THESES OF THE PH.D. DISSERTATION

Effect of montmorillonite nanoplatelet, cellulose micro- and nanocrystal on the properties of poly(lactic acid) matrix

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INTRODUCTION

Poly(lactic acid) or PLA is a biobased thermoplastic polyester which can be produced from lactic acid derived from the fermentation of different natural available polysaccharides. Furthermore PLA is a biodegradable and compostable plastic with relative good properties compared to the other biodegradable, biobased plastics, thus PLA has got its potential in many applications such as medical, drug delivery and textile or packaging applications. However, PLA is too brittle for many applications, softens at relatively low temperatures, has a weak water vapor and gas barrier properties compared to commercial polymers. To extend the application field the improvement of its properties (barrier, thermal, mechanical) is required. There have been taken many efforts to improve the week properties of PLA with different kind of materials including blending/compounding with other polymers, plasticizers (e.g. poly(Ɛ-caprolacton), thermoplastic starch, poly(ethylene glycol)s, tributil-citrates), reinforcing materials in micro (e.g. natural fibers, starch particles, cellulose micro crystals) and nanosize (layered silicates, carbon nanotubes, biobased nanoparticles or nanocrystals).

Special properties of heterogenic polymer based systems containing nanoreinforcements can be related not only to the presence of the reinforcement phase (eg. in reducing the water vapor and gas transmission through physical barrier created by nanoclays) but also to the polymer phase in the interfacial area, which has remarkably different properties than the bulk polymer matrix. Reinforcements in the nano range (<100 nm) have large surface area which facilitates plenty interfacial interactions to be formed with the polymer chains even using very little quantities. To obtain high amount of interfacial areas with unique properties achievement of proper dispersion and distribution is required. However it is a big challenge due to the high surface area and reactivity of the nanosized reinforcements, thus applying surface modification and/or compatibilizing agents is often necessary. Processing techniques (meaning the preparation of the nanoreinforcements as well) have also a high impact on the properties of the nanocomposites. Nanosized reinforcements can improve the mechanical properties, reduce the brittleness, enhance the toughness and the impact resistance, through the crystal nucleating effect the reinforcements can enhance the crystallinity, the speed of the crystallization, reduce the size of the spherulites (thus improve the transmittance), furthermore the nanoclays, nanoparticles can improve the fire resistance, the heat stability and also the barrier or even the degradation properties if they are dispersed and distributed properly in the polymer matrix.

OBJECTIVES OF THE RESEARCH

The aim of the research was to investigate the effect of montmorillonite nanoclay, cellulose micro- and nanocrystal (which was obtained from the ultrasonic treatment of the MCC) on the properties of the poly(lactic acid), ultimately to improve the weak properties of the PLA. The objectives of the research included:

- preparation of cellulose nanocrystals from MCC without acidic hydrolysis using sonication in a media which removal is not required thus preventing the aggregation, agglomeration of the cellulose nanocrystals
- comparison of the effect of MCC and MCC treated with ultrasound on the properties of the PLA
- improving the mechanical, thermal and barrier properties of the PLA with montmorillonite nanoclay and cellulose particles while preserving the transparency of the polymer system.

MATERIALS AND METHODS

The poly(ethylene glycol) (PEG400) (Macrogola 400, with average molecular weight of 400g/mol) was used not only as a plasticizer of the PLA, but as dispersion, distribution enhancing compatibilizing agent, and as a medium for ultrasonic treatment of the microcrystalline cellulose.

To prepare PLA based MCC containing composites 20μm particle size of highly pure microcrystalline cellulose was used (from Sigma Aldrich). To reduce the particle size of cellulose the MCC was sonicated in PEG400 media. Because the power of the ultrasonic rod treatment (with 20 kHz and 32 μm) seemed to be too high and caused the degradation of the PEG400, the direct sonication time was reduced to 15 min and the further sonication was carried out indirectly in an ultrasonication bath (with dual-frequency unit - transducers frequencies of 25 and 75 kHz) for 40 min. Prior the treatment, the microcrystalline cellulose was swelled in the poly(ethylene glycol) (also in case of MCC without sonication) for 24 hours. To obtain nanosized cellulose chemicals were not used in order to keep the process "green". In order to verify the effectiveness of the ultrasonic treatment, samples containing pure MCC and MCC+PEG400 were prepared.

