FIXATION OF REINFORCING FABRIC FOR ION EXCHANGE MEMBRANE

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Abstract: *A reinforcing fabric is an integral part of heterogeneous ion exchange membranes (IEMs). It guarantees the mechanical resistance of IEMs. Thermal fixation of the fabric is one of the most important refining operations, which is also reflected in the production of IEMs during lamination on heated cylinders. The influence of the fixation temperature (grey variant, 120, 160 and 215°C) of the Ulester 31HDA polyester fabric with a twill weave on the production of IEMs was studied. DSC, iodine sorption value measurement and dimensional stability during the additional heat load were studied for commercially supplied fabrics Ulester 31HDA. The values were compared with a model series of fabrics prepared in laboratory drying under precisely defined conditions (temperature and time). The principle of fixation is the rearrangement of the internal fiber structure associated with the change of the crystalline phase. The reinforcing fabric is dimensionally stable up to the fixation temperature. Iodine sorption value decreased with the increasing temperature of fixation. No changes were seen from SEM images or density measurements. DSC analysis did not show the predicted dependence for the model series of fabric. Dimensional changes after temperature loading increased with temperature.*

Keywords: *heterogeneous ion exchange membrane, preparation of membrane, reinforcing fabric, iodine sorption value, differential scanning calorimetry, shrinkage of reinforcing fabric.*

1 INTRODUCTION

Heterogeneous ion exchange membranes (IEMs), which are used in electroseparation processes, consist of a polymeric matrix, an ion exchange resin which contributes to the transport of ions through the membrane and also a reinforcing fabric that guarantees good mechanical properties [1-3]. Heterogeneous IEMs can be prepared by extrusion of a polymer and ion exchange resin mixture, with the simultaneous incorporation of a reinforcing fabric on heated rolls [2, 3]. In this manufacturing process, it is important to have a properly fixed fabric in terms of temperature. If the reinforcing fabric is insufficiently fixed, additional shrinkage occurs during lamination of IEMs, which affects the quality of the produced IEMs, decreases the free area of the reinforcing fabric and thus also increases the electrical resistance of the manufactured IEMs [4]. Production is more demanding - extending the runway time, adjusting the entire production line, quality of the fabric is transferred to the manufactured IEMs quality. It is also necessary to buy a larger width of fabric to keep the required width of the manufactured IEMs. These factors increase the price of the reinforcing fabric and the IEMs.

For synthetic fiber fabrics, fixation is one of the most important refining operations. The desired touch and shape stability is a result of simultaneous heat-fixation and stretching of the fabric. The main change in synthetic fibers during fixation is the increase of the content of the crystalline fraction [5]. The fabric should be dimensionally stable up to the fixation temperature. The degree of fixation can be determined by several procedures, for example, by measuring DSC (differential scanning calorimetry), ISV (iodine sorption value), fiber density, critical time measurement, temperature, concentration or measurement of dimensional changes before and after thermal loading in a laboratory press.

The aim of the work was to characterize the commercially supplied grey reinforcing fabric and fixed fabrics at 120, 160 and 215°C and then to test them in the process of manufacturing IEMs. First, it was necessary to create a model line of fixed fabrics at defined temperatures and times, which was characterized by DSC and ISV. The commercially available reinforcing fabrics Ulester 31HDA were compared to the model series and additionally the dimensional changes at 120, 140 and 160°C, mechanical properties and density were determined. Cylinders used for laminating IEMs are normally set to these temperatures.

2 EXPERIMENTAL

2.1 Materials

The reinforcing woven fabric Ulester 31HDA (Silk & Progress, Czech Republic) in 4 variants was used to test the degree of fixation and quality of IEM preparation. Basic parameters of the fabrics are shown in Table 1.

Table 1 Properties of used reinforcing fabrics

Reinforcing fabric	Temperature of fixation [°C]	Thickness [μm]	Warp/weft [1 cm^{-1}]	Free (open) area [%]
Ulester 31HDA grey	-	263	27.7 / 30.5	40.6
Ulester 31HDA 120	120	249	28.5 / 30.5	39.8
Ulester 31HDA 160	160	260	29.8 / 30.2	39.2
Ulester 31HDA 215	215	242	29.2 / 30.4	39.1

Ulester 31HDA is a polyester woven fabric with a twill (2:2) weave, consisting of a monofilament of 150 μm in warp and 100 μm in weft direction. Ulester 31HDA grey was not washed and fixed. Other fabrics (Ulester 31HDA 120, 160 and 215) were already washed and fixed at 120, 160 and 215°C at Alligard (Czech Republic). The fabrics were stretched to the frame during the fixation, the duration of the heat was 2 minutes. Ulester 31HDA grey was used to prepare the model fabric series that were fixed at 120 - 215°C for 1 or 2 minutes in the laboratory drying oven.

