CELLULOSE CHEMISTRY AND TECHNOLOGY

MICROCRYSTALLINE CELLULOSE FILLERS FOR USE IN HYBRID COMPOSITES WITH POLYETHYLENE AND LIGNIN

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Microcrystalline cellulose (MCC) fillers were obtained for hybrid composites with high-density polyethylene and lignin. The fillers were obtained from bleached kraft pulp and cotton fibres. The raw materials were treated by the thermocatalytic destruction method and then ground in a ball mill. Treatment conditions were developed for each raw material. MCC powder samples were obtained, which contained microparticles of different shape and size. Composite samples, which contained polyethylene, 50% of lignin, 20% of MCC and a coupling agent, were produced. It was established that the mechanical properties of composites were improved to a greater extent by the MCC filler obtained from cotton fibres. This can be related to the fact that it contained longer fibre fragments in comparison with wood pulp MCC. The higher degree of crystallinity of cotton cellulose also played a part.

Keywords: thermocatalytic destruction, microcrystalline cellulose, lignin, polyethylene, hybrid composites

INTRODUCTION

Recently, cellulose fibres and lignocellulosic materials, such as papermaking fibres and textile industry wastes, wood processing residues, technical lignins etc., have aroused considerable interest due to the their use as fillers in thermoplastic materials.[1-6] They represent highly filled composites, which contain up to 60% organic fillers. Compared with classic mineral-organic fillers, they have several advantages. Lignocellulosic fillers are biodegradable, bio-based, exhibit a low density and usually have a low cost. The rational use of by-products is the basis for the development of wasteless production, enhances its economic efficiency, increases the output and favours the environmental protection. However, the composites on the basis of thermoplastics with cellulose fibres or lignocellulosic fillers not always possess satisfactory mechanical indices.[7] The application of these materials is hindered because of the lack of the compatibility between the polar, hydrophylic cellulose-containing fillers and the hydrophobic thermoplastic matrix. The poor interfacial adhesion reduces the mechanical properties and favours the degradation caused by the moisture and biological attack. Therefore, coupling agents such as polyethylenimine,[8] silane,[9] isocianates,[10] maleic acid anhydride grafted polymers[11] and others are used in composites, which improves the compatibility. Using coupling agents and performing fibre modification, for example, by benzoylation and/or laurylation reactions, composites with improved thermal stability and mechanical properties were obtained.[12-14]

One of the best fillers used for improving the mechanical properties of thermoplastic polymers are man-made cellulose fibres. At the Fraunhofer Institute for Applied Polymer Research (Fraunhofer Institute IAP), composites were processed and investigated on the basis of polypropylene, polyethylene, polypropylene/

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ethylene block copolymer, high impact polystyrene, poly(lactic acid), thermoplastic elastomer and other polymers with 10 up to 40 wt% of man-made cellulose fibres (Rayon tyre cord yarn from Cordenka GmbH).[15-18] It was established that these fibres considerably improved the mechanical properties of thermoplastic polymers. Thus, for example, the man-made cellulose fibres increased the modulus of elasticity and tensile strength of composites on the basis of polyethylene and polypropylene threefold and Charpy notched impact strength fivefold.[19] The composites on the basis of poly(lactic acid) reinforced with Rayon are biobased and biodegradable, with excellent mechanical properties. Three partially conflicting properties are significantly improved at the same time, for example stiffness, tensile strength and impact strength.[20]

The aim of the present work was to obtain microcrystalline cellulose fillers for use in composites with high-density polyethylene, thermoplastic lignin preparations and a coupling agent.

EXPERIMENTAL

Materials

In composites, high-density polyethylene (SABIC HDPE HDPE M80064), standard softwood kraft lignin from a sulphate process, the coupling agent – maleic acid grafted high-density polyethylene (HDPE-g-MAH) (DuPont Fusabond E-MB 100-D) and cellulose-containing fillers were used.