The other reinforcement was an organophilic montmorillonite (Cloisite ®30B), a surface modified (quaternary ammonium salt with long alkyl chains and hydroxyl groups) layered silicate (specific surface area:750g/m^2, aspect ratio: 70-150). It is difficult to separate the nanoplatelets and to achieve a delaminated, intercalated structure especially in case of during melt process. To facilitate the separation of the layers, prior the melt processing of the composite, the MMT was swelled in PEG400 for 24 hours. In order to increase the delamination 5 minutes sonication was applied in ultrasonic bath. Large degree of swelling was observed, the highly mobile PEG chains entered into the interlaminar space of the montmorillonite.

The components were mixed in a COLLIN ZK25T four zoned compact laboratory twin screw co-rotating extruder where the a screw speed of 50 rpm and the temperature profile of 170-185-190-190°C were found to be optimal. The composite films were prepared on Scientific twin screw extruder with melt pump and LBRC – 150

chill roll cast line (180-185-190-195°C, 45 rpm, rolling speed: 4,3 m/min). The composition of the composite films can be seen in table 1.

Table 1. Composition of the PLA based composite films

sample name	PEG400 (wt%)	MCC (wt%)	MMT (wt%)
neat PLA	-	-	-
PEG5	5	-	-
PEG10	10	-	-
1M_P	10	-	1
3M_P	10	-	3
5M_P	10	-	5
1C	-	1	-
3C	-	3	-
5C	-	5	-
1C_P	10	1	-
3C_P	10	3	-
5C_P	10	5	-
1C_P_UH*	10	1	-
3C_P_UH*	10	3	-
5C_P_UH*	10	5	-

* samples containing MCC sonicated in PEG400

The manufactured PLA based films were characterized by several kinds of methods like UV-VIS spectrophotometry, FT-IR spectroscopy, wide angle powder X-ray diffraction (WAXD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), thermogravimetry (TG), tensile and tear test, scanning electron microscopy (SEM) and water vapor transmission rate test.

SUMMARY OF THE RESEARCH

Transmission electron microscopic images (Figure 1) showed that it is possible to obtain cellulose nanocrystals (spherical in form) with the ultrasonic treatment of MCC in PEG400, eliminate the acidic hydrolysis. According to the TEM images (Figure 2) in case of samples containing MMT a homogenous distribution and delamination was achieved with the applied pretreatment and processing parameters. The highest exfoliation was observed in case of 1 wt% MMT. In case of 5 wt% MMT content an intercalated and exfoliated structure was formed which was proved by WAXD as well. WAXD showed that samples 1M_P and 3M_P contained not fully delaminated layers too, but less than sample 5M_P. PLA based composites with montmorillonite are real

nanocomposites, while composites with ultrasonic treated MCC are hybrid systems containing both micro- and nanocrystals.

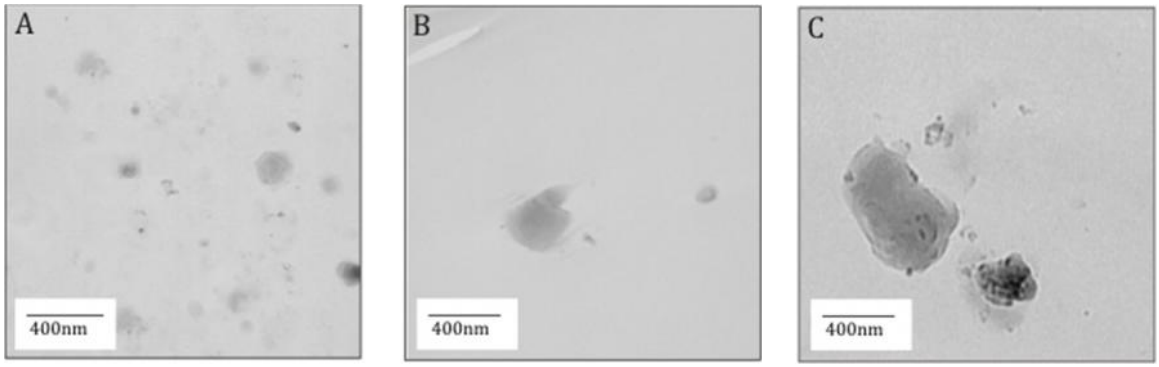

Figure 1. TEM images of PLA based samples containing MCC treated with ultrasound, A: 1C_PU, B: 3C_PU, C: 5C_PU