2.2 Methods

Model reinforcing fabrics were characterized by DSC and ISV. Commercially supplied reinforcing fabrics (Ulester 31HDA grey, 120, 160 and 215) were characterized using SEM (scanning electron microscopy) and DSC. Dimensional changes before and after the thermal loading in the laboratory press, the ultimate force and strain, ISV and the density by pycnometry were determined. All commercial reinforcing fabrics were subsequently tested in the production of IEMs on the continuous lamination line in MemBrain s.r.o. and the influence of the degree of fixation on the production and quality of IEMs was evaluated.

SEM – scanning electron microscopy

The structure of the reinforcing fabrics was investigated using a FEI Quanta 250 FEG scanning electron microscope. The SEM measurement conditions were 10 kV voltage, in low vacuum (80 Pa) with LFD (large field detector) for secondary electrons.

Dimensional changes during temperature loading

Shrinkage in the warp and weft direction was determined at 120, 140 and 160°C for all fabrics according to ČSN 80 0823 [13] in the laboratory press. Testing was only in dry conditions; the reinforcing fabrics were placed between cold metal sheets.

DSC – differential scanning calorimetry

The purified sample was placed in a DSC PT 10 (Linseis) pan. DSC analysis was performed during heating and cooling. Two cycles of heating and cooling were measured in Ar atmosphere. The heating rate was 15°C min^{-1}, the cooling rate was 2°C min^{-1}. The maximum temperature was 305°C. The melting point and melting enthalpy were evaluated from DSC curves. Crystallinity [%] was calculated using the enthalpy of melting ΔH_m from the 1st cycle according to the equation:

$$\text{Crystallinity} = \frac{\Delta H_\text{m}}{\Delta H_\text{m}^0}\ 100\ \% \tag{1}$$

where ΔH_m^0 is the enthalpy of melting for 100% crystallinity of polyester from 2nd cycle.

ISV – iodine sorption value

Sorption of I_2 [5-8] into the amorphous regions of the fabric was determined by the iodine sorption value (ISV) [mg I_2.g^{-1}]. First the solution of 40 g KI + 5 g I_2 + 50 ml of water was prepared. The samples were degreased and dried. 1.2 ml of the prepared solution was added to 0.2 g reinforcing fabric. After 5 minutes, 100 ml of water was added. After 1 hour, 75 ml of the solution was taken and titrated with 0.02 M sodium thiosulphate of the exact concentration. Starch was used as an indicator. ISV was calculated according to the equation:

$$\text{ISV}\left(\frac{\text{mg I}_2}{\text{g}}\right) = \\ = \frac{\left(V_\text{blind} - \frac{V\ (101{,}2)}{V\ (75)} V_\text{titer}\right)\ c\ (\text{Na}_2\text{S}_2\text{O}_3)\ M\ (\text{I}_2)}{m} \tag{2}$$

where V_{blind} is the volume of blind sample, V_{titr} is the volume of titer with sample, c ($Na_2S_2O_3$) is the concentration of sodium thiosulfate, M (I_2) is molar weight of iodine.

Mechanical properties

The mechanical properties of the reinforcing fabric were measured with samples of dimensions of 50x200 mm (clamping length) according to the ISO 13934-1 [14] using an H5KT (Tinius Olsen) tensile testing machine with a test speed of 100 mm.min^{-1}. The stress was in the warp and weft direction.

Density

Density was measured using the Pycnomatic ATC automatic helium pycnometer (ThermoFisher Scientific).

Preparation of IEMs

IEMs were prepared from an anion exchange resin and polyethylene. The mixture was extruded through a flat head between the rolls, onto which the Ulester 31HDA (grey, 120, 160 and 215°C) commercially available fabric was introduced. The temperature of the rolls for all fabrics was 140°C, the temperature of the extruded mixture was 136°C. The continuous lamination line speed was 1 m.min^{-1}. IEMs were laminated on both sides. IEMs were rolled up after cooling [9].

3 RESULTS AND DISCUSSION

The dimensional changes (length - warp direction, width - weft direction, thickness) of commercial Ulester 31HDA after additional heating at 120, 140 and 160°C was tested by the laboratory press. The reinforcing fabric was fixed by cold metal sheets and was inserted into the heated press to the desired temperature. Sample sizes were determined before and after exposure. The results for the warp and for the weft are shown in Figure 1.

