Development and characterization of starch - based nanocomposite materials

M Zoumaki1,*, D Tzetis2 and G Mansour1

1Department of Mechanical Engineering, Laboratory of Machine Tools and Manufacturing Engineering, Aristotle University of Thessaloniki, Greece
2International Hellenic University, School of Science and Technology, Greece

Email: mariazita687@gmail.com

Abstract. Nature has developed several biodegradable materials which can be used in architectural and civil engineering to address the challenges of a more sustainable construction and housing industry to mitigate and adapt to climate change. Nowadays, there is an increasing interest in using biodegradable polymers from renewable resources such as starch and cellulose derivatives in the global plastic industry in order to reduce the environmental pollution caused by the petroleum-based traditional synthetic plastic waste. In this study, conventional composite and nanocomposite films of plasticized corn starch were prepared with sodium montmorillonite clay by a solution mixing procedure with glycerol as a plasticizer. The obtained nanocomposite microstructures were ascertained by XRD and SEM techniques and the tensile properties were investigated as a function of clay and plasticizer contents, in order to analyze the mechanical properties of the films.

1. Introduction
Researchers, engineers and designers have argued for a more interdisciplinary research on biodegradable structural materials from renewable resources, trying to design solutions for a more sustainable construction and housing industry to prepare society to adapt and mitigate the consequences of climate change [1- 4]. Starch, as a promising semi-crystalline natural biopolymer, has the advantages of renewability, biodegradability, compostability, abundance and low cost, and has received great attention in various pharmaceutical, biomedical, agricultural, food and biomaterial industrial applications and production of bioplastic and novel construction materials.[5-8] Thermoplastic starch can be obtained by mixing native starch with a plasticizer at a temperature above a characteristic critical value[5,6]. To overcome the disadvantages associated with the hydrophilic character and inadequate mechanical properties of starch-based biodegradable films, the incorporation of natural materials such as nanofillers into the plasticized starch matrix is an effective way of improving physical and mechanical properties of gelatinized starch [7-15]. In this study, conventional composite and nanocomposites films of plasticized corn starch were prepared with sodium montmorillonite (NaMMT) clay by a solution mixing procedure with glycerol/water plasticizer. The obtained nanocomposite microstructures were ascertained by XRD and SEM techniques and the tensile properties were investigated as a function of clay and plasticizer contents.
2. Materials and methods
A commercial corn starch (containing approximately 23% amylose) was used in the experiments. The moisture content of starch was 12 wt% as determined by drying to constant mass. The unmodified NaMMT clay Ma (supplied by Southern Clay Products, USA) was used to prepare composites of different types with thermoplastic starch. Glycerol (G) was also used as plasticizer and supplied by Mallinckrodt Chemical Works, USA [16,17]. Plasticized starch films were prepared by a solution mixing procedure, as discussed in previous studies [10, 12, 18, 19]. The glycerol content was varied between 10 and 100 wt%, while the clay content was varied between 0 and 25 wt% (based on the amount of dry starch) and the starch concentration of the solution was 6.5 wt%. The mechanical properties, tensile strength, percentage of elongation at break and elastic modulus (Young’s modulus) of conventional composite and nanocomposite films of plasticized corn starch were evaluated using tension tests. The tensile properties of the composite film samples were determined according to ASTM D882 standard test methods for tensile properties of thin plastic sheeting and films. The dimensions of the tensile specimens were 10x100 mm and the testing cross head speed was 20 mm/min [20]. The obtained nanocomposite structure of the films was confirmed by a wide angle X-ray scattering method (Rigaku MiniFlex II XRD) and scanning electronic microscopy (JEOL JSM-840A SEM).

3. Results and discussion
The films obtained in this study were macroscopically isotropic, homogeneous, smooth, flexible and sufficiently transparent, although the starch/clay nanocomposite films were less transparent as illustrated in figure 1 than the conventional starch films, plasticized with glycerol and water.

Figure 1. The physical appearance of the conventional (left) and NaMMT/nanocomposite (right) corn starch films

Comparison of conventional composite films of plasticized corn starch with increasing glycerol content (g/100 g starch) generally showed a decrease in tensile strength and elastic modulus but a marked increase in elongation at break (figure 2a). This could be attributed to the hydrogen bond interactions (during plasticization process) between hydrophilic glycerol molecules and starch chains and the subsequent disruption of the strong hydrogen bonds between the amylose and amylopectin that increased the mobility of starch chains [5, 9, 10]. The influence of different levels of glycerol (G20, G30 and G40 wt%) and NaMMT clay (between 0 and 25 wt% based on the amount of dry starch) on
the tensile properties (tensile strength, elastic modulus and elongation-at-break of the investigated TPS nanocomposite films) is also presented in figures 2b, 2c and 2d.