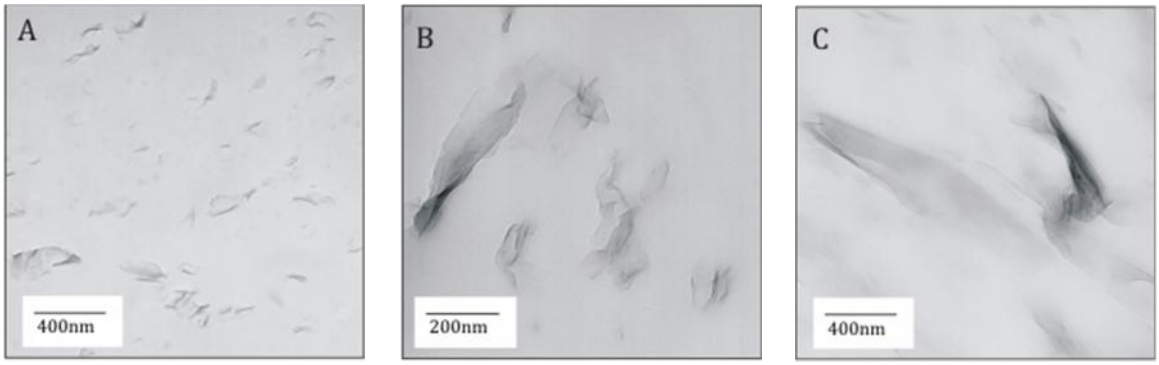

Figure 1. TEM images of PLA based samples containing montmorillonite nanoplatelets, A: 1M_P, B: 3M_P, C: 5M_P

According to the WAXD and DSC measurements due to the relatively fast cooling large amorphous fraction remained in the matrix, however the DSC showed that the modified samples, except the samples containing only pure MCC, have higher crystallinity due to the nucleating effect of the reinforcements and the chain mobilizing effect of the PEG400. In case of samples 1C, 3C and 5C, presumably caused by the reduced chain motions due to the strong interfacial interactions between the MCC and the PLA, the micro-Brown motions started at higher temperatures, the glass transition temperatures increased with 16.4, 16.0 and 14.9°C, respectively. Melting temperatures did not change significantly, except the double melting peak that was observed in case of neat PLA (also in case of 1C, 3C and 5C) and which was formed to be one peak caused by reduced amount of imperfect crystals. The UV-VIS spectrophotometry showed that the transmittance of the 1M_P sample (due to delamination and perhaps the smaller spherulites) was slightly, but higher than the neat PLA's. Montmorillonite nanoplatelets affected less the transparency than cellulose particles. The least reduction in transmittance was observed when ultrasonic treated MCC was used. TG results showed that the onset temperature (T_{ons}) of thermal degradation was shifted to higher

temperature even in case of samples containing plasticizer. The highest increase in T_{ons} was observed at samples 1C, 3C and 5C where the T_{ons} increased with 28.4, 29.7 and 20.9°C, respectively. Sample 5M_P had higher T_{ons} as well, where the increasement was 12°C compared to the neat PLA. According to the derivative thermogravimetry the T_{max} was shifted to higher temperatures only in case of samples containing 1, 3 and 5 wt% of pure MCC, other samples showed slightly decrease.

Tear index of the modified PLA became greater both in the machine and in cross direction. The highest improvement was observed in case of 3M_P and 5M_P samples – in machine direction the improvement was 625 and 717% and in cross direction 142 and 166%, respectively. In cross direction the 1C_P_UH sample showed also a remarkable improvement compared to the neat PLA. According to the stress-strain curves given by tensile tests the tensile properties of the samples differed in the machine and in cross direction which could be originated from the orientation of the reinforcements and/or the spherulites and the polymer chains in the amorphous phase. Stress at peak and stress at break (and also Young-modulus) were decreased almost every case, however, the strain at peak and at break was improved in many cases. Stress at peak in cross direction was higher almost for each modified sample, in the greatest extent at PEG10, 5M_P and 3C_PU with 87.52, 84.77 and 112.84%, respectively. Improvement is strain was even higher in machine direction, sample 1C_PUH and 3C_P_UH showed a 105.75 and 97.72% greater strain at peak compared to the neat PLA. Strain at breaks showed even greater improvement. In cross direction the improvement was 2847 and 3328%, respectively in case of samples 3M_P and 5M_P. Significant improvement was observed in the case of samples containing sonicated MCC as well, where the improvement was 444, 235 and 216%, respectively with the ultrasonically treated MCC content. All the samples showed greater strain at breaks at machine direction, the highest improvement (which have not been observed before in the literature) occurred using 3 and 5 wt% montmorillonite, where the strains were 103 and 132 times higher, respectively, than the strain at break of the neat PLA. Using ultrasound treated cellulose high improvement was observed, 108, 82 and 65 times higher stains were observed in case of samples 1C_P_UH, 3C_P_UH and 5C_P_UH. Samples with high strains showed cold drawing and neck forming, the neck could be observed along the whole samples. Strain hardening could not be seen, which was probably due to the orientation of the lamellae during the foil processing method. Deformations in the beginning were caused by shear band formation especially in case of samples containing MMT. The main mechanism was shear yielding (with the appearance of crazing as well) at samples containing MMT, crazing at samples containing MCC, cavitation and shear yielding in case of samples with ultrasound treated MCC. Material with high toughness can be prepared applying proper processing parameters and using ultrasonically treated MCC in PEG400 media and MMT swelled in PEG400.

