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Mercerisation of Rapeseed Straw Investigated with the Use of WAXS Method

Abstract

The aim of this research project was to investigate the mercerisation process of natural rapeseed straw used to manufacture composites with thermoplastic polymers. Alkali treatment of the native cellulose causes polymorphic transition to cellulose II and, consequently, improvement of mechanical properties of natural lignocellulosic materials. Different concentrations of alkali solutions were employed in the course of the rape (*Brassica napus*) mercerisation of Kaszub and Californium varieties: 5, 10, 12.5, 15, 17.5, 20, & 25%, and the process lasted for 1, 2, 3, 4, 5, 7.5, 10, 15, 30, 60, 90 and 120 minutes, respectively. The structural transformation from cellulose I to cellulose II for rapeseed straw after alkali treatment with sodium hydroxide was investigated by means of the wide-angle X-ray scattering (WAXS) method. The X-ray diffraction pattern was recorded within the angle range of $5 - 30^\circ 2\theta$. The polymorphic transition was calculated on the basis of the individual areas under the peaks of both cellulosic forms. It was found that the amount of cellulose II in wooden parts of rapeseed straw depended on the concentration of alkali solution as well as on the time of chemical treatment. It was further found that the great efficiency of Cellulose I \rightarrow Cellulose II transition (over 50%) was observed for both experimental varieties at a wide range of the concentrations applied, from 12.5 to 20%, when the process was conducted for at least 5 minutes. This result indicates a different behaviour of rapeseed straw in comparison with such other lignocellulosic materials as wood or natural fibres. There were no structural differences found between various rapeseed straw varieties in the mercerisation process. On the basis of the degree of cellulose crystallinity in rapeseed straw after alkali treatment, no degradation of lignocellulosic material was found to occur in the above-mentioned conditions.

Key words: rapeseed straw, composite fillers, mercerisation, cellulose, polymorphic transition, WAXS.

Introduction

World crops of rape oilseed are estimated at over 50 million tons and exhibit a steady growing trend. Rapeseed straw is a waste material and can be used for the production of composites with thermoplastic polymers [1, 2].

The biodegradability of fillers and their origin from renewable sources are important factors of research and for the application of such composite materials. Our earlier investigations confirmed the good mechanical properties of isotactic polypropylene/rapeseed straw composites [3, 4]. In addition, detailed investigations are conducted with the aim to determine the impact of rapeseed straw on propylene crystallisation [5], the thermal properties of composites in oxidation conditions [6] as well as on the degradability of such composites [7].

In general, the properties of composites depend on the type of natural materials and on the matrices and adhesion between them [8]. In order to make natural components like wood, natural fibres etc. more compatible with aliphatic polymers, it is advisable to modify them. The first step of modification before chemical reactions like esterification, etherification, and treatment with isocyanates or organosilanes is the mercerisation pro-

cess, which causes changes in the crystal structure as well as eliminates a large amount of hemicelluloses and lignin. Moreover alkali treatment removes waxy and other natural impurities [9 - 14]. Other researchers stress that alkalisation increases the relative cellulose content and causes greater crystallinity in wheat straw fibre [15].

However, the most important aspect of the alkali treatment of native cellulose is that it results in the phase transformation of cellulose I \rightarrow cellulose II, improving the mechanical properties of natural lignocellulosic materials [15 - 19].

Investigations on beech and pine wood mercerisation were performed by Borysiak and Doczekalska [20, 21]. The soda lye concentrations applied ranged from 15% to 25% and the mercerisation process was conducted at room temperature for a period of 15 to 90 minutes. The highest efficiency of polymorphic transformation from cellulose I to cellulose II was noted at the highest concentration of sodium hydroxide solution. In addition, the amount of the cellulose II obtained also depends on the time of the mercerisation process. For example, for beech wood, the highest effectiveness of the structural phase transition was reached when the concentrations of NaOH ap-

plied were 20 and 25%, in which case over 40% of cellulose was transferred into the second polymorphic phase. Moreover it was found that the degree of cellulose crystallinity following the mercerisation process declined in pine wood. It is evident from the investigations performed that pine and beech wood sensitivity to alkali action varies.

The mercerisation process is commonly carried out at room temperature. Ouajai and Shanks investigated the process of hemp fibre mercerisation at a temperature of 30 °C [11]. However, Suardan et al. [22] carried out this process for 1 h at an oven temperature of 95 °C. Different concentrations of the sodium base were applied. After the mercerisation process, hemp fibres were rinsed with tap water to eliminate any NaOH solution sticking to the fibre surface and then dried. It was found that 4 wt.% NaOH-treated fibre composites demonstrated good mechanical properties. It is clear from these studies that a considerable temperature increase of the mercerisation process makes it possible to apply considerably smaller concentrations of the sodium base in comparison with the processes conducted at a temperature of 20 °C.

