Effect of E-beam treatment of ligno-cellulosics on the rheological properties of the ionic liquid solutions

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ABSTRACT

In this study, we evaluated the effect of electron beam irradiation (E-beam treatment) on the DP of ligno-cellulosics and the rheological properties of their solutions in an ionic liquid (IL). Various low refined birch pulps were produced by using a conventional kraft pulping method. The pulps were then subjected to E-beam treatment at radiation dosages of 10, 20 and 30 kGy. The pulps were evaluated in terms of intrinsic viscosity and molar mass distribution using gel permeation chromatograph (GPC). Subsequently, the treated pulps were dissolved in [DBNH][OAc] and the shear rheology of the respective dopes was analyzed. Finally, the rheological properties were related to the spinnability of the dopes through a previously established spinning procedure.

INTRODUCTION

The IONCELL-F process is a novel air-gap spinning process using 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) as a solvent for the manufacture of regenerated cellulose-based fibers.[1] The major factor that governs the spinnability is the visco-elasticity of the spinning dope. The rheological properties of the polymer solution are related to the dope concentration and, most importantly, the degree of polymerization (DP) of the ligno-cellulosics.[2,3] To achieve the production of a suitable spinning dope, the DP of the ligno-cellulosics has to be adjusted to a certain level. Electron beam (E-beam) irradiation has been proposed as an efficient method for DP adjustment of ligno-cellulosics.[4] It is a more environmentally friendly and cost and chemical efficient method compared to conventional wet-chemical DP adjustment methods such as acid or enzyme (endoglucanase) treatments because no yield losses and waste water emissions are generated.[5]

EXPERIMENTS

Birch kraft pulps with a high residual lignin content were produced with an effective alkali charge of 20% on od wood, a sulfidity of 40%, a liquor-to-wood ratio of 4:1 at 160°C and H-factors of 25 (H25), 50 (H50) and 125 (H125), respectively. Fiber sheets of these pulps were subjected to an E-beam treatment at LEONI Studer AG, Switzerland. The E-beam dosages 10, 20 and 30 kGy were selected for all the samples. Both the kraft pulps and E-beam treated pulps were characterized by means of chemical compositional (HPAEC-PAD), molar mass distribution (GPC) and intrinsic viscosity analyses. The samples were delignified with chlorite solution prior to GPC and Intrinsic viscosity measurement.

The spinning dopes with polymer concentration of 13 wt% were prepared by using a vertical kneader. Air-dried pulp, after grinded with a Wiley mill (1 mm

mesh), was mixed with IL and kneaded for 1.5 h at 80°C and 10 rpm at reduced pressure (50 – 200 mbar). The solutions were filtered through a hydraulic press filter device (metal filter mesh with 5 µm absolute fineness, Gebr. Kufferath AG, Germany) applying 2 MPa pressure at 80°C to remove undissolved substrate.

The rheological properties of the spinning dopes were measured by using an Anton Paar MCR 300 rheometer with a parallel plate geometry (25 mm plate diameter, 1 mm measuring gap). The complex viscosity and dynamic moduli (storage modulus G' and loss modulus G'') were determined by performing a dynamic frequency sweep from 50 to 100°C over an angular frequency range of 0.1–100 s^{-1}. The zero shear viscosity was determined by fitting the complex viscosity data with a Cross model.

Multi-filaments were spun on a customised laboratory piston spinning system (Fourn_ Polymertechnik, Germany). The solidified solution was placed in the cylinder, in which the dope was heated to 70 oC to form a highly viscous, air-bubble-free spinning dope. The molten solution was then extruded through a 36-hole spinneret with a capillary diameter of 100 µm and a length to diameter ratio (L/D) of 0.2. After they passed through a 1 cm air gap, the filaments were coagulated in a water bath (10 to 15 oC) in which the filaments were guided by the Teflon rollers to the godet couple. The extrusion velocity (Ve) was set to 1.6 ml/min (11.4 m/min), and the take-up velocity (Vt) of the godet varied from 5 to 85 m/min depending on different samples. The DR can be calculated as DR=Vt/Ve. The fibres were washed off-line in hot water (60 °C) and air-dried.

