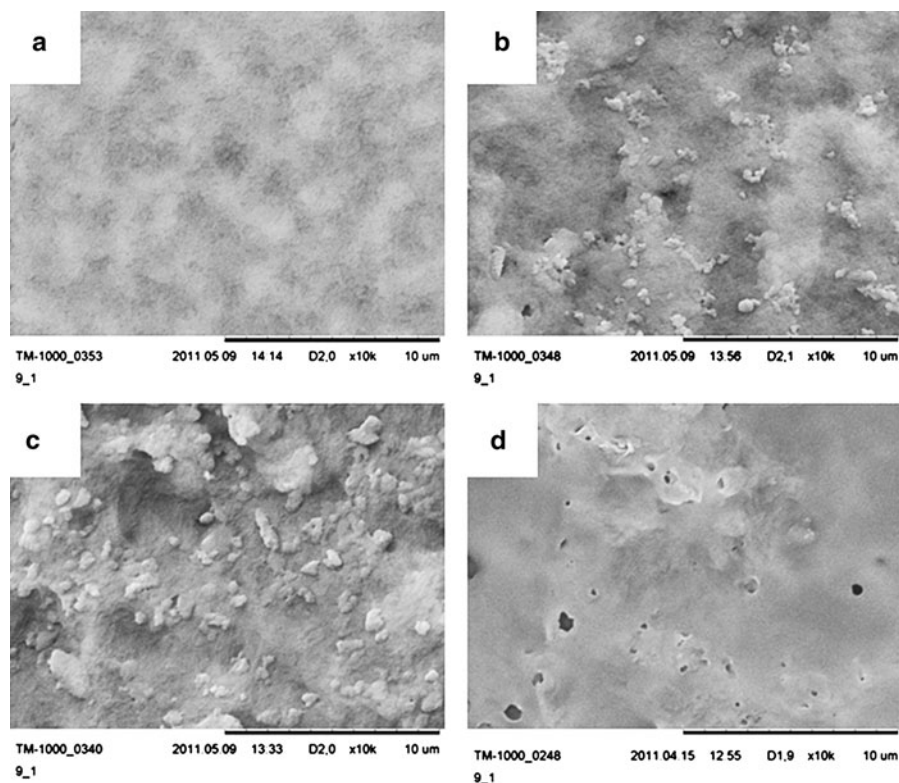


Fig. 6 The SEM-micrographs of **a** neat cellulose, **b** Cell-75, **c** Cell-50, and **d** leached Cell-50 film samples. The magnification is 10,000

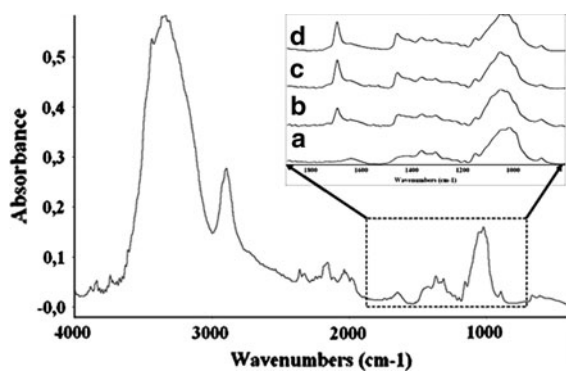


Fig. 7 FTIR-ATR-spectra of neat cellulose. Inlet, **a** neat cellulose, **b** Cell-75, **c** Cell-50, and **d** leached Cell-50 film samples

cellulose/PE-co-AA blends is that the phases were well mixed. This enables large interfacial area between cellulose and PE-co-AA which would intensify any weak nucleation effects. This explanation would also support the above leaching results if we consider that the PE-co-AA phase was out of reach of toluene leaching due to the well mixed morphology.

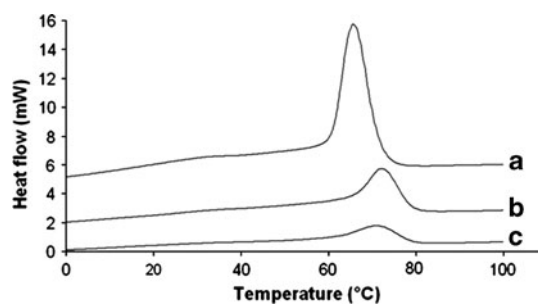


Fig. 8 DSC-crystallization curves of **a** neat PE-co-AA, **b** Cell-50, and **c** Cell-75 obtained at cooling rate of 10 °C/min. Sample amount ~ 10 mg

Conclusions

A wide variety of analyses were conducted to study the possibility to prepare well mixed cellulose/PE-co-AA polymer blends via solution mixing procedure. The rheological studies with corresponding results from microscopic pictures and centrifugation tests demonstrated the evolution of the alkaline polymer/polymer

suspension during mixing. This evolution was a sum of many factors, including cellulose gelation, and it was controlled to some extent by varying the mixing procedure. In our study, a uniform quality suspension and the best possible mixing between the cellulose and poly(ethylene-co-acrylic acid) solutions were obtained using a method in which the suspension was frozen and melted between the mixing. Finally, the analyses of the dried blends also indicated that the polymers were well mixed in the blend. According to SEM, IR, and DSC studies the polymers were dispersed, at least, in 1 μm scale. As a final result it can be stated that the solution mixing procedure proved to be an effective and easy way of preparing a blend from cellulose and PE-co-AA, two polymers with totally different characteristics.

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