Different NaOH concentrations of the mercerisation process are employed e.g. up to the of 25 wt.% for flax fibres [8]. However, it was observed that for hemp fibres structural disruption was found to occur following higher alkaline concentration, 20 wt.%, and longer scouring time [11].

As mentioned earlier, it is advantageous to perform the mercerisation process before chemical modification, which leads to the improvement of adhesion between the polypropylene matrix and lignocellulosic reinforcement. However, it should be stressed that numerous research articles have been published which did not take into account the mercerisation process. Lignocellulosic materials such as wood and natural fibres are first subjected to chemical modification, for example, by acetic acid anhydride [4, 23]. When analysing the mercerisation process from the point of view of the utilisation of lignocellulosic materials, Borysiak reported that cellulose I and cellulose II present in pine wood nucleated polypropylene matrix crystallisation on their surface in

a different way following the mercerisation process [24].

The aim of this research project was to investigate the mercerisation process of natural rapeseed straw used for manufacturing composites with thermoplastic polymers at various concentrations of sodium hydroxide solution and activation times. Up to now, the polymorphic transformation of cellulose I to cellulose II for rapeseed straw has not been dealt with in literature data. The first fragmentary experiments on the mercerisation of rapeseed straw were carried out in our earlier investigations [25], in which a narrow range of base concentrations was applied (16 – 25%). It was observed then that the maximum amount of cellulose II in rapeseed straw after 5 minutes was achieved. The objective of this study was the comprehensive evaluation of the mercerisation process of rapeseed straw in a wide range of NaOH concentrations and at different durations of the process.

■ Experimental

Materials

In order to characterise the mercerisation process of wooden parts of the stem of winter rape, two rape varieties were used: *Kaszub* and *Californium*. The rapeseed straw used was obtained from fields of the Plant Breeding and Acclimatisation Institute (IHAR) in Poznan from the 2009 crop. For our study, we used dried rapeseed straw.

The samples were prepared in the following way: parenchyma was removed from sections of the rape stem, subsequently wooden parts of the rapeseed straw were mechanically crumbled, and 0.5 – 2.0 mm particles were separated with the use of sieves.

Alkali treatment

The dried particles of rapeseed straw (the mass of individual samples was 1.65 g, as this was the amount required to perform roengenographic measurements) were immersed in NaOH at different concentrations of alkali solution. The chemical used in this study was sodium hydroxide (NaOH; P.P.H. STANDARD, Lublin Sp.z.o.o.).

For the *Kaszub* and *Californium* varieties applied, the following concentrations and

times were used: 5, 10, 12.5, 15, 17.5, 20, & 25%, and 1, 2, 3, 4, 5, 7.5, 10, 15, 30, 60, 90 and 120 minutes. The mercerisation process was carried out at a temperature of 20 °C.

After alkali treatment, the materials investigated were immediately washed with water and filtered in order to remove NaOH and to bring the rapeseed straw to neutral reaction. Next the material was dried.

The selection of this method of process termination at such a small mass of the lignocellulosic material subjected to the alkalisation process guaranteed its rapid neutralisation without exposure to unpredictable structural changes, for example, as a result of treatment with an acid.

WAXS investigations

Structural investigations of the rapeseed straw samples were carried out by means of the wide angle X-ray scattering method (WAXS) using a CuK_α radiation wavelength of 1.5418 Å and employing nickel filtering. The following parameters were applied: voltage - 30 kV and anodic current - 25 mA. The X-ray diffraction pattern was recorded at an angle range of 5 – 30° (2 θ), with a counting step of 0.04° (2 θ).

Structural analysis

The resolution of the multi-peaks was performed employing the method proposed by Hindeleh and Johnson [26], improved and programmed by Rabiej [27]. The degree of transformation of cellulose I to cellulose II was calculated on the basis of separated areas under the peaks of both polymorphic forms. The method of calculation of the amounts of crystalline phase cellulose I and cellulose II has described in detail previously [8, 20, 28].

The degree of crystallinity (X_c) was calculated from the areas under crystalline peaks and that under the amorphous curve.

■ Results and discussion

According to literature data, the mercerisation process begins at a 9 - 10% NaOH concentration [29, 30]. Other sources maintain that the process can also take place at lower NaOH concentrations [11, 15]. Therefore, in this study, the lowest alkali concentration used was 5%.