Lignin had a molecular weight of 5010 g/mol, a polydispersity of 25.3 and a glass transition temperature of 148 ºC. The metoxy groups per phenyl propane unite (PPU) were about 0.9. The chemical composition determined from elemental analysis was: C=63.45%, H=5.84%, N=0.70%, O=27.24%, S=1.44%.

Cellulose-containing fillers, obtained from bleached birch kraft pulp (Metsä Fibre, Finland), bleached mixed softwood (pine and spruce) kraft pulp (Metsä Fibre, Finland) and cotton fibres (Uzbekistan), were used.

Thermocatalytic destruction and grinding

Cellulose fibres and lignocellulosic materials were destructed by the thermocatalytic method developed at the Latvian State Institute of Wood Chemistry.[21] According to this method, the raw materials were impregnated with a catalyst (weak hydrochloric acid solution) and then thermally treated at elevated temperatures until the moisture content in the samples reached 3%. The destruction of cellulose was characterised by changes of its degree of polymerization (DP).

To obtain cellulose-containing powders, the acid treated materials were ground in a ball mill.

Composites preparation

Before the compounding, lignin powder and MCC powders were pre-dried overnight in a vacuum oven at 80 °C.

After that, HDPE, 50 wt% lignin, 20 wt% MCC powders, as well as a coupling agent, were compounded using a Brabender W350 kneader at 170 °C for 5 min.

After pelletising the compounds, standard test specimens were prepared according to DIN EN ISO 527-2 (for tensile test) and DIN EN ISO 179 (for Charpy impact test) using an injection moulding machine (MiniJet) at a temperature of 170 °C and an injection pressure of 600 bar. The mould temperature was 50 °C with a cycle time of 14 seconds.

The production scheme is shown in Fig. 1.

Investigation of the properties of prepared cellulose-containing fillers and composites

The structural and physico-chemical properties of the obtained cellulose-containing fillers were investigated. The shape and size of the powder particles were studied using a LEICA CTR 5500 microscope and a TESCAN 5136 scanning electron microscope. Water retention value (WRV) was determined by centrifugation.[22] Physico-chemical properties (solubility, pH value, weight loss after drying, etc.) were determined by the methods specified in the European Pharmacopoeia.[23] DP of cellulose was calculated from the intrinsic viscosity of cellulose cadoxen solution.[24]

The mechanical properties of composites, i.e. tensile strength (σ_{max}), tensile modulus (E-Modulus), and elongation at break (ε_b) were determined under quasi-static stress in accordance with the standard DIN EN ISO 527, on a Zwick 1445 tensile testing machine. The impact properties, i.e. Charpy impact strength (a_c) as well as Charpy notched impact strength (a_{cN}), were determined according to the standard DIN EN ISO 179 on a pendulum impact tester, using a 0.5 J and 1 J hammer, respectively. All test specimens were conditioned for 24 h in a climate-controlled test laboratory at 23 °C and 50% relative humidity.

RESULTS AND DISCUSSION

Development of appropriate thermocatalytic treatment conditions

As it was shown earlier,[25] at the temperature of 110 ºC, with increasing concentration of the hydrochloric acid solution, DP first decreases rapidly, then at 0.03% HCl in the case of hardwood and at 0.04% in the case of softwood, cellulose reaches a constant value – the levellingoff degree of polymerisation (LODP), when the amorphous part is destructed, while the crystalline one remains almost intact. At a constant hydrochloric acid concentration (0.04%), with increasing thermal treatment temperature, LODP is reached at 90 ºC and 110 ºC for hardwood and softwood cellulose, respectively.

As a result, the following thermocatalytic treatment conditions for reaching LODP were established: concentration of hydrochloric acid solution 0.04-0.07% and 0.05-0.1%; thermal treatment temperature 90-120 ºC and 110-130 ºC for hardwood and softwood pulp cellulose, respectively.

After grinding the thermally destructed pulp in a ball mill, hardwood microcrystalline cellulose (HW MCC) and softwood microcrystalline cellulose (SW MCC) powders were obtained.