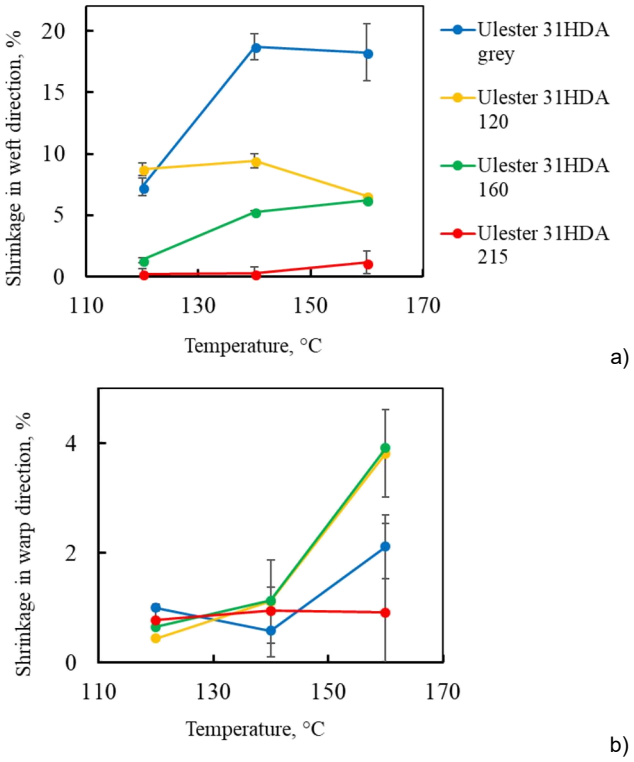

Figure 1 Shrinkage of reinforcing fabrics Ulester 31HDA in the weft (a) and warp (b) direction

The thickness of the samples increased in all cases due to the shrinkage of the fibers in the crossing of fabric. During the IEMs lamination, additional shrinkage occurred only in the weft direction. The warp is stretched by the roll from which it is unwound. Dimensional changes increased with higher temperature in the warp and weft directions. Dimensional changes in the warp direction were much lower than in the weft direction. This is due to the process of fixation and weaving, where the anisotropy of the reinforcing fabric properties occurs [10]. Ulester 31HDA grey had the highest shrinkage. The shrinkage decreased with the increasing Ulester 31HDA fixation temperature, which we anticipated.

The results did not show significant differences of fabric density and mechanical properties. Average values for ultimate force have an increasing tendency, but they are within the measurement error. The ultimate strain in the weft direction also showed a slight increase (Table 2). The anisotropy of mechanical properties in the weft/warp direction was already published by many authors [10-12]. The impact of stress on mechanical properties is enormous. The anisotropy of fabric properties is given by the fabric structure based on the perpendicular threads in the warp and weft. It can also affect the relative shifts of individual threads and the interaction of the threads at the bonding points.

During the fixation, the internal structure is rearranged, increasing the content of the crystalline fraction. From a thermodynamic point of view, it is the establishment of new conformational equilibria of the polymer chains in the threads deformed during the refining operation. I_2 sorption is the basic method for determining the degree of fixation of synthetic fibers. I_2 is absorbed only into the amorphous regions of the threads at polar sites (NH, CO). The proportion of crystalline regions in the fiber increases with the increasing degree of fixation and the sorption of I_2 decreases [5-8]. From the model series and commercially available fabric Ulester 31HDA, it is seen that ISV decreased with the increasing fixation temperature. The decreasing dependence is well evident in Figure 2. The ISV is determined with a relatively high error. For more accurate measurement of the fabric with an unknown fixation temperature, the method should be adjusted.

From DSC analysis, it was possible to calculate the crystallinity of the material, which varied according to the temperature history of the sample. There was a melting peak in the DSC curve, which did not change with the temperature of the fixation of the reinforcing fabric. Crystallinity was calculated from the 1st cycle (heating and cooling) when the sample still had a temperature history due to the fixation temperature. The problem with DSC measurement for fabrics was the small sample weight at the detection limit and poor heat transfer from the pan to the sample. The heat transfer was improved in the 2nd cycle (fabric is in the sheet form), but the temperature history of the sample was not visible on the DSC curve.