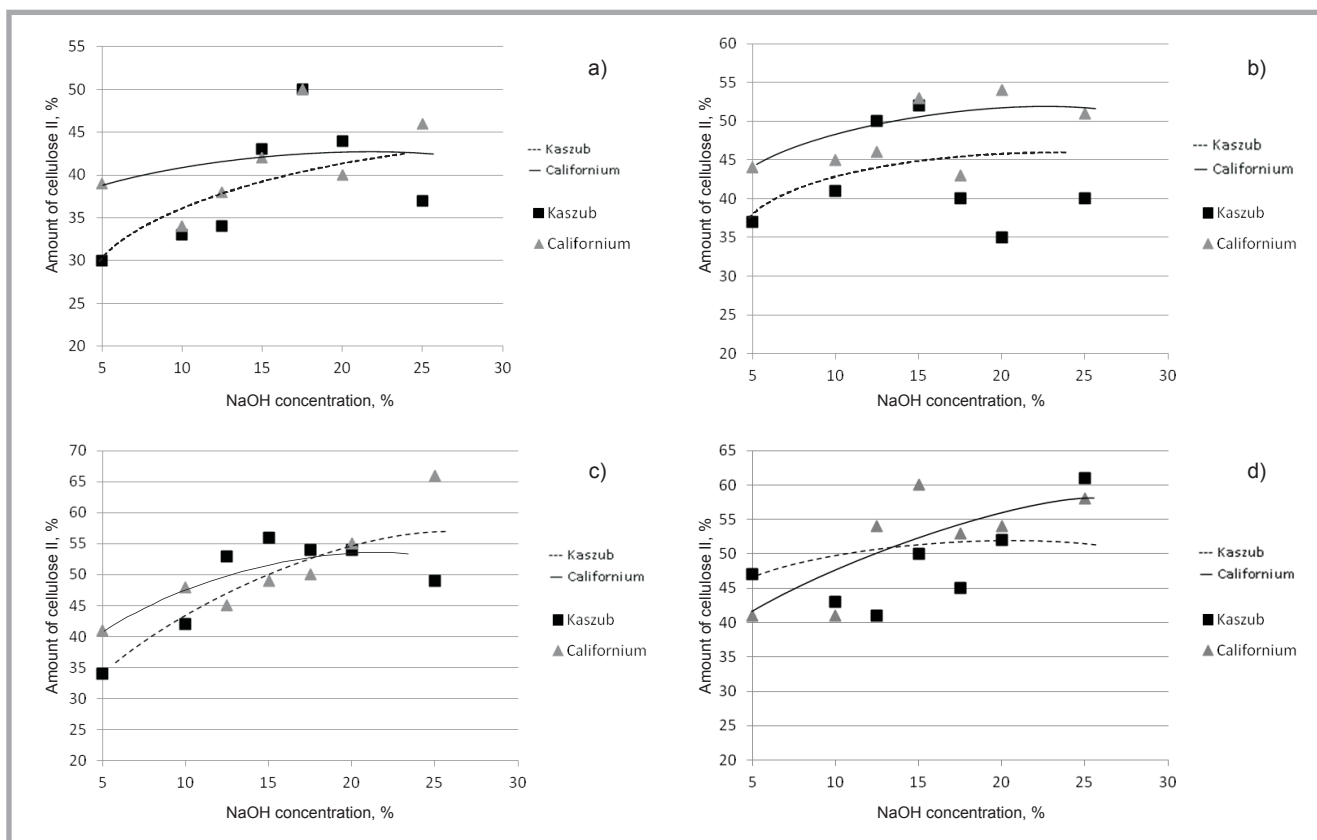


Figure 1. Amount of cellulose II vs. NaOH concentration for: a) 1 min. b) 5 min. c) 30 min. d) 120 min. of mercerisation.

In industrial conditions, the shortest times applied in these investigations are difficult to achieve. However, they are important from a cognitive point of view.

Figure 1.a shows the dependence of the amount of cellulose II on the concentration of the base for the process carried out for a period of 1 minute.

It should be emphasised that for the two experimental rapeseed varieties employed, the amount of cellulose I which underwent transformation to cellulose II already after one minute mercerisation in 5% base ranged from 35 to 40%. For comparison, in the course of the same period of time (1 minute), the rate of flax fibre transformation treated with 10% NaOH solution reached 25% [8], while that of rapeseed straw amounted to 40%. This confirms the greater sensitivity of the lignocellulosic material examined in this study to the mercerisation process, when compared with flax fibres.

