

JACEK W. KACZMAR¹⁾, JOANNA PACH^{1),*}, CHRISTOPH BURGSTALLER²⁾

The chemically treated hemp fibres to reinforce polymers

Summary — The effect of different chemical treatments of hemp fibres, carried out by alkali treatment, acetylation and modification with maleic anhydride, on their physical, thermal and chemical properties as well as their surface characteristic was discussed in this paper. The morphology of the fibres was investigated by SEM. Thermal properties were investigated by TGA and DTA methods and the chemical composition of fibres by FT-IR spectroscopy. Chemical modifications resulted in the lowered content of lignin, pectin and hemicellulose, what is especially observable with mercerised fibres. Another effect of the chemical treatment applied is related to the removal of waxy substances from the surface, which was indirectly ascertained by SEM observation, which revealed a relatively smooth hemp fibres surface. TGA results showed that the applied chemical fibre treatment resulted in the lowered thermal degradation of the treated fibres, after the removal of non-cellulose components, especially lignin.

Keywords: hemp fibres, chemical treatment, alkali treatment, acetylation.

WŁÓKNA KONOPNE MODYFIKOWANE CHEMICZNIE PRZEZNACZONE DO WZMACNIANIA POLIMERÓW

Streszczenie — Włókna konopne modyfikowano metodą alkalizacji, acetylowania lub za pomocą bezwodnika maleinowego. W celu zbadania zmian chemicznych włókien konopnych po zastosowaniu modyfikacji wykonano analizę widm w podczerwieni (FT-IR) (rys. 2). Określono również wpływ przeprowadzonych modyfikacji na stabilność termiczną włókien (rys. 4 i 5). Analiza termogravimetryczna pokazała, że włókna niemodyfikowane wykazują nieco gorszą stabilność termiczną i ich degradacja rozpoczyna się w niższej temperaturze niż w przypadku pozostałych analizowanych włókien. Włókna modyfikowane są stabilne termicznie do ok. 250 °C, co może wynikać z usunięcia podczas modyfikacji mniej stabilnych składników włókien, jak np. hemiceluloza, której rozkład rozpoczyna się w temp. 150 °C. Za pomocą SEM zbadano i porównano topografię powierzchni włókien surowych i modyfikowanych chemicznie (rys. 3). Modyfikacja chemiczna spowodowała usunięcie warstwy wosków, co objawiło się tym, że włókna elementarne w wiązkach zostały bardziej wyodrębnione. Usunięcie substancji woskowych z powierzchni włókien lignocelulozowych spowodowało odsłonięcie powierzchniowych grup hydroksylowych i zmianę topografii powierzchni włókien, czyniąc powierzchnię bardziej szorstką.

Słowa kluczowe: włókna konopne, modyfikacja chemiczna, alkalizacja, acetylowanie.

Lignocellulosic fibres have been used since time immemorial for manufacturing of clothing, ropes and strings, paper and other articles of daily use. Today they are also used for the reinforcement of thermosets and thermoplastics, improvement in various properties, such as their mechanical performance. Polymer based composite materials reinforced with natural fibres are used in the automotive industry for the manufacture of some parts of the interior, in the building industry, furniture industry and others.

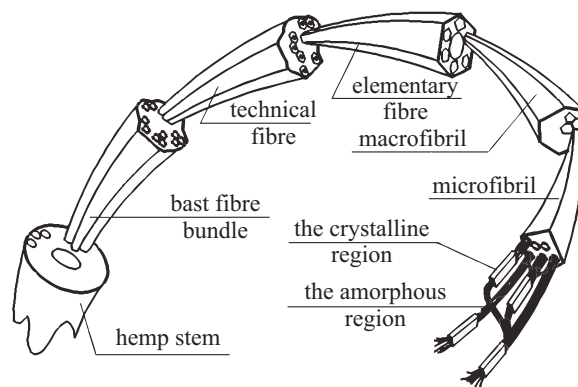


Fig. 1. Schematic view of hemp fibres structure, according to [1, 2]

Lignocellulosic fibres show very complex structure. As an example, the schematic view of hemp fibres is

¹⁾ Wrocław University of Technology, Institute of Production Engineering and Automation, Laboratory of Polymers, ul. Łukasiewicza 5, 50-371 Wrocław, Poland.