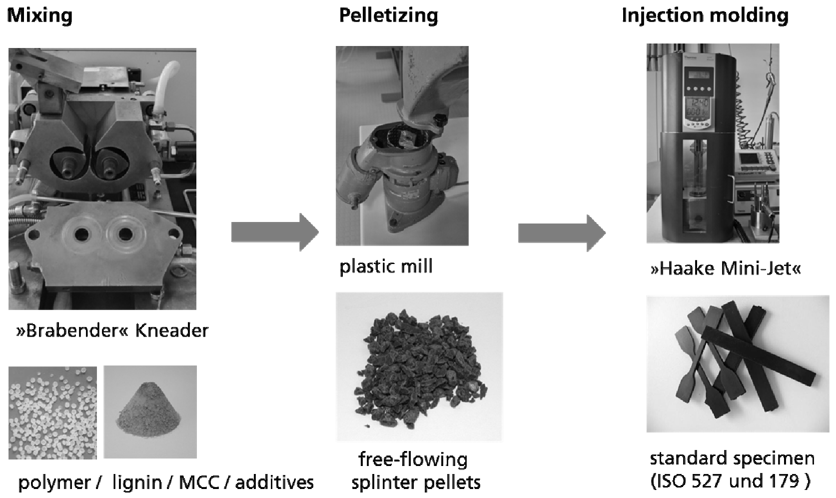

Figure 1: Production scheme of composites

Table 1
Characteristics of the obtained MCC samples

Sample No.	Raw material	Abbreviation	Thermocatalytic hydrolysis conditions	DP
1	Birch kraft pulp	HW MCC1	c_{HCl} = 0.04%, T = 115 ºC	410 (LODP)
2	Birch kraft pulp	HW MCC2	c_{HCl} = 0.04%, T = 70%	490
3	Birch kraft pulp	HW MCC3	c_{HCl} = 0.02%, T=120 ºC	500
4	Softwood (pine and spruce) kraft pulp	SW MCC	c_{HCl} = 0.05%, T = 120 ºC	320 (LODP)
5	Cotton fibres	C MCC	c_{HCl} = 0.1%, T = 120 ºC	400

However, after testing the initial composites (Fraunhofer IAP), it was concluded that reinforcing cellulose fillers with a higher aspect ratio is beneficial for the tensile and impact properties. For obtaining such powders, relevant conditions were developed by changing the treatment temperature and hydrochloric acid concentration. It was established that a higher aspect ratio of the cellulose particles can be obtained using treatment conditions, which correspond to the destruction of wood pulp up to a cellulose DP of 500-600 units. For hardwood pulp, it takes place either in the case when the hydrochloric acid concentration is 0.02% and treatment temperature 110-120 ºC, or when the hydrochloric acid concentration is 0.04% and treatment temperature 75 ºC.

In further experiments, the thermocatalytic treatment conditions were also developed for cotton cellulose. It is well known that the size of crystallites in cotton cellulose is comparatively higher, reaching 110-120 nm. Therefore, it is possible to obtain cotton fibre fragments, which are larger than those of wood cellulose. Besides, cotton fibres have a higher DP (3000-5000) as compared to the wood cellulose, and higher degree of crystallinity, i.e., 70%[26] (for wood cellulose 61-65%). Different raw materials and the applied thermocatalytic treatment conditions are listed in Table 1.

Structural properties of the obtained wood pulp MCC samples

Fig. 2 shows the percentage distribution graphs of the number of particles in the longitudinal and transversal size of the hardwood and softwood MCC samples.

Table 2 shows the number (%) of hardwood and softwood MCC particles with different size in longitudinal and transversal direction.

As can be seen from Fig. 2 and Table 2, the majority of particles, obtained from hardwood and softwood pulp, had the size of 20-40 μm in longitudinal direction. The particle size of samples HW MCC2 and HW MCC3, obtained at a lower temperature and a lower acid concentration, was higher in comparison with that of samples HW MCC1 and SW MCC, obtained under thermocatalytic conditions, corresponding to the LODP of cellulose. The maximal size of these samples exceeded 100 μm and in some cases 200 μm. The majority of the particles had a size of 10-20 μm in transversal direction. Therefore, the aspect ratio for particles of the samples HW MCC2 and HW MCC3 could reach 10 units.