RESULTS AND DISCUSSION

E-beam treatment

The chemical composition of the H25, H50 and H125 pulps is listed in Table 1. It is assumed that the E-beam treatment does not alter the chemical composition. Figure 1 reveals the course of the intrinsic viscosity of the three pulps after E-beam irradiation with dosages of 0, 10, 20 and 30 kGy. It is clearly seen that the most pronounced decrease in viscosity occurs at 10 kGy while the subsequent depolymerisation proceeds more moderate when the dosage is further increased to 20 and 30 kGy, respectively. This proves that E-beam irradiation is an efficient pre-treatment for kraft pulps, by which the polymer was degraded due to random chain scission. When 10 kGy and 20 kGy were applied, the viscosities of the pulps are close to the optimum pulp viscosity (425-450 ml/g) for stable spinning.[1]

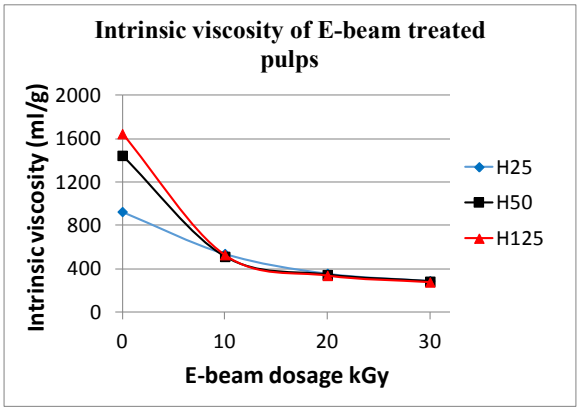

Figure 1. Intrinsic viscosity of E-beam treated samples.

Table 1. Chemical compositions of the birch kraft pulps H25, H50, and H125

	Cellulose	Hemicelluloses	Lignin
H25	53.7	22.4	23.9
H50	56.4	21.8	21.8
H125	60.0	23.6	16.4

To further confirm the chain scission of cellulose, the molecular weight distribution of the E-beam treated pulps were analyzed by using GPC. Figure 2 shows the molecular weight distribution of E-beam treated H25, H50 and H125 pulps. Typically, a bimodal molecular weight distribution was obtained for all the measured samples. It is clearly

demonstrated that the high molecular weight domains shifted to lower molar mass, while the molecular weight of the short-chain fraction remained unchanged. This is in agreement with the intrinsic viscosity measurement where the viscosity decreases as E-beam dosage increases.

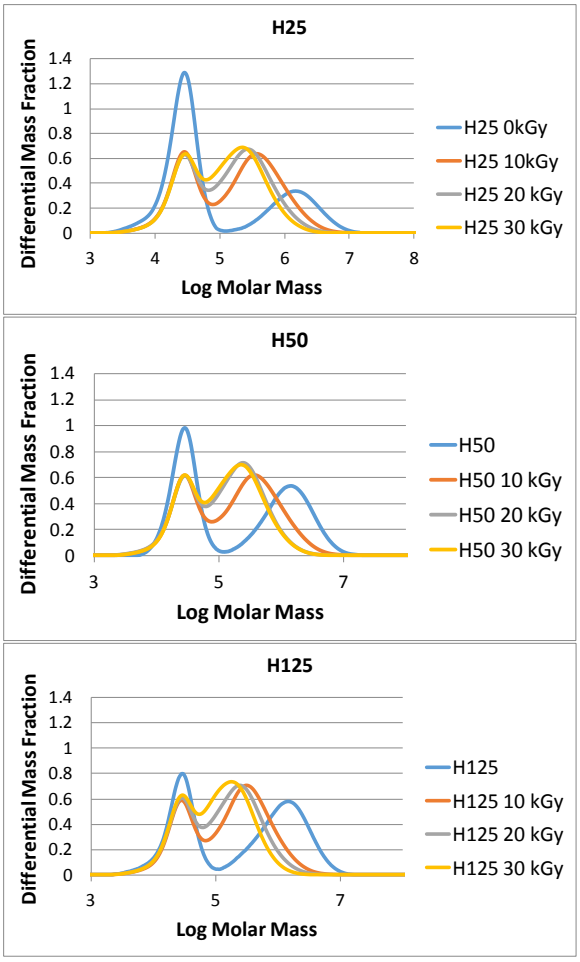

Figure 2. Molecular weight distribution of E-beam treated pulps.