²⁾ Transfercenter für Kunststofftechnik GmbH, Franz Fritsch Strasse 11, 4600 Wels, Austria.

* Correspondence author; e-mail: joanna.pach@pwr.wroc.pl

shown in Figure 1. The chemical composition of hemp fibres is quite complex. These fibres consist of cellulose, hemicellulose, lignin, as well as small amounts of waxes, pectin and minerals [3]. The knowledge of the chemical composition of the components is important because this would help understand reactions occurring during chemical modification of hemp fibres. Cellulose belongs to the group of polysaccharides insoluble in water, consisting of D-anhydroglucopyranose units joined by β -1,4-glycosidic bonds. Each of the six-element heterocyclic rings consists of alcoholic groups of primary and secondary character of different reactivity, which could be possible bonding partners for several chemical compounds. Furthermore cellulose contains functional oxygen groups like ether and carbonyl groups.

Hemicellulose, like cellulose, contains functional oxygen groups, although, compared to the latter this is a polysaccharide containing several units of sugar. Moreover it is characterised by the small molecular mass and small water solubility.

Lignin is a complex polymer composed of aliphatic and aromatic groups and bonds cellulose and hemicellulose. It can be considered as the glue which bonds the cellulose fibrils together to form the fibres. The last components are pectins, which belong to the heterosaccharides, mainly composed of polygalacturon acid and waxes, which cover the lignocellulosic fibres and are insoluble in water, as described elsewhere [1, 4].

Table 1. Properties of selected natural fibres in comparison to properties of glass fibres according to [5]

Fibre	Young's modulus GPa	Tensile strength MPa	Elongation at break, %	Density g/cm ³	Specific strength*) km
glass	72	2000–3400	1.8–3.2	2.56	79.1–135.4
flax	45–100	600–1100	1.5–2.4	1.4–1.50	43.7–80.1
ramie	128	500–1000	1.2–4.0	1.4–1.50	36.4–72.8
hemp	35	390	1.1–1.6	1.4–1.50	28.4
jute	43	320–550	1.7	1.3–1.45	23.3–40.0

*) Specific strength – value of tensile strength divided by density and acceleration of gravity.

Although the mechanical resistance of synthetic fibres like glass or carbon fibres is higher than that of natural fibres, the relatively high specific strength and the low price of natural fibres make them very interesting as reinforcing elements in polymer based composite materials. A comparison of the mechanical and physical properties of selected natural fibres with glass fibres is shown in Table 1. It can be seen that especially flax fibres exhibit good specific strength, which corresponds to the specific strength of glass fibres widely applied to reinforce polymer based composite materials.

Furthermore, not only the mechanical but also other properties of the natural fibres have to be considered.

One aspect is the processing of natural fibre reinforced polymers, which is less complicated than in case of glass fibre reinforced ones, as well as recycling of the former is easier due to less fibre damage during the production process [5–7].

Probably the most important factor affecting the mechanical properties of polymer based composite materials reinforced with the natural fibres is the adhesion at the interface between the polymer matrix and the reinforcing fibres. The difference in the chemical composition of the matrix polymer and the natural fibres and the resulting polarity difference weakens the adhesion forces at the interface. An example for such polarity difference is the system polypropylene-flax, where the adhesion between matrix and fibres is relatively poor. To improve the adhesion between fibre and matrix at the interface, additives like coupling agents (or compatibilizers) can be used. One type of such coupling agents is maleic anhydride grafted polyolefins, which can interact with the polar fibres as well as the non-polar matrix due to their combination of polar groups with non-polar polymer chains.