Fig. 3 shows micrographs of the samples HW MCC1, HW MCC2 and HW MCC3. The sample HW MCC1 has fine particles, while the samples HW MCC2 and HW MCC3, besides fine particles, also have fibre fragments.

Fig. 4 shows scanning electron micrographs of HW MCC1 and SW MCC particles. It can be seen that, in both cases, the MCC powder contains particles that are similar in longitudinal and transversal direction.

Table 2
Number of hardwood and softwood MCC particles with different size in longitudinal (l) and transversal (d) direction

Sample		<3 μm	3-10 μm	10-20 μm	20-40 μm	40-60 μm	60-80 μm	80-100 μm	>100 μm
		Number of particles (%)							
HW MCC1	l	0	6	41	43	9	1	0	0
	d	1	26	49	19	5	0	0	0
HW MCC2	l	0	0	14	44	30	8	2	2
	d	0	9	46	41	5	0	0	0
HW MCC3	l	0	1	7	39	25	11	5	12
	d	0	10	45	35	8	2	0	0
SW MCC	l	0	5	44	49	2	0	0	0
	d	1	20	60	19	0	0	0	0

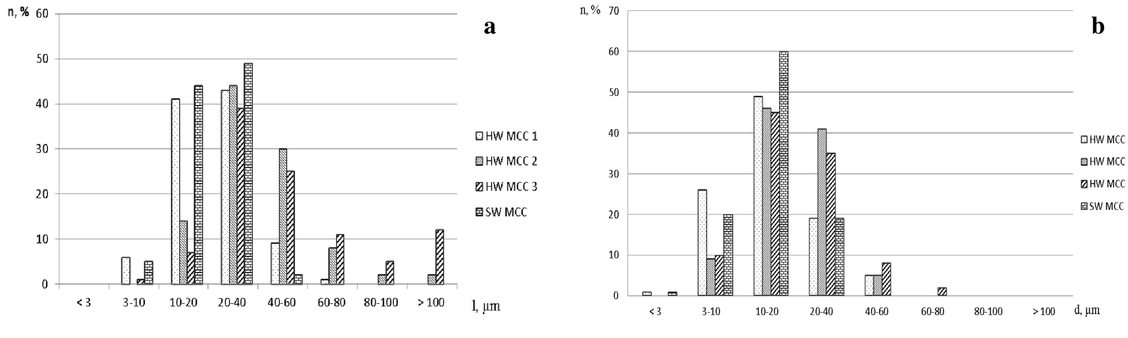

Figure 2: Percentage distribution graphs of the number of particles in (a) longitudinal size l, and (b) transversal size d of softwood and hardwood MCC samples

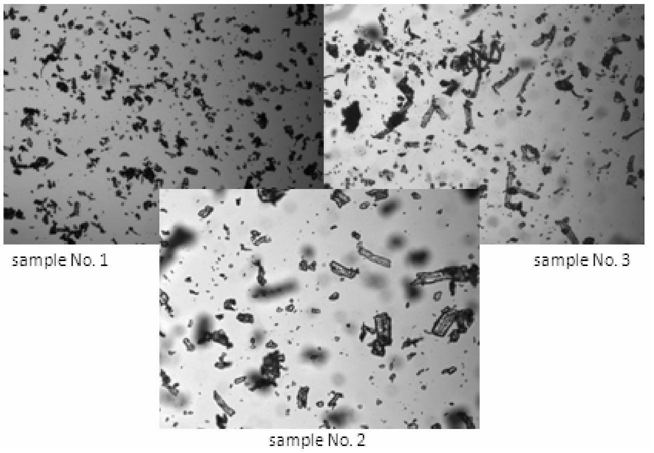

Figure 3: Micrographs of samples HW MCC 1 (No. 1), HW MCC 2 (No. 2) and HW MCC3 (No. 3); magnification x100