Figure 1.b presents the dependence of the quantity of cellulose which underwent phase transformation vs. the base concentration for the process lasting 5 minutes. It is worth noting that the results of investigations carried out for merceri-

sation times lasting 2, 3 and 4 minutes followed courses exhibiting similar tendencies as those for processes lasting 1 or 5 minutes.

It is also worth emphasising that an amount of cellulose II of the order of 50% was obtained after a period of 5 minutes following the application of a 12.5 - 15% base concentration. Such a quantity of cellulose II in beech and pine wood is reached only after 40 minutes of the process and at considerably higher NaOH concentrations of 20 and 25% [20, 21].

Thus in the case of the previous interval, which was not presented graphically, research results obtained for mercerisation times of 7.5, 10 and 15 minutes showed runs of a similar trend as for processes lasting 5 and 30 minutes.

Figure 1.c presents the dependence of the quantity of cellulose which underwent phase transformation on different base concentrations for the process lasting 30 minutes.

It is evident from **Figure 1.c** that when a base of 10% concentration was applied, the amount of cellulose II for the Kaszub

variety exceeded 40%, and for the Californium variety it was close to 50%. Higher concentrations resulted in the formation of this polymorphic variety in quantities exceeding 50%. It can be said that from the point of view of industry, it would be advantageous to employ a time interval not shorter than 5 minutes accompanied by a fairly broad concentration interval ranging from 12.5 to 20%.

Research results for the successive times tested (for 60 and 90 minutes) failed to exhibit any changes with reference to the trends observed. On the other hand, **Figure 1.d** presents research results for the process lasting 120 minutes.

It is evident from **Figure 1.d** that already at a NaOH concentration of 10%, the level of transformation of cellulose I to cellulose II reached 40 to 50%, and a further increase in the base concentration above 12.5% did not increase the quantities of crystalline phase cellulose II significantly.

In order to have a different look at the phenomenon observed, in **Figure 2** (see page 22) the authors have presented the quantity of cellulose II in the crystalline

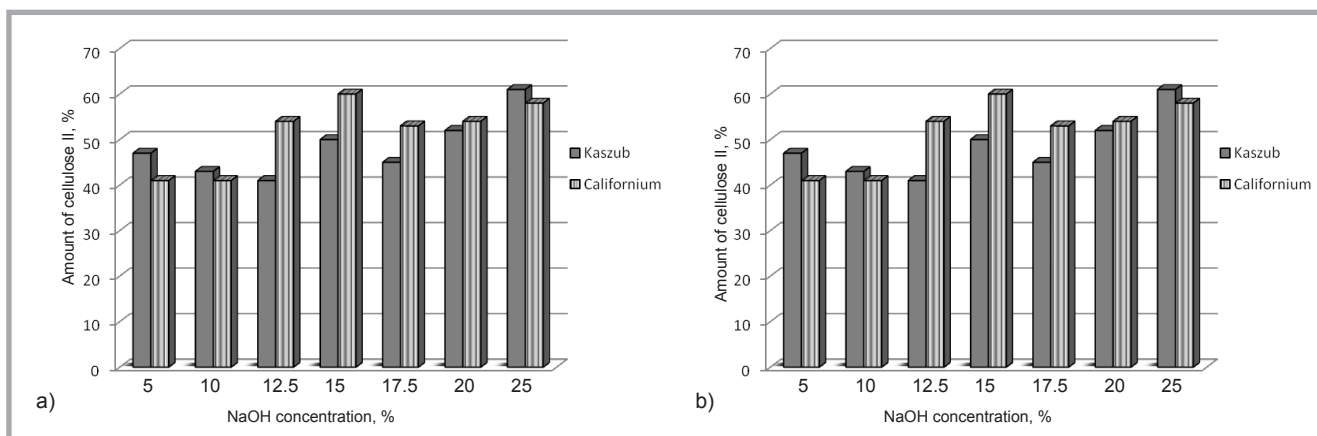


Figure 2. Amount of cellulose II after: a) 15 min. and b) 120 min. of alkali treatment.

phase after 15 and 120 minute treatment with a base of differing concentrations.

Figure 2 show that the mercerisation process was affected positively when the base concentrations applied exceeded 15%. In such a case, the conversion rate reached a value of 50% for both rapeseed varieties tested. Furthermore, a period of 15 minutes was sufficient to carry out an optimal process of mercerisation.