Rheological measurements

Small amount of dopes were first produced from H25 and H50 for rheological measurements. The complex viscosity development of 13 wt% IL solutions (at 70 °C) of the E-beam treated H25 and H50 pulps is exhibited in Figure 3. Owing to the reduction of DP, the complex viscosity of spinning dopes decreases as the E-beam irradiation dosage increases. For the H25 pulps, the dissolution of the original and the 10 kGy treated pulps in IL results in gels as the complex viscosity is not stabilized at low angular frequency. As a result of gel formation, no crossover points (of storage and loss modulus, see Figure 4) were observed for these two dopes. Dopes with a good solution state were obtained with E-beam dosages of 20 and 30 kGy. In case of the H50 pulp, the rheology of dopes is quite similar to that of the H25 pulp, except that the dope starts to show a good solution state by using pulp with 10 kGy. The zero shear viscosity of the dopes of both 20 kGy pretreated pulps is at the same level as that prepared from our standard pulp (Bahia) comprising the same concentration of 13 wt% (30000 Pa.s). These two pulps can be potentially used as a suitable spinning dope for the Ioncell-F spinning process.

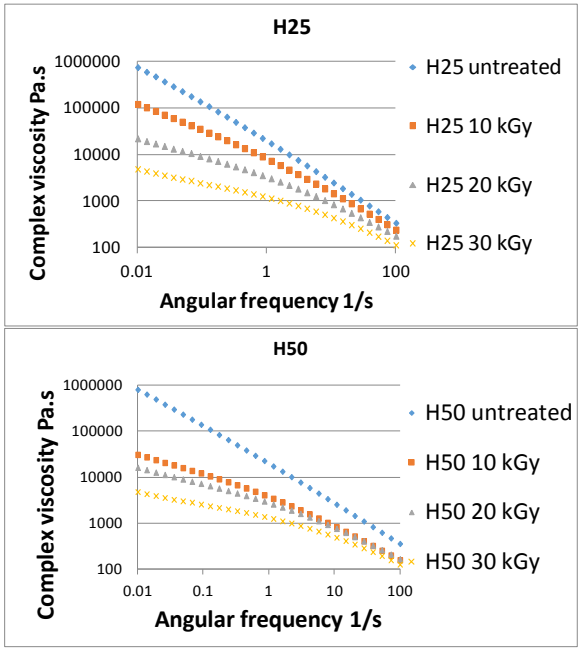

Figure 3. Complex viscosity of dopes from H25 and H50 pulps and their E-beam treated pulps.

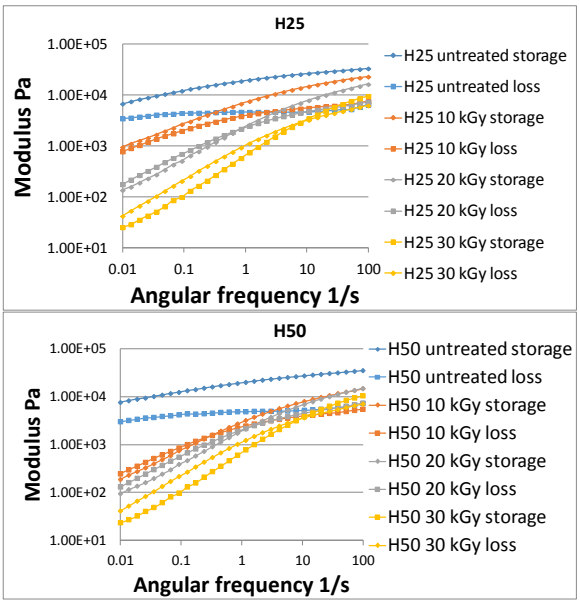

Figure 3. Dynamic modulus of dopes from H25 and H50 pulps and their E-beam treated pulps.