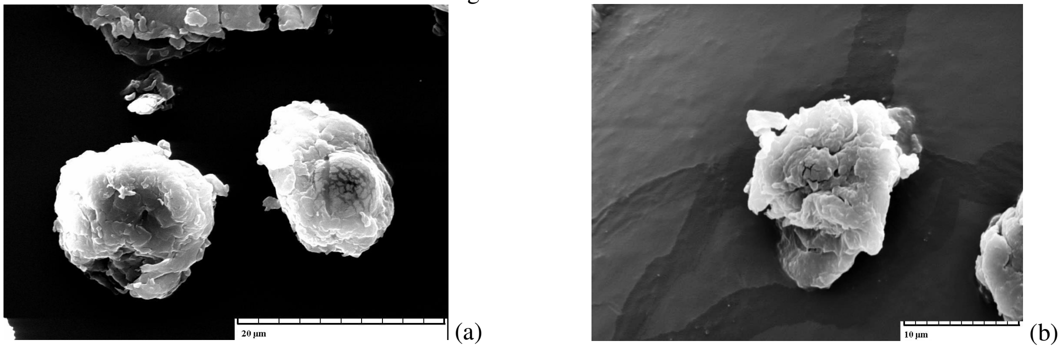

Figure 4: Electron micrographs of sample HW MCC1 (a) and SW MCC (b) particles

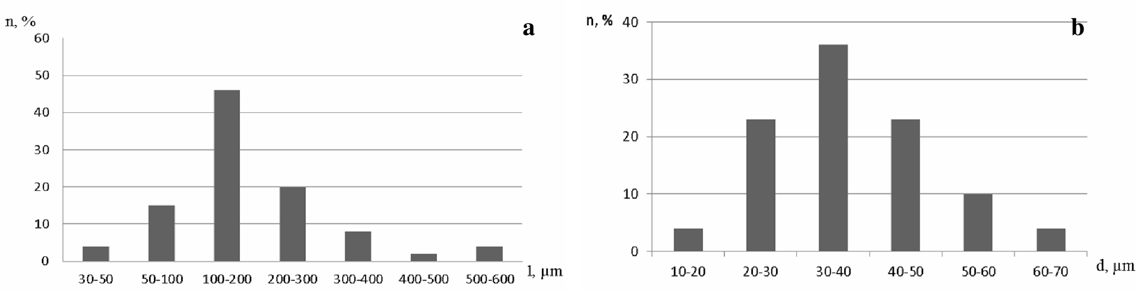

Figure 5: Percentage distribution graphs of the number of particles (fibre fragments) (a) in longitudinal size l, and (b) in transversal size d for the C MCC sample

Table 3
Number of particles (fibre fragments) with different size in longitudinal and transversal direction for cotton C MCC

	Size in longitudinal direction (µm)						
	30-50	50-100	100-200	200-300	300-400	400-500	500-600
Number of particles (%)	4	15	46	20	8	2	4
	Size in transversal direction (µm)						
	10-20	20-30	30-40	40-50	50-60	60-70	
	4	23	36	23	10	4	

The SW MCC sample obtained from softwood pulp under thermocatalytic treatment conditions, leading to close to LODP, had the lowest DP values (Table 1). From hardwood MCC samples, the HW MCC1 sample obtained under treatment conditions leading to LODP had a low DP value. The samples obtained at the lower acid concentration or lower temperature exhibited a higher DP.

Structural properties of cotton MCC samples

MCC powder, obtained from cotton fibres, had fibre fragments with greater length and aspect ratio. The DP value was 400 ± 20 units.