With micro- and nanoreinforcements and with poly (ethylene glycol) composite foils with different kinds of properties and applications can be created. The modifications can extend the application field of the PLA. Reducing the brittleness bags,

heat formed packaging or extrusion coating with longer lifetime can be prepared. The reinforcements give better water vapor barrier properties to the material thus expanding the shelf-life of products packed in PLA.

THESES

1. **Thesis**
   Cellulose nanocrystals can be effectively produced via ultrasonic treatment in poly(ethylene glycol) (Mw=400) media excluding the usage of other chemicals. CNCs formed during sonication in PEG400 have spherulite appearance. The sonically produced CNCs can be directly used with the PEG400 media to modify the poly(lactic acid). Removal of the CNCs and further treatment is not required.

2. **Thesis**
   Brittleness of poly(lactic acid) foils can be reduced remarkably using little amount of MCC that was ultrasonically treated in PEG400. Beside the high improvement in toughness of the melt produced hybrid material, the transmittance and the heat stability remains satisfying. The water vapor transmission rate of either the PEG400 plasticized or the neat PLA foil can be significantly reduced using 1wt% of sonicated cellulose.

3. **Thesis**
   Optical microscopic images showed that the main deformation mechanism in case of samples containing MCC without ultrasonic treatment is crazing, while the main mechanism at samples containing sonicated MCC is void formation caused by the cohesive fracture of the cellulose particles rather than the termination of the interfacial interactions between the reinforcement and the matrix.

4. **Thesis**
   With PEG400 it is possible to combine the advantages of solution casting and melt process in case of montmorillonite reinforced PLA nanocomposites. Using PEG400 no solvent is needed since the MMT is able to swell in the liquid poly(ethylene glycol) which promotes the delamination. PLA based nanocomposites containing organophilic montmorillonite swelled in PEG400 have intercalated and exfoliated structures after the melt process. MMT with PEG400 can significantly enhance the plastic deformation of the PLA, can increase the transmittance, the crystallinity and reduce the water vapor transmission of the PEG400 plasticized PLA.