Figure 2. (a) Tensile strength and elongation at break of conventional corn starch films as a function of glycerol content. The influence of different levels of glycerol and clay (Ma) on the tensile properties: (b) tensile strength, (c) Young’s modulus and (d) elongation-at-break of the investigated TPS nanocomposites films

It is clear from the results that the interactions between the glycerol molecules, starch chains and clay content greatly affect the formation of nanostructure and influence the mechanical properties of the nanocomposite films. Films prepared with the same clay content, lower glycerol concentrations were generally associated with better mechanical strength (figure 2b) and modulus of elasticity (figure 2c) and low elongation at break (figure 2d) than higher glycerol concentrations. Even though the films obtained in this study showed a smooth and homogeneous appearance, the standard deviations of the tensile measurements were relatively large. It is important to note that at higher glycerol content (above about 50 wt%) the additional formation of hydrogen bonds between glycerol and starch resulted in lowering the reinforcing ability of the unmodified clay filler. As the clay Ma content increases, the tensile strength increases from around 38 MPa up to approximately 58 MPa, from 11 MPa to 26 MPa and from 6 MPa to 15 MPa with glycerol contents of 20, 30 and 40 w/w%, respectively (figure 3b). Compared to other studies [10, 12, 18, 19], the films obtained in this study
showed a higher increase in tensile strength, as can be clearly seen in figure 2. For the nanocomposite films, the tensile properties were enhanced even at lower clay content. The best results were obtained with NaMMT nanocomposites in the 10–15 wt% Ma range and glycerol concentration of 20 – 30 wt% in agreement with previous publications [18, 19].

From the findings of this study, it is revealed that sodium NaMMT had a significant reinforcing effect on the tensile properties of corn starch-based films. This enhanced effect can be attributed to interactions between plasticizer, starch and montmorillonite during diffusion of glycerol molecules and starch chains inside the clay galleries. The degree of clay intercalation and exfoliation depends not only on the glycerol content but also on the type of clay [5, 21, 22] The formation of an intercalated nanocomposite structure in the polymer matrix was also confirmed by XRD analysis. [23]

![XRD diffraction patterns](image)

**Figure 3.** XRD diffraction patterns of (a) corn starch and conventional composites G5 and G30 with 5 and 30 wt% glycerol concentrations, respectively, and (b) NaMMT (Ma) and G20-Ma3, G20-Ma5, G20-Ma10, G20-Ma15 and G20-Ma25 nanocomposites containing 3, 5, 10, 20 and 25 wt% NaMMT Ma clay, respectively, with 20 wt% glycerol concentration.
Corn starch shows characteristic XRD diffraction peaks with strong reflections at 2θ angles of about 15° and 23° and double peaks at 17° and 18°, exhibiting a typical A-type crystalline structure, whereas the absence of these peaks and the presence of a small broad peak in the XRD pattern of thermoplastic starch films is indicative that most of the original crystalline structure was destroyed during the solution mixing process (figure 3a). It follows from figure 3b that the XRD pattern of NaMMT shows an intense diffraction peak at approximately 2θ ≈ 7.3°, corresponding to an interlayer basal spacing of 1.21 nm. In the case of nanocomposite films with 3 wt% of nanoclay loading, the broad small double peak in XRD pattern (at diffraction angles 2θ between 3° - 5°) indicated that intercalation is non-uniform. The obtained nanocomposite films with 5 - 25 wt% of nanoclay loading show a peak shift to lower diffraction angles (2θ ≈ 5.1° - 5.3°) than the pure NaMMT (Ma), indicating an increase in interlayer spacing of silicate layers (≈ 1.68 - 1.70 nm). It is therefore evident that the shifting of XRD peaks towards lower angles (figure 3b) is indicative of an intercalated nanocomposite structure where starch chains and glycerol molecules are incorporated between the silicate layers, with subsequent increasing of the interlayer distance. The mechanical properties presented in Figure 2 are in a good agreement with the XRD results shown in figures 3a and 3b, where the formation of an intercalated nanocomposite structure was identified.

![Figure 4. Scanning electron micrographs taken from the (a) G20 conventional composites with 20 wt% glycerol concentration and (b) G20-Ma5 nanocomposites containing 5 wt% NaMMT Ma clay with 20 wt% glycerol concentration.](image)

The structures of the obtained nanocomposites were characterized by a wide angle X-ray scattering method and the morphology of the samples and the degree of dispersion of clay platelets in the plasticized starch matrix were examined by scanning electron microscopy (SEM). The results of XRD analysis were supported by SEM analysis which clearly illustrates that the films presented surfaces without noticeable pores, cracks or breaks with fairly homogeneous distribution of clay particles into the starch matrix (as shown in the SEM micrographs taken from the G20 and G20-Ma5 composites and presented in figures 4a and 4b, respectively). Similar morphology and homogeneous clay distribution were observed in all composite samples analyzed from each film. In summary, the above results support the conclusion that the incorporation of NaMMT into the starch matrix increased film stability in a wide range of clay content (from 3 wt% to 25 wt%) and improved the tensile properties of the nanocomposites obtained in this study.