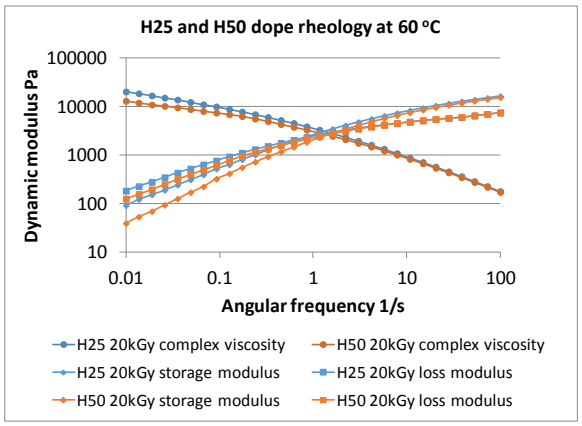

Figure 4. the complex viscosity and dynamic modulus of dopes prepared from H25 and H50 with 20 kGy E-beam dosage at 60 °C.

Table 2. zero shear viscosity and crossover point of storage and loss modulus of dopes prepared from H25 and H50 with 20 kGy E-beam dosage at 60 °C.

	Zero shear viscosity	Cross-over point	
	η0* (Pa.s)	ω (1/s)	G (Pa)
H25 20kGy	22809	0.7918	2246
H50 20kGy	13256	1.5198	2708

Fibre spinning

In the rheological measurement of small scale dopes, it shows promising complex viscosity and dynamic moduli when samples were treated with 20 kGy E-beam dosage at 70 °C. To validate the behaviour of the dopes during the spinning, large scale H25 and H50 pulp samples were prepared followed by E-beam treatment with 20 kGy. However, the dope prepared from large scale pulp samples showed slightly lower complex viscosity. Thus the spinning temperatures were lowered to 60 °C to ensure stable spinning. Figure 4 demonstrates the complex viscosity and dynamic modulus of dopes prepared from H25 and H50 with 20 kGy E-beam dosage. Table 2 presents their the zero shear viscosity and crossover points of storage and loss modulus.

In previous studies, the visco-elastic properties for a stable spinning of [DBNH][OAc]-based dopes (13 wt% eucalyptus pulp) were discovered at an angular frequency of the crossover point of approximately 1 s-1, a modulus at the crossover point of 3000 – 5000 Pa and a zero shear viscosity of 25000 - 35000 Pa.s. However, the addition of lignin decreases the complex viscosity and the dynamic moduli of the spinning dope.[6] As shown in table 2, both of the viscosity and the dynamic moduli at crossover point are lower than that from the model spinning dope. However, the spinning of both dopes were stable and the filaments were nicely extruded, even though the rheology of the spinning dopes didn't seem to be promising. Table 3 illustrates the spinnability and tensile properties of the fibres at the maximum draw ratio. In both cases, draw

ratio of 9.72 was reached (17.7 with the model dope). The spinning was acceptable considering the chemical composition of the raw materials. Due to relative low draw ratio, the fibres show higher titer. The tenacities of the fibres from both dopes are considerably low compared to that from model dope. However, they are still in the range of viscose fibres.

Table 3. Filament draw ratio and tensile properties of the fibres from E-beam treated H25 and H50 pulps.

	Draw ratio	Titer dtex	Dry tenacity cN/tex	Dry elongation %
H25	9.7	2.0	23.0	8.1
H50	9.7	2.1	24.4	7.4
Model dope	17.7	1.2	50.5	8.5

CONCLUSION

Generally, the intrinsic viscosity of the pulp has to be adjusted to 450 – 420 ml/g to ensure stable spinning. However, viscosity adjustment by acid-catalysed hydrolysis is commercially not feasible owing to unacceptably high charges of acid and thus high losses of hemicelluloses. Alternatively, E-Beam treatment can be utilized because it is a reliable and efficient treatment for the DP adjustment of (kraft) pulps. The intrinsic viscosity of low refined kraft pulps can thus be adjusted to the target value using moderate E-beam dosages as revealed by GPC measurements. As expected, the rheological characteristics of the dopes prepared from E-beam treated pulps can be influenced by the radiation dosage. As the E-beam dosage increases, the complex viscosity of the dope decreases. A radiation dosage of 20 kGy resulted in optimal rheological characteristics of the prepared dopes ensuring stable spinning behaviour. The actual spinning of the pulps treated with 20 kGy E-beam dosage were stable. Even though the rheological properties are lower than that from the optimum properties, the filaments extrusions were promising.

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