The ability of the natural fibres to absorb water, which is due to cellulosic structure, results in a further release in processing, because at the elevated processing temperatures necessary for polymer processing, the water evaporation causes problems with the wetting of the fibres with the polymer. In order to avoid such problems one is well advised to dry the fibres prior to processing and keep them in the dry state to yield composites with sufficient interfacial adhesion.

Decreasing the hydrophilic nature of natural fibres and then the improvement in the adhesion on the interface can be achieved by fibre modification, which can be performed by chemical or physical methods. The physical treatment affects only the surface structure of fibres whereas the chemical composition of fibres remains unchanged. Examples for such physical treatment, as corona treatment [8, 9], cold plasma treatment [10] and thermal treatment [11] can be found in literature.

On the other hand, surface modifications of natural fibres applying chemical compounds change the chemical composition of the surface and therefore can improve the adhesion between the fibres and the polymer matrix. An important method of chemical modification is chemical coupling [1] which can be performed *via* fibre treatment with maleic anhydride-polypropylene copolymers for improving the interface between cellulose based fibres and polypropylene [12]. Other common chemical modification methods, applied for natural fibres are graft copolymerization [13], acetylation [14], alkalization [15] and silanization [16].

The aim of this work was to investigate the effect of different methods of the chemical treatment of hemp fibres, carried out by alkali treatment, acetylation and modification with maleic anhydride, on their physical and thermal properties as well as their surface morphology.

EXPERIMENTAL

Materials

The hemp fibres (*Cannabis sativa*) used in this study were delivered by the Institute of Natural Fibres in Poznań (Poland), and have been cut in order to achieve the mean length of 4 mm. Prior to the treatment, the fibres were dried at 105 °C for two hours in a hot air cabinet.

Sodium hydroxide, acetic anhydride, maleic anhydride, toluene and acetone were supplied by Sigma-Aldrich.

Fibres modification

For alkali treatment, the pre-dried hemp fibres were soaked in an aqueous solution of sodium hydroxide (8 wt. % solution of NaOH) for two hours at room temperature (20 °C). Afterwards, the fibres were rinsed with distilled water until the filtrate reached pH = 7. Next, the fibres were dried again at 105 °C, until a constant mass was reached.

Acetylation was carried out *via* soaking the fibres in a solution of acetic anhydride (5 wt. %) in toluene for two hours at elevated temperatures (66 °C). Afterwards, the fibres were rinsed to obtain pH = 7 and dried at 105 °C until constant mass was observed.

Maleic anhydride modification was carried out in the same way as the acetylation, but a solution of 10 wt. % maleic anhydride in acetone at temperature 55 °C was used. The rinsing and drying steps were carried out afterwards in the same manner.

Fibre analysis

FT-IR spectra of the fibres were recorded in reflection mode by means of a Perkin Elmer infrared spectroscope, equipped with an ATR-bridge (attenuated total reflection). The fibres were compressed and put under the ATR measuring crystal. For each sample, ten spectra were recorded (with a resolution of 1 cm⁻¹), and the average spectrum of these was used for the evaluation.

Thermogravimetric analysis (TGA) was carried out using Mettler Toledo TGA/SDTA 851 device in air atmosphere in a temperature range from 50 to 550 °C at a heating rate of 10 deg/min. About 10 mg of fibres were placed in a 0.07 cm³ aluminium oxide crucible and put into the apparatus, where the mass loss was determined.

The differential thermal analysis (DTA) measurements were carried out at a Mettler Toledo DSC 822e apparatus, in a temperature range of -50 °C to 600 °C at a heating rate of 10 deg/min under air atmosphere. About 5 mg of the fibres were placed in an aluminium crucible, and the temperature difference between the sample and the reference crucible was recorded.