4. Conclusions
The most recent and comprehensive research predicts that warming climate will increase the frequency of extreme weather-related natural disasters, and this may impose many challenges for
future buildings. Recently growing interest has been shown in applications of biopolymers in packaging films industry and as alternative novel construction biomaterials, such as corn starch-based building materials, as a possible partial replacement for concrete. In the present paper, a simple method was developed for synthesis of corn starch-based films with enhanced tensile properties for various applications of biodegradable materials. The obtained intercalated nanocomposite microstructures were confirmed by XRD and SEM techniques and the tensile behaviour was investigated as a function of clay and glycerol contents. At a given glycerol concentration, the tensile properties of nanocomposite films were enhanced even at lower clay content. Films prepared with the same clay content, lower glycerol concentrations were generally associated with better mechanical properties than higher glycerol concentrations. The best results were obtained with sodium montmorillonite nanocomposites at glycerol concentration of about 20 wt% and clay content of about 10 wt%. Compared to other studies, the obtained nanocomposites showed a higher increase in tensile strength, as can be concluded from the above findings. This enhanced effect may be attributed to better dispersion of unmodified clay particles in the starch matrix and strong interactions between glycerol, starch and sodium montmorillonite during diffusion of glycerol molecules and starch chains inside the clay galleries. Based on the above analysis, a further study will be carried out to investigate the possibility of developing advanced materials, resulting from the welding of the obtained nanocomposites, suitable for lightweight architectural constructions, in order to develop bio-inspired building envelopes.

**Acknowledgements**

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Program «Human Resources Development, Education and Lifelong Learning» in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research” (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

**References**

[1] Thomsen M R, Tamke M, Gengnagel C, Faircloth B and Scheurer F 2015 Modelling Behaviour: Design Modelling Symposium Springer ISBN 978-3-319-24208-8

[2] Ashby M F 2009 Materials and the Environment: Eco-informed Material Choice Butterworth-Heinemann 15 594-595

[3] Pacheco-Torgal F, Labrincha J A, Diamanti M V, Yu C P. and Lee H K 2015 Biotechnologies and Biomimetics for Civil Engineering Springer ISBN 978-3-319-09287-4

[4] Lyons A 2010 Materials for architects and builders Elsevier ISBN: 978-1-85617-519-7

[5] Madhumitha G, Fowsiya J, Mohana-Roopen S and Vijay Kumar Thakur 2018 Int. J. of Polym. Analysis and Characterization DOI: 10.1080/1023666X.2018.1447260

[6] Averous L and Boquillon N 2004 Carbohydrate Polymers 56 111

[7] Souza A C, Benze R, Ferrão E S, Ditchfield C, Coelho A and Tadini C 2012 LWT–Food Sci. and Technol. 46 110

[8] Zhang R, Wang X and Cheng M 2018 Polymers doi:10.3390/polym10101172

[9] Tang X Z, Alavi S and Herald T J 2008 Carbohydrate Polym. 74 552

[10] Pandey J K and Singh R P 2005 Starch-Starke 57 8

[11] Chen B Q and Evans J 2005 Carbohydrate Polym. 61 455

[12] Chivrac F, Pollet E, Dole P and Averous L. 2010 Carbohydrate Polym.s 79 941

[13] Chung Y L, Ansari S, Estevez L, Hayrapetyan S, Giannelis E P and Lai H M 20 Carbohydrate Polym. 79 391

[14] Cyras V, Manfredi L, Ton-That M and Vazquez A 2008 Carbohydrate Polym.73 55

[15] Arora A, Choudhary V and Sharma D 2011 J. Polym. Res. 18 843

[16] Marra S and Zuburtikudis I 2012 Journal of Applied Polymer Science 124 2999

[17] Christidis G and Scott P 1997 Mineralium Deposita 32 271

[18] Müller P, Kapin E and Fekete E 2014 Carbohydrate Polymers 113 569
[19] Bertuzzi M, Gottifredi J and Armada M 2012 *Brazilian Journal of Food Technology* **15** 219
[20] American Society for the Testing of Materials – ASTM 2012 *Standard Test Methods for Tensile Properties of Thin Plastic Sheeting* ASTM D882 USA 182-190
[21] Ray S and Bousmina M 2005 *Progress in Materials Science* **50** 962
[22] Chivrac F, Pollet E and Averous L 2009 *Materials Science and Engineering* Report **67** 1
[23] Van Soest J, Hulleman S, deWit D and Vliegenthart J 1996 *Crops and Products* **5** 11