Table 2 Density, ultimate force and strain for commercial reinforcing fabrics

Reinforcing fabric	Density - pycnometry [g.cm^{-3}]	Ultimate force - warp/weft [N 5 cm^{-1}]	Ultimate strain - warp/weft [%]
Ulester 31HDA grey	1.380	1260±25 / 543±12	46±3 / 28±2
Ulester 31HDA 120	1.393	1240±35 / 571±13	46±3 / 28±1
Ulester 31HDA 160	1.380	1330±16 / 621±9	44±1 / 34±3
Ulester 31HDA 215	1.385	1290±65 / 635±6	42±4 / 36±1

An increasing proportion of the crystalline phase to temperature was only apparent for commercially available Ulester 31HDA samples (Figure 2). For the model series of samples, the increasing proportion of the crystalline phase was not confirmed. This was probably due to insufficient heat transfer from the pan to the sample or low sensitivity of the DSC.

SEM pictures of commercially supplied Ulester 31HDA are shown in Figure 3. No significant changes during fixation were visible on the threads. The increasing fixation temperature only slightly decreased of the free (open) area of the reinforcing fabrics (Table 1) in the order of percentages.

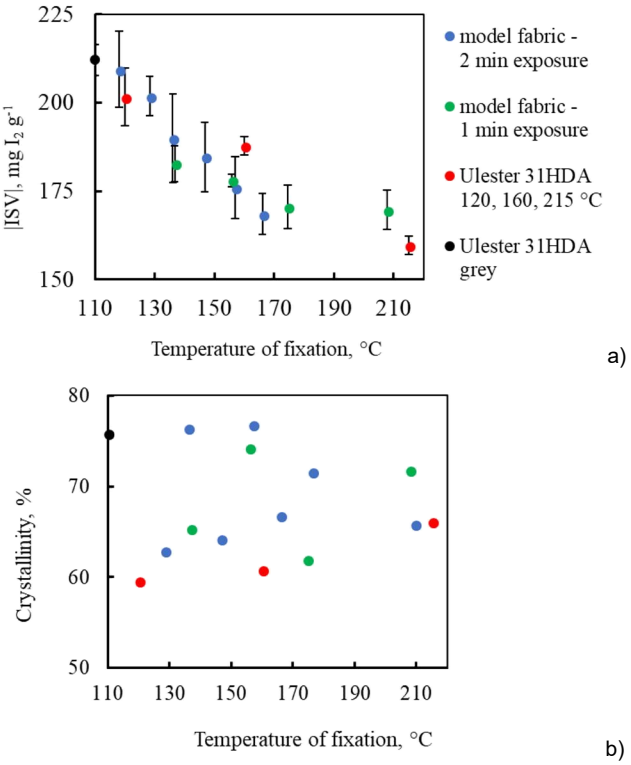

Figure 2 Iodine sorption value ISV (a) and crystallinity (b) of model fabric and commercially supplied Ulester 31HDA

The production of IEMs with Ulester 31HDA 215 and 160 took place without any significant problems. The Ulester 31HDA 215 and Ulester 31 HDA 160 on 140°C warm rolls had a shrinkage of 0.4%, respectively 2.6% in the weft direction. Values correspond to the measured data from the laboratory press at 140°C. Production of IEMs took place at lower temperatures (140°C) than the temperature of the fixation of the reinforcing fabric (160 and 215°C). Textiles were stable at this temperature.

IEM production with Ulester 31 HDA grey and 120 was more problematic. Greater parameter changes and setting of pressures on rolls had to be done. The Ulester 31HDA grey and Ulester 31 HDA 120 on 140°C warm rolls shrinked by 16.7%, respectively 10.2% in the weft direction. These values also correlate with the measured data presented in Figure 1.