Scanning electron microscopy (SEM) was applied (after sputtering the fibres) to get deeper insights into the

fibre surface morphology JEOL-JSM 5800LV microscope were used. Ten samples of fibers for each modification were prepared and analyzed.

RESULTS AND DISCUSSION

FT-IR Results

The aim of infrared spectroscopy was to trace the changes in the chemical composition of the surface. A closer look at the spectra, shown in Figure 2, reveals several absorption peaks. The main absorption bands and their assignment to the different groups are shown in Table 2. The peak found at about 2300 cm⁻¹ is due to the presence of CO₂ (from the air) in the sample, which can not be eliminated completely in attenuated total reflection measurements.

Table 2. Characteristic bands of the FT-IR spectra of the hemp samples studied and described in [4, 18]

Wavenumber, cm ⁻¹	Functional group	Assignment
3489–3100	C-H, O-H stretching in alkyl or aryl	
2900, 2851	CH stretching vibrations	
1740	C=O stretching of acetyl or carboxylic acid	hemicellulose + lignin + pectin
1650	COO ⁻	pectin
1550	C=C stretching of the aromatic ring	lignin
1465	C-H asymmetric bending in CH ₃	lignin
1430	CH ₂ bending	cellulose
1372	O-H bending vibrations (in plane)	
1343	O-H in plane bending	cellulose
1317	CH ₂ wagging	cellulose
1155	C-O-C asymmetric bridge stretching	cellulose
898	Asymmetric, out of phase ring stretching	cellulose

The different spectra of the untreated and alkali or maleic anhydride treated fibres do not show any significant differences. This is not surprising due to the fact that in case of the alkali treatment, no new groups are introduced to the fibres, and therefore no big difference can be found. In case of the maleic anhydride treated fibres, the problem is that the acid groups, which are introduced with this treatment, are also found in the structure of the untreated fibres, in the lignin as well as in the cellulose itself, and therefore it is not possible to distinguish the source of the peaks.

Only the acetylated fibres exhibit two distinct bands at 1740 and 1230 cm⁻¹, respectively, which can be assigned to ester and C-O bonds. This is due to the fact that with acetylation many ester bonds are established in the fibres [17].

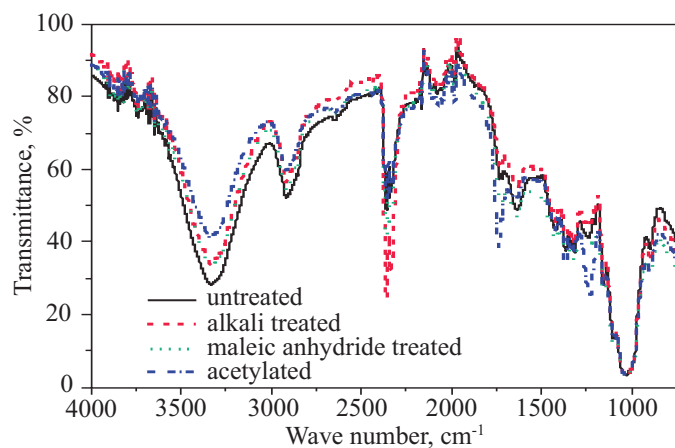


Fig. 2. ATR-FT-IR spectra of unmodified raw hemp fibres and fibres after acetylation, maleic anhydride and alkali treatment

The band for 1740 cm^{-1} is attributed to the C=O stretching of the acetyl groups of hemicellulose [4, 18]. This band is not present in the alkali treated samples. According to the literature [19], the removal of hemicellulose from the fibre surfaces makes this disappear.

