USE OF ACETYLATED STARCHES IN BIODEGRADABLE PLASTICS AND COMPOSITES WITH MONTMORILLONITE

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Introduction

Preservation of our planet with responsive utilization of fossil raw materials is *conditio sine qua non* for our and future generations. Plastics are an example of indispensable material class of everyday life used widely in packaging; nevertheless their often non degradable nature and bad carbon footprint are bottlenecks affecting plans for increasing production and consumption. Fully recyclable/biodegradable materials make one of proper ways. Starch-based plastics are basic very common biodegradable structures. The limitations of these formulations have been in their physical properties: poor water resistance and modest strength. Various strategies have been employed to get around these problems – like to combine biopolymer with a synthetic one (e.g. polyethylene) with known demanded properties. The aim of a biopolymer blend is to achieve a rapid fragmentation of the plastic film plus possible enhacement of degradation by using photoadditives. [1]. Starch material reinforcement by different materials (both organic like cellulose whiskers, or inorganic like clay platelets) is also a possibility of improving properties. [2]. We will report utilization of modified starches and montmorillonite for biodegradable nanocomposite material.

Experimental

Materials

Native potato starch (indicated as sample 1) as well as acetylated starches (less substituted with DS = 1,40 – 1,80, indicated as sample 2; more substituted with DS = 2,0 – 2,40, indicated as sample 3) were kindly supplied by Lyckeby Amylex a.s., Czech Republic. Sodium montmorillonite (Cloisite Na®, MMT) was supplied by Southern Clay Products Inc., USA. Sabenil® bentonite was kindly supplied by Keramost, a.s. Most, Czech Republic. Analytical grade glycerol (Lach-Ner s. r. o., Czech Republic) was used as received.

Apparatus

X-ray diffraction (XRD) experiments were conducted using X´Pert PRO MRD diffractometer (PANanalytical B.V., The Netherlands) using CuK_{α} radiation at $\lambda = 0.15406$ nm).

The tensile test measurements were carried out at temperature 22^{O} C and relative humidity 60% with Zwick/Roell Z5 device at crosshead speed 50 mm/min.

Procedures

Clays were suspended in water (1 g in 100 g of distilled water) under vigorous stirring to achieve perfect delamination. Samples of all thermoplastic starches (TPS) were prepared by gelatinization using water and glycerol at 85^{o}C. Starch composites with clays were prepared in the same manner with 2.5 and 5.0 % of the filler (w/w).

The film sheets were prepared by casting on PVC pad after proper degassing of suspension.

Results and Discussion

Prior to synthesis of thermoplastic acetylated starches and composites with clays, morphology of clay platelets in the hybrid material has been investigated by means of XRD analysis. The records reveal that incorporation of both natural potato and acetylated starches into the mineral structure leads to high degree of MMT exfoliation. It is important that this was found not only for the pure MMT mineral (Cloisite Na) having the diffraction peak at 12.07 Å but also for the natrified industrial bentonite with maximum at 12.6 Å (Figs. 1 - 3, respectively).

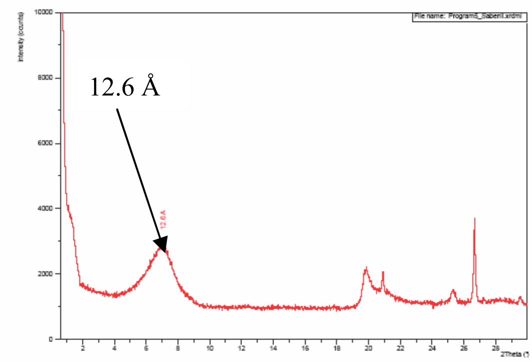

Fig. 1 X-Ray Diffraction Pattern of Sabenil bentonite

These mostly exfoliated structures obtained with acetylated starches differ from morphology of composites based on cationized starches and MMT [3].

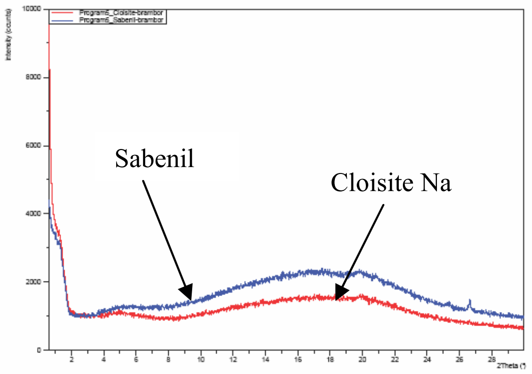

Fig. 2 X-ray diffraction pattern of clay/pristine potato starch composites

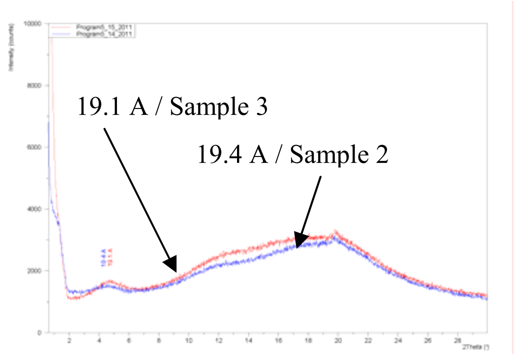

Fig. 3 X-ray diffraction pattern of Cloisite Na/acetylated starches composites

Mechanical properties of plastics based on acetylated starches were measured immediately after preparation and after 30 days of ageing. The results are summarized in Table 1.

Table 1 Mechanical properties of the starch matrix

Sample	Tensile strength [MPa]		Elongation at break (%)	
	Fresh	After 30 days	Fresh	After 30 days
1	7.5	6.2	92.4	92.2
2	4.3	2.6	193.6	247.4
3	4.4	3.5	237.5	245.7

In general, materials prepared on basis of the pristine potato starch exhibited the best mechanical behaviour. Ageing of the plastic matrix prepared with acetylated starches lowers the material strength (but enhances its elasticity) which corresponds to delayed retrogradation of chemically modified/crosslinked starches [4]. The reinforcement of the material by a pure MMT or bentonitic clay in two different concentrations is given in Tables 2 and 3, respectively.

Table 2 Mechanical properties of clay/starch composites / 2.5 % wt. of clay

Sample	Tensile strength [MPa]		Elongation at break (%)	
	Fresh	After 30 days	Fresh	After 30 days
1+Cloisite	8.7	6.9	52.4	48.9
2+Cloisite	5.8	6.0	130.4	101.0
3+Cloisite	5.9	3.9	66.7	117.4
1+Sabenil	9.9	7.2	60.5	80.10

Table 3 Mechanical properties of clay/starch composites / 5.0 % wt. of clay

Sample	Tensile strength [MPa]		Elongation at break (%)	
	Fresh	After 30 days	Fresh	After 30 days
1+Cloisite	5.44	5.72	70.9	68.2
2+Cloisite	4.92	5.48	125.3	125.8
3+Cloisite	5.29	5.96	80.4	69.5
1+Sabenil	8.82	6.43	64.7	75.1

Introduction of MMT into the starch matrix improves the strength significantly; even the industrial natrified bentonite showed the best results. Addition of more nanofiller had a negative effect. Presence of MMT in the nanocomposite enabled a higher share of retrogradation compared the plastic acetylated - starch matrix.

Conclusion

The mechanical properties of nanocomposites based on acetylated starches and clays showed a distinct reinforcement effect of the exfoliated MMT. The best strength results were achieved for the industrial bulk-volume clay (bentonite) surprisingly, and for the pristine potato starch.

References

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