Figure 6: Micrographs of cotton sample C MCC particles; magnification x100

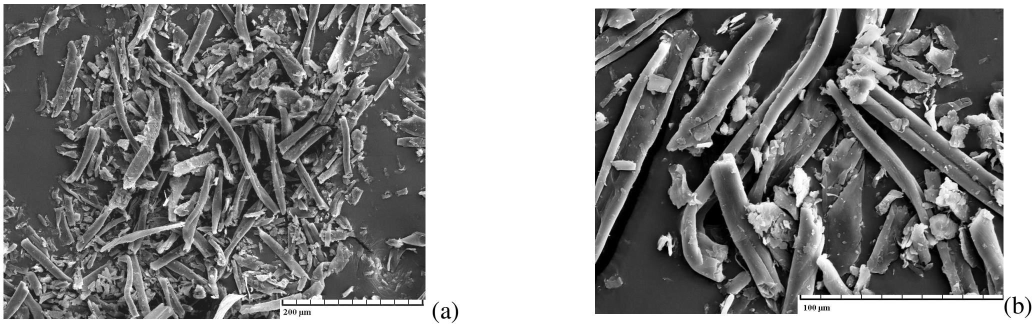

Figure 7: Electron micrographs of sample C MCC particles; magnification x1000 (a) and x1500 (b)

Table 4
Physico-chemical and quality indices of cellulose particles

Indices	HW MCC	SW MCC	C MCC
Solubility	Practically insoluble in water, 96% ethanol, diluted acids, acetone, toluene	Practically insoluble in water, 96% ethanol, diluted acids, acetone, toluene	Practically insoluble in water, 96% ethanol, diluted acids, acetone, toluene
pH	3.4 for non-washed from acid 5.0 for washed	3.4 for non-washed from acid 5.0 for washed	3.7 for non-washed 6.0 for washed
Weight loss upon drying (%)	3.9-4.1	5.3-5.5	3.9-4.3
Water-soluble substances (%)	1.24-1.67	3.22-3.35	1.20-1.72
Ether-soluble substances (%)	0.33-0.47	0.40-0.42	0.31-0.55
Sulphate ash (%)	0.71-0.92	0.20-0.29	0.73-0.96
Starch and dextrins	Does not contain	Does not contain	Does not contain
WRV (%)	72-85	50-55	-

Fig. 5 shows the percentage distribution graphs of the number of particles (fibre fragments) in longitudinal and transversal direction for the sample C MCC, and Table 3 shows the number of particles (fibre fragments) with different size in longitudinal and transversal direction for the sample C MCC.

It can be seen from the distribution graphs (Fig. 5 and Table 3) that the majority of cotton MCC particles (fibre fragments) have the size of 100-300 µm in longitudinal direction, and some particles exceed 500 and 600 µm. In transversal direction, the size of most particles is 20-40 µm. Therefore, the longitudinal and transversal size ratio reaches 30.

Fig. 6 shows micrographs of cotton MCC particles at the magnification x100, and Fig. 7 demonstrates electron micrographs of these particles. In all these micrographs, fibre fragments and fine particles among them can be seen. The average size of the fine particles in longitudinal and transversal directions is 11 µm and 7 µm, respectively.

Physico-chemical properties of the obtained samples

Table 4 lists the physico-chemical and quality indices of the investigated samples.

It can be seen that all the samples are practically insoluble in water, 96% ethanol, diluted acids and organic solvents. Before washing, their pH is ~4, and after washing from acid pH=5-6. They have a comparatively high amount of water-soluble and ether-soluble substances and sulphate ash. However, despite the sufficiently low chemical cleanliness, all powders can be used in composites with other materials.

Utilisation of obtained MCC samples in composites

Table 5 and Fig. 8 show mechanical indices such as tensile strength (σ_{max}), modulus of elasticity (E), relative elongation at break (ε_B), notched Charpy impact strength (a_{cN}) and Charpy impact strength (a_c) of the investigated composites, containing different MCC powders, and their increase.