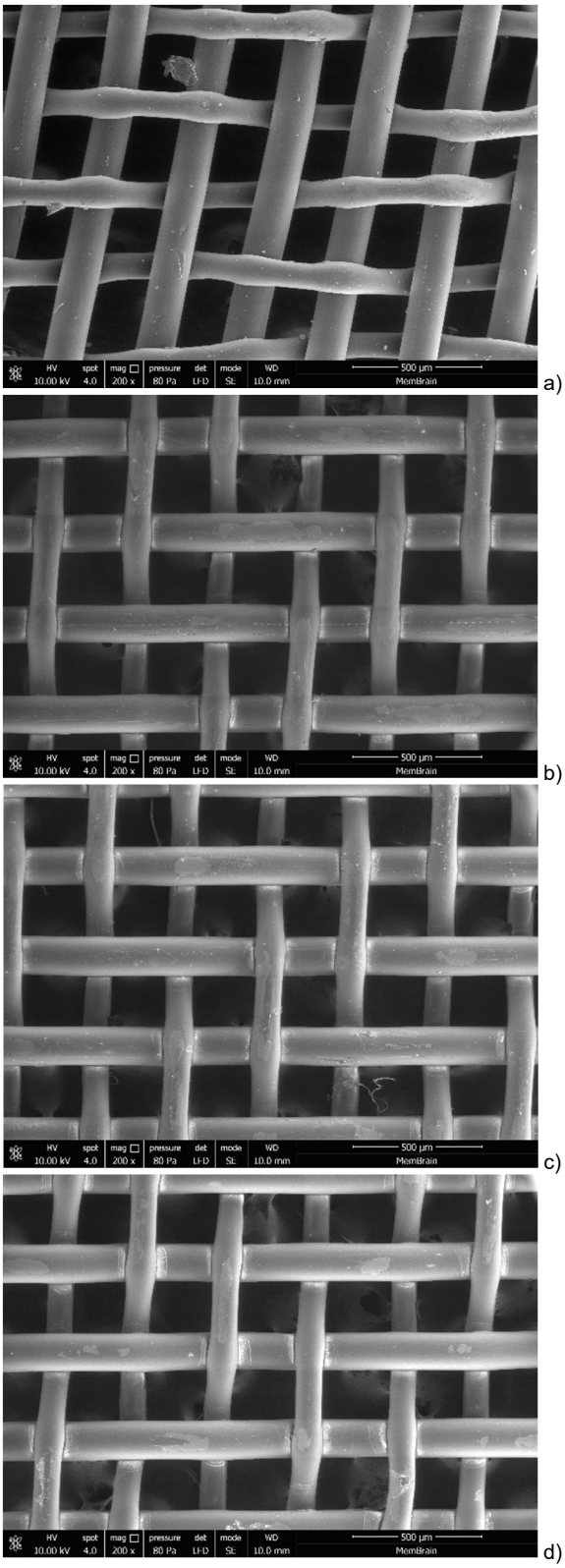

Figure 3 SEM pictures of Ulester 31HDA grey (a), Ulester 31HDA 120 (b), Ulester 31HDA 160 (c) and Ulester 31HDA 215 (d)

The formation of wrinkles and fabric duplication occurred with high shrinkage of the reinforcing fabrics on the rolls, where there is uneven tension and material distribution. The defects are visible in Figure 4. In some places, the reinforcing fabrics were folded and rolled into the IEM in two layers. Another problem was the formation of surface wrinkles formed by the imprinting of PET foil which is used to separate IEM from heated rolls. The reinforcing fabric rumpled the PET foil because of its high shrinkage and wrinkles from PET foil were imprinted on the IEM surface.

Figure 4 Images of unsatisfactory production of IEMs; wrinkles caused by high shrinkage of the fabric on the warm rolls

These IEMs were then marked as unsatisfactory. Despite the difficulties, it was eventually possible to start production with this type of reinforcing fabric, so all variants would be used in the production of IEMs.

4 CONCLUSIONS

The effect of the fixation temperature of reinforcing fabric Ulester 31HDA on IEM production and their characterization was investigated using basic methods such as DSC, ISV measurements or dimensional changes before and after the temperature exposure.

ISV decreased with the fixation temperature due to lower sorption of iodine in crystalline regions. However, the method is not sensitive enough to determine the precise fixation temperature of reinforcing fabrics. Dimensional changes at temperatures below the fixation temperature of the fabric were within 5%. Shrinkage increased with increasing temperature. Below the fixing temperature, the fabric is still thermally stable. The crystallinity was determined from DSC analysis. An increasing trend was demonstrated only in commercial samples Ulester 31HDA. From SEM, density, or ultimate force and strain measurements, there was not visible difference between reinforcing fabrics treated at different temperatures. All types of Ulester 31HDA textiles can be used in the manufacture of IEMs by lamination. In some cases, it is necessary to increase the correction of the individual parameters of continuous lamination line. The price of fixation of the reinforcing fabric is around 20% of the purchase price of the reinforcing fabric. Production problems with the reinforcing fabric fixed at lower temperature than the production temperature of the IEM are large and there is the large amount of unsatisfactory production. Thus, other IEM components are also drawn. The price of fixation of the reinforcing fabric thus appears to be more advantageous. It is also recommended to fixation at 160 or 215°C.

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