As is evident from Figure 2, the amount of cellulose II formed for the longest time was only slightly smaller than during the treatment lasting 15 minutes (similarly, for 30 or 60 minutes). A similar tendency could be observed in investigations conducted by Borysiak and Garbarczyk during their experiments of flax fibres [8]. In the case of the NaOH concentration of 25% applied, once the process lasting 2 minutes achieved its maximum, the quantity of cellulose II formed in the mercerised sample exhibited a declining tendency. Since in literature no opposite process can be found described, the trend observed occurring in the investigations presented in this paper can barely be interpreted in terms of the destructive influence of the sodium base of high concentration on the cellulosic material examined. On the other hand, investigations carried out by Mwaikambo et al on sisal, hemp, jute and kapok

confirmed the degradation of cellulose between 0.8 – 8% NaOH, beyond which the degradation was found to be marginal. Moreover there was a marginal drop in the crystallinity index of hemp fibre, while sisal, jute and kapok fibres showed a slight increase in crystallinity at a caustic soda concentration of 0.8 - 30% [12].

That is why it was decided to subject the mercerised straw to analysis with respect to the degree of crystallinity. The degree of cellulose crystallinity in native rapeseed straw amounted to 68% for the Californium variety and 69% for the Kaszub variety. Table 1 presents the dependence of the degree of cellulose crystallinity on the time of conducting the process for the Californium variety for three concentrations selected.

It is worth mentioning that degrees of crystallinity for the remaining concentrations as well as for the Kaszub variety were similar. Analysing changes in the crystallinity degree, it can be concluded that a slight decline in the degree of crystallinity, which could have contributed slightly to degradation processes of the lignocellulosic material, could be observed only when the base concentration was 25%. This is in keeping with the diagrams on which a slight decline in the cellulose II content at the crystalline phase was observed for the above-men-

tioned concentration. This phenomenon will be the objective of further investigations. However, recapitulating, on the basis of the degree of rapeseed straw crystallinity after alkali treatment, it can be said that no degradation of lignocellulosic material was found to occur in the above-mentioned conditions.

Summary and conclusions

As is evident from the experimental results obtained and literature data, there were significant differences in the influence of NaOH solution on phase transformations of native cellulose to cellulose II in various materials (pine and beech wood, flax and hemp fibres and rapeseed straw). It seems that the differences observed can be attributed to the morphology as well as to the slightly different chemical composition of rapeseed straw [31]. Rapeseed straw showed the most extensive transformations under the influence of the alkali applied, which might be due to its “softness”. This softness probably facilitated the infiltration of water and base molecules into the lignocellulosic material. This problem will be investigated in our later experiments. The results of the investigations performed failed to demonstrate significant differences in the mercerisation process between the varieties of rapeseed straw applied. The research results obtained are in keeping with those of our earlier experiments [32]. It should be emphasised that the properties of the lignocellulosic material in employed filler derived from the annual plant can depend, to a considerable extent, not only on a specific variety but also on other factors, for example, climatic conditions or soil fertility.

Table 1. Degree of cellulose crystallinity for different times of the duration of the process for 5, 15 and 25% NaOH base concentrations.

| Min. | 5% | 15% | 25% |
|------|----|-----|-----|
| 1 | 72 | 62 | 66 |
| 5 | 68 | 67 | 73 |
| 15 | 74 | 73 | 72 |
| 30 | 71 | 71 | 64 |
| 60 | 76 | 71 | 64 |
| 120 | 72 | 67 | 63 |

It is worth stressing that for both of the varieties examined, very high efficiency (over 50%) of Cellulose I → Cellulose II transition was found in the case of a wide range of the concentrations applied, from 12.5 to 20%, and for a duration of the process of at least 5 minutes. This finding may be of considerable significance in the case of industrial utilisation of rapeseed straw for composite production, for example, with a polypropylene matrix. Moreover on the basis of the degree of crystallinity of cellulose in rapeseed straw after alkali treatment, it was found that no degradation of lignocellulosic material occurred during the mercerisation process.

On the basis of the results presented in this study, it is possible to draw the following conclusions.

- There were significant differences in the influence of NaOH solution in phase transformations cellulose I → cellulose II on rapeseed straw compared with other lignocellulosic materials, like natural fibres and wood.
- From the point of view of industrial utilisation of the mercerisation process, it can be said that optimal conditions for the process occur at base solution concentrations ranging from 12.5 to 20%, with process continuing for at least 5 minutes.
- There were no structural differences found between various rapeseed straw varieties during the mercerisation process.
- On the basis of the degree of crystallinity of cellulose in rapeseed straw after alkali treatment, it was found that no degradation of lignocellulosic material in the above-mentioned conditions occurred.

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