Scanning Electron Microscopy results

For comparison purposes, SEM micrographs of the fibre surface from the differently treated fibres were

taken and presented in Figure 3. The fibre surface of the untreated fibres shows a layer of non-cellulose components, which are suspected to be waxes, hemicellulose or lignin. The alkali treated fibres look somewhat cleaner, as well as the fibre bundle structure itself can be seen better than for the untreated fibres. This is due to the fact that the waxes as well as some lignin are removed from the fibres. Removing noncellulosic substances as fats, waxes, pectins, lignins and hemicelluloses, as a result of alkali treatment of hemp fibre is also described in other papers [19–21]. The ESEM images presented by Sgriccia *et al.* [19] showed that the interfibrillar material, hemicellulose and lignin, were etched away by the alkali treatment. Also, according to the Kostic *et al.* [20] and Wang *et al.* [21] lignin cannot be totally removed by the alkali process because degradation or fragmentation of lignin is very limited due to the presence of strong carbon-carbon linkages and other chemical groups such as aromatic groups, which are very resistant to chemical attack.

In case of the two remaining treatments, namely maleic anhydride treatment and acetylation, the fibre bundles are quite well separated. In the micrograph, the elementary fibres, with a fibre diameter around $20\text{ }\mu\text{m}$ and a very clean surface, can be observed. This can emerge from the two treatments carried out at raised temperature, where some of the fibre constituents can be solved and therefore removed from the fibre surface.

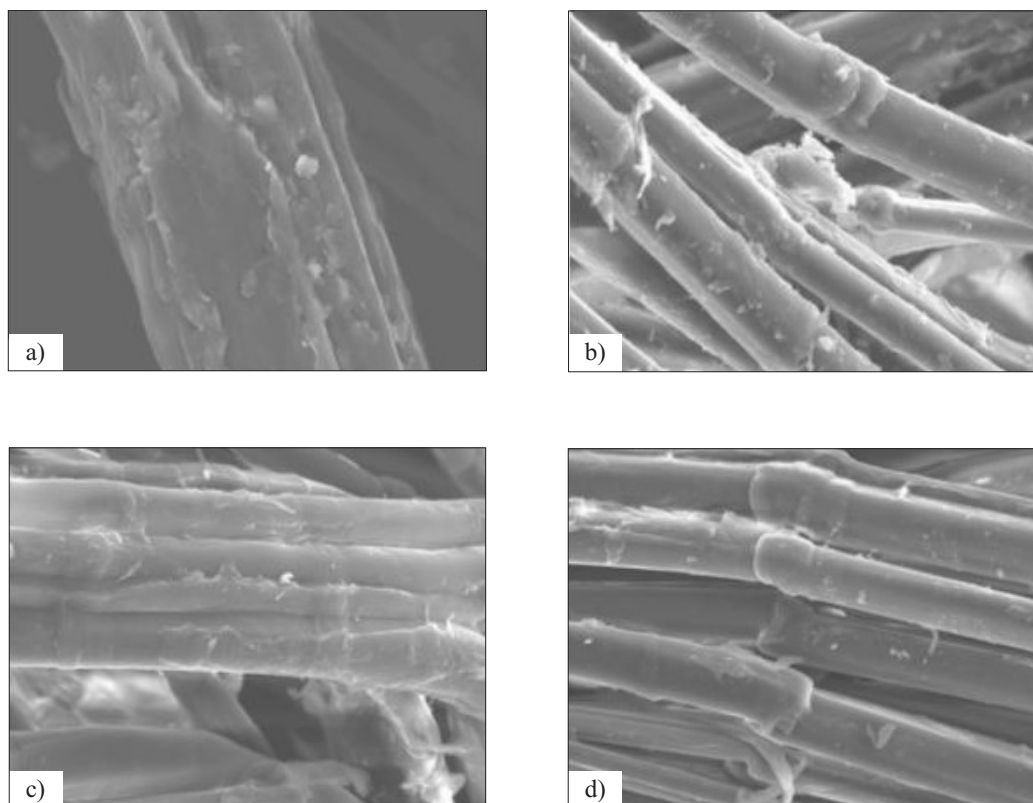


Fig. 3. SEM micrographs ($\times 1200$) of hemp fibres, a) raw, non-modified hemp fibres, b) acetylated fibres, c) alkali treated fibres, d) fibres modified with maleic anhydride