It can be seen that all kinds of MCC fillers improve the mechanical properties of composites, which contain high-density polyethylene, softwood kraft lignin and a coupling agent. The MCC filler obtained from cotton fibres (sample C MCC) improves the mechanical properties of composites to a greater extent in comparison with the MCC fillers obtained from wood pulp. It is related to the fact that the cotton MCC powder contains fibre fragments with a higher aspect ratio and the single fibres are stiffer and stronger due to the higher degree of crystallinity. At 20% filler content, the tensile strength, modulus of elasticity, notched Charpy impact strength and Charpy impact strength of composites with the MCC filler obtained from cotton fibres increase by 30, 64, 50 and 15%, respectively, and elongation at break decreases by 20%. In the same way, the MCC filler obtained from hardwood pulp (HW MCC3) also sufficiently improves the mechanical properties of composites. In this case, tensile strength, modulus of elasticity, and notched and unnotched Charpy impact strength increase by 32, 51, 60 and 14%, respectively, whereas elongation at break does not change.

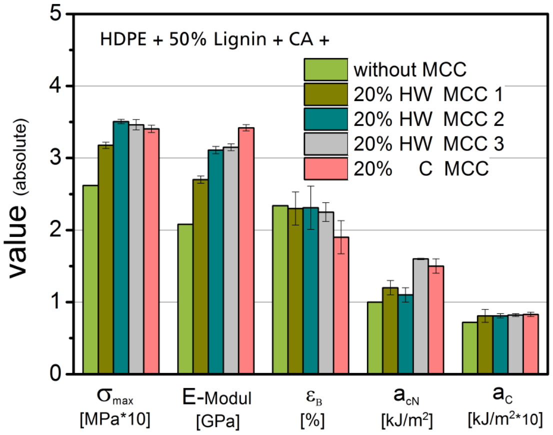

Figure 8: Mechanical indices for the obtained composites, containing differently shaped MCCs

Table 5
Mechanical indices of the investigated composites, containing different MCC powders

Composition PE+50% Lignin+CA	σ_{max} [MPa]	$\Delta\sigma_{max}$ [%]	E [GPa]	ΔE [%]	ε_B [%]	$\Delta\varepsilon_B$ [%]	a_{cN} [kJ/m^2]	Δa_{cN} [%]	a_c [kJ/m^2]	Δa_c [%]
	26.2	0	2.08	0	2.3	0	1.0	0	7.2	0
+20% HW MCC1	31.8	+31	2.70	+30	2.3	0	1.2	+20	8.1	+12
20% HW MCC2	35.1	+34	3.11	+50	2.3	0	1.1	+10	8.1	+12
20% HW MCC3	34.6	+32	3.15	+51	2.3	0	1.6	+60	8.2	+14

Therefore, the obtained MCC fillers can be used in blends with polyethylene and lignin to improve tensile properties and help overcome the embrittlement. There are no special requirements to the quality of cotton raw material for producing MCC. In these experiments, we have used residues from the textile industry.

However, the rayon fibre filler enhanced the mechanical properties of the investigated composites, especially the impact strength, much more in comparison with MCC powder fillers (Table 5).

It could be explained by the high tenacity parameter and, in particular, the higher aspect ratio (l/d=100 units) of man-made rayon fibres.The investigations performed at Fraunhofer IAP have shown that, using the rayon fibre filler instead of the MCC fillers, the tensile strength, modulus of elasticity, notched and unnoched Charpy impact strength and relative elongation at break of composites, which contain PE, 50% of lignin and a coupling agent, increase 2.7, 2, 10, 4.4 and 1.9-fold, respectively. However, since the rayon fibre filler is not economically attractive, in some cases, when high impact strength is not necessary, MCC fillers can be used to improve the mechanical properties of composites.

CONCLUSION

Thermocatalytic treatment conditions were developed to obtain wood pulp and cotton microcrystaline cellulose MCC powder fillers for their use in composites with high-density polyethylene and softwood kraft lignin.

It has been established that the obtained MCC powder fillers can be used in the investigated composites to improve their mechanical properties.

Greater improvement of the mechanical properties of composites was established using the MCC powder filler obtained from cotton fibres, which is connected with the fact that this filler contains fibre fragments with higher aspect ratio and mechanical properties in comparison with other fillers.

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