PUBLICATIONS FROM THE TOPIC OF THE DISSERTATION

1. Katalin Halasz, Levente Csoka: Plasticized biodegradable poly(lactic acid) based composites containing cellulose in micro and nano size, JOURNAL OF ENGINEERING 1:(1) pp. 1-9. (2013)
2. Alpár T., Halász K. Fa-cement rendszerek, Politejsav alapú, montmorillonitot és cellulózt tartalmazó nanokompozitok, Sopron: Nyugat-magyarországi Egyetem, Hungary, 2013. 151 p, (book) ISBN:978-963-359-017-1
3. Katalin Halasz, Levente Csoka, Rita Rakosa: The effect of cellulose on the properties of poly(lactic acid) from the range of nano to micro size, 66th International Convention of Forest Products Society., Washington, DC, USA, 2012 pp. 1-4. (proceedings and oral presentation)
4. Katalin Halasz, Mandar Badve, Levente Csoka: Poly(lactic acid) based hybrid composite films containing cellulose from micro to nano size, Third International Conference on Natural Polymers, Bio-Polymers, Bio-Materials, their Composites, Blends, IPNs and Gels Polyelectrolytes and Gels: Macro to Nano Scales, Kerala, India, 2012.10.26-2012.10.28. p. 139. (oral presentation)
5. Katalin Halasz, Andras Winkler, Levente Csoka, Rita Rakosa: Nanocellulose produced via ultrasonic treatment as a reinforcement for biodegradable poly(lactic acid) matrix, TAPPI International Conference on Nanotechnology for renewable Materials, Montreal, Canada, 2012.06.04-2012.06.07. TAPPI Press, Motreal, 2012. p. 37. (oral presentation), ISBN:978-1-59510-216-4
6. Katalin Halasz, Levente Csoka, Rita Rakosa: Application of nano and micro sized cellulose crystals in poly(lactic acid), The Impact of Urbanization, Industrial and Agricultural Technologies on the Natural Environment : International Scientific Conference on Sustainable Development and Ecological Footprint, Sopron, Hungary, 2012.03.26-2012.03.27. Budapest: Nemzeti Tankönyvkiadó; Nyugat-magyarországi Egyetem, 2012. pp. 1-6. (proceedings and oral presentation), ISBN:978-963-19-7352-5
7. Halász Katalin, Csóka Levente: Montmorillonittal és polietilén-glikollal módosított politejsav fóliák előállítása és vizsgálata, PAPÍRIPAR 51:(1-2) pp. 3-7. (2011)
8. Halász K., Rakosa R, Csóka Levente: Properties of Poly(Lactic Acid) Based Nanocomposites, Second International Conference on Natural Polymers, Bio-Polymers, Bio-Materials, their Composites, Blends, IPNs and Gels Polyelectrolytes and Gels: Macro to Nano Scales. , Kerala, India, 2011.09.24-2011.09.26. p. 28. (oral presentation)
9. Halász K, Csóka L, Rákosa R: Nanométeres mérettartományba eső erősítőanyagok hatása a politejsav mátrixra, MKE 1. Nemzeti Konferencia, Sopron, Hungary, 2011.05.22-2011.05.25., Budapest: Magyar Kémikusok Egyesülete, 2011. p. 88. (oral presentation), ISBN:978-963-9970-11-3

10. Halász K, Csóka L, Rákosa R: Cellulose-Reinforced Poly(Lactic Acid) Composites, 65th International Convention: Forest Products Society, Portland, OR, USA, 2011.06.19-2011.06.21. p. 1. (poster presentation, 1. price)
11. Halász Katalin, Rákosa Rita, Csóka Levente: Politejsav tulajdonságainak javítása nanométeres tartományba eső erősítőanyagok felhasználásával, Regionális Innovációs Kiállítás és Találmányi Vásár, 2010. április 16., Győr, Hungary(poster presentation) (2010)
12. Halász Katalin: Politejsav módosítása nanométeres tartományba eső erősítőanyagokkal MTA Műszaki Osztályának Szál- és Kompozittechnológiai Bizottsági Ülés, NYME, 2009. november (2009) (oral presentation)
13. Halász Katalin: PLA biopolimer fólia hazai fejlesztése, Csomagolástechnológus és papíros szakmai nap, BMF, 2009. május (oral presentation) (2009)
14. Halász K, Rákosa R, Csóka L: Politejsav alapú nanokompozitok vizsgálata, Magyar Kémikusok Egyesülete Környezetvédelmi Analitikai és Technológiai Társaság, Környezetvédelem és élelmiszerminőség a III. évezredben: IX. Környezetvédelmi Analitikai és Technológiai Konferencia, Sopron, Hungary, 2009.10.07-2009.10.09. Budapest: Magyar Kémikusok Egyesülete, 2009. p. 68. (oral presentation), ISBN:978-963-9970-00-7

OTHER PUBLICATIONS

15. Halász Katalin, Csóka Levente: Improving the barrier properties of poly(lactic acid) bottle by applying Lb-technique, TAPPI International Conference on Nanotechnology for Renewable Materials, Stockholm, Sweden, 2013.06.25-2013.06.27., USA: TAPPI Press, 2013. p. 117. (oral presentation) ISBN:978-1-59510-225-6
16. George Grozdits, Katalin Halasz: Paper Mill Residue Utilization to Make Thinner, Stronger Papers with Targeted Specific Paper Properties: The combination of layer-by-layer nanocoating and molecular mitigation technologies, TAPPI International Conference on Nanotechnology for renewable Materials, Montreal, Canada, 2012.06.04-2012.06.07., TAPPI Press, 2012. p. 38. (poster), ISBN:978-1-59510-216-4
17. Csóka Levente, Halász Katalin: Ultrasound in the Pulp and Paper Industry, Recent advances in high-power ultrasound research in Hungary – a Possible new way of technology, Sopron, Hungary, 2009.10.22 Sopron: Nyugat-magyarországi Egyetema, 2009. pp. 1-4. (proceedings and oral presentation), ISBN:978-963-988