Thermal analysis results

The thermogravimetric analysis results are presented in Figure 4. The measurements were carried out in the atmosphere of air. The first mass loss observed occurs at around 100 °C, which is due to the loss of water. This can be observed for all the investigated samples. Afterwards, the untreated fibres show slightly lower stability than the treated ones. Degradation starts at lower temperatures than for the treated ones, which are stable up to about

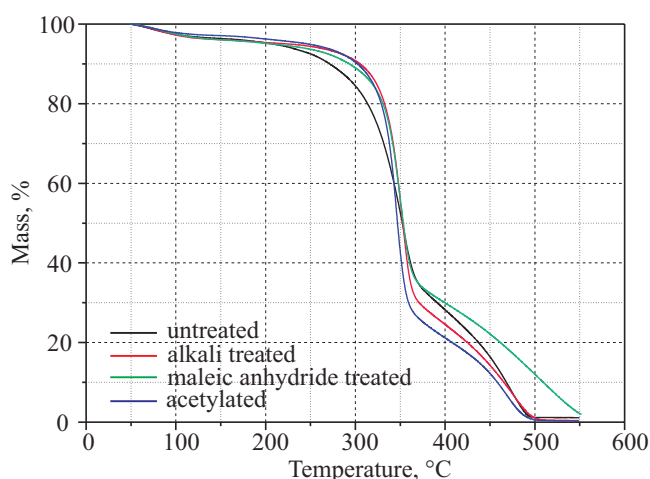


Fig. 4. Thermogravimetric analysis (TGA) of untreated and treated hemp fibres

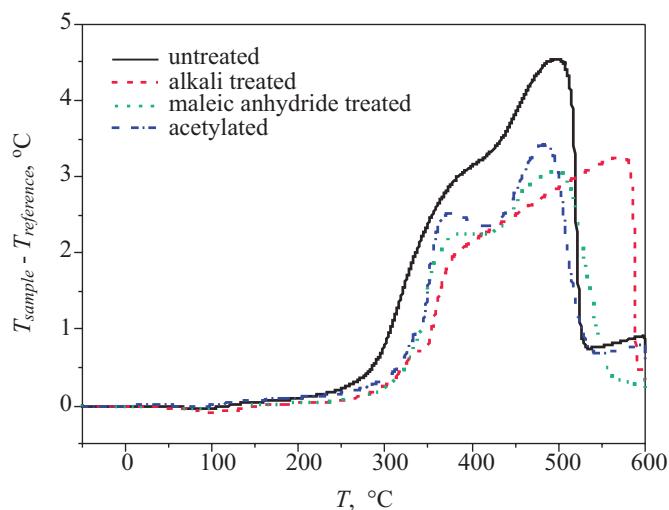


Fig. 5. Differential thermal analysis (DTA) of untreated and treated hemp fibres

250 °C. It could be due to the fact that some components of the cellulosic fibre, like hemicellulose or lignin, are removed during the treatment process. Therefore the main remaining part is cellulose itself, which is stable against thermal degradation up to about 250 °C.

The results of differential thermal analysis, which are shown in Figure 5, are in good accordance with the ones

from the TGA. First, a small endothermic peak can be observed at about 100 °C due to the loss of water [22]. Afterwards, the fibre degradation takes place. DTA results confirm that the untreated fibres start to degrade earlier than the treated ones. The three treated types (acetylated, alkali and maleic anhydride treated) show a similar behaviour over the range of degradation. The reason for that could be again the removal of some fibre components like hemicellulose or lignin due to the treatment process.

CONCLUSIONS

As shown in this work, the chemical treatment can alter the properties as well as the morphology of hemp fibres. The applied chemical modifications affected the presence of waxes and hemicellulose at the fibre surface, which could be seen in SEM micrographs. Results of TGA and DTA measurements proved that thermal stability of fibres was increased after the application of all treatment methods. This was due to the removal of some non-cellulose compounds of the hemp fibres, which were degraded earlier than the cellulose itself.

The only modification which yielded a different ATR FT-IR spectrum, in comparison with spectrum of untreated fibres, was acetylation. This was due to the fact that during this type of treatment numerous groups should be introduced into the fibre, therefore yielding a spectral response. The other treatments did not introduce new chemical groups (alkali treatment) or the introduced groups (maleic anhydride treatment) yield similar absorption bands than the hemp fibre itself.

The application of chemical modification and especially alkali treatment can be very beneficial for getting good bonding at the interface between a polymer matrix and the modified hemp fibres.

Chemically modified hemp fibers were used as reinforcement of polypropylene matrix composites. The mechanical properties of composites are presented in another paper [23] and confirmed the effectiveness of applied chemical modification of hemp fibres.

REFERENCES

1. Bledzki A. K., Gassan J.: *Prog. Polym. Sci.* 1999, **24**, 221.
2. Bos H. K., Müssig J., van den Oever M.: *Composites Part A* 2006, **37**, 1591.
3. Tserki V., Zafeiropoulos N. E., Simon F., Panayiotou C.: *Composites Part A* 2005, **36**, 1110.
4. Abdel-Nasser A., El-Hendawy: *J. Anal. Appl. Pyrolysis* 2006, **75**, 159.
5. Kaczmar J. W., Pach J., Kozłowski R.: *Polimery* 2006, **51**, 722.
6. Herrera-Franco P. J., Valadez-Gonzalez A.: *Composites Part B* 2005, **36**, 597.
7. Steller R., Meissner W.: *Polimery* 2002, **47**, 332.
8. Ke G., Yu W., Xu W., Cui W., Shen X.: *J. Mater. Process. Technol.* 2008, **207**, 125.

9. Sakata I., Morita M., Tsuruta N., Morita K.: *J. Appl. Polym. Sci.* 1993, **49**, 1251.
10. Wang Q., Kaliaguine S., Ait-Kadi A.: *J. Appl. Polym. Sci.* 1993, **48**, 121.
11. Li X., Tabil L. G., Oguocha I. N., Panigrahi S.: *Compos. Sci. Technol.* 2008, **68**, 1753.
12. Bledzki A., Faruk O.: *Appl. Compos. Mater.* 2003, **10**, 365.
13. Ghosh P., Dev D., Samanta A. K.: *J. Appl. Polym. Sci.* 1998, **68**, 1139.
14. Gomex-Bueso J., Westin M., Torgilsson R., Olesen P. O., Simonson R.: *Holz Roh Werkst.* 1999, **57**, 178.
15. Joseph K., Thomas S., Pavithan C.: *Polymer* 1996, **37**, 5131.
16. Cantero G., Arbelaz A., Llano-Ponte R., Mondragon I.: *Compos. Sci. Technol.* 2003, **63**, 1247.
17. Chang S. T., Chang H. T.: *Polym. Degrad. Stabil.* 2001, **71**, 261.
18. Colom X., Carrillo F., Nogues F., Garriga P.: *Polym. Degrad. Stabil.* 2003, **80**, 543.
19. Sgriccia N., Hawley M. C., Misra M.: *Composites Part A* 2008, **39**, 1632.
20. Kostic M., Pejic B., Scundric P.: *Bioresour. Technol.* 2008, **99**, 94.
21. Wang H. M., Postle R., Kessler R., Kessler W.: *Text. Res. J.* 2003, **73**, 664.
22. Ouajai S., Shanks R. A.: *Polym. Degrad. Stabil.* 2005, **89**, 327.
23. Pach J., Kaczmar J.: *Polimery* 2011, **56**, 385.

*Received 13 IX 2010,
in revised form 12 V 2011.*