Budapest University of Technology and Economics
Faculty of Chemical Technology and Biotechnology
„George Olah" Doctoral School

Nanofillers: properties, surface modification and applications

Thesis Book

Author: Nóra Hegyesi
Supervisor: Béla Pukánszky

Polymer Physics Research Group
Institute of Materials and Environmental Chemistry
Research Centre for Natural Sciences

Laboratory of Plastics and Rubber Technology
Department of Physical Chemistry and Materials Science
Budapest University of Technology and Economics

2020

1 Introduction

Layered silicate, especially smectite nanocomposites created much interest about three decades ago when the researchers of Toyota polymerized ε-caprolactam among the layers of montmorillonite and applied it as the timing belt cover of the model Toyota Starlet[1,2]. The advantageous properties of the material obtained started a hype and intensive research; many groups launched projects to explore the possibilities of this new group of materials. Our group started research on layered silicate nanocomposites as early as 1998, which resulted in the preparation of four PhD theses. The initial goal was to explore the factors determining the properties of layered silicate composites, which later led to the detailed analysis of surface characteristics, interfacial interactions and the role of processing parameters on composite structure and properties.

Interfacial interactions are among the four main factors which determine the properties of heterogeneous polymer systems[3] and are of utmost importance in the use of nanofillers and the preparation of nanocomposites because these latter have enormously large specific surface area. The improvement of the stiffness, strength and dimensional stability of composites is expected already at very small silicate contents, at least compared to traditional fillers or fiber like reinforcements. However, only exfoliated structure can fulfill these expectations because individual discs have large specific surface area and not the particles.

Two main approaches were studied in the literature for the preparation of nanocomposites and for the achievement of exfoliated structure. *In situ* intercalative polymerization was the first method applied by the Toyota group for the preparation of layered silicate nanocomposites. They incorporated ε-caprolactam among montmorillonite layers, and then initiated its ring opening polymerization[1,2]. Quite a few at-

---

[1] Kurauchi T, Okada A, Nomura T, Nishio T, Saegusa S, Deguchi R. *SAE Tech. Pap.*, (1991)

[2] Okada A, Fukushima Y, Kawasumi M, Inagaki S, Usuki A, Sugiyama S, et al., *US4739007A* (1988)

[3] Pukánszky B. In: Karger-Kocsis J, editor. *Polypropylene: Structure, Blends and Composites*. London: Chapman and Hall; 1995. p. 1-70.

tempts were made to polymerize various monomers among the layers of the silicate afterwards including olefins[4,5], styrene[6], acrylates[7,8], etc. As most commercial polymers are processed and molded by melt mixing technologies, the obvious approach is to prepare nanocomposites in the melt state. However, the delamination of silicate layers and the achievement of large extent of exfoliation is practically impossible by this method[9,10]. Silicates exfoliate in larger extent in composites prepared by *in situ* intercalative polymerization resulting in better thermal and mechanical properties [5,6,11]. Direct exfoliation in the melt state is hindered by strong silicate/silicate interactions due to their large surface energy[12] and their 2D shape[13]. Surface energy can be reduced with surface modification with long alkyl chains in an ion exchange reaction but weaker particle/particle interactions go hand in hand with weaker polymer/particle interactions[14,15].

Our previous works pointed out that layered silicate composites can surpass the reinforcing effect of commercial fillers only in a very narrow composition range because of structural effects, i.e. the lack of exfoliation and the lack of controlled structure[16]. The results indicate that the traditional approaches utilized in the last few decades do not work, the exchange of interlayer cations to organic cations with long aliphatic chains does not achieve the desired effect, the separation of

[4] Asensio M, Herrero M, Núñez K, Gallego R, Merino JC, Pastor JM. *Eur. Polym. J.*, **100**:278-289, (2018)

[5] Rong J, Jing Z, Li H, Sheng M. *Macromol. Rapid Commun.*, **22**:329-334, (2001)

[6] Zeng QH, Wang DZ, Yu AB, Lu GQ. *Nanotechnology*, **13**:549-553, (2002)

[7] Lee DC, Jang LW. J. *Appl. Polym. Sci.*, **61**:1117-1122, (1996)

[8] Herrera NN, Persoz S, Putaux J-L, David L, Bourgeat-Lami E. J. *Nanosci. Nanotechnol.*, **6**:421-431, (2006)

[9] Kato M, Usuki A, Okada A. J. Appl. Polym. Sci., 66:1781-1785, (1997)

[10] Laus M, Francescangeli O, Sandrolini F. J. Mater. Res., 12:3134-3139, (2011)

[11] Tung J, Gupta RK, Simon GP, Edward GH, Bhattacharya SN. *Polymer*, **46**:10405-10418, (2005)

[12] Heinz H, Koerner H, Anderson KL, Vaia RA, Farmer BL. *Chem. Mater.*, **17**:5658-5669, (2005)

[13] Chiu C-W, Huang T-K, Wang Y-C, Alamani BG, Lin J-J. *Prog. Polym. Sci.*, **39**:443-485, (2014)

[14] Kádár F, Százdi L, Fekete E, Pukánszky B. *Langmuir*, **22**:7848-7854, (2006)

[15] Pukánszky B, Fekete E, Tüdós F. *Macromol. Symp.*, **28**:165-186, (1989)

[16] Hári J, Horváth F, Móczó J, Renner K, Pukánszky B. *Express Polym. Lett.*, **11**:479-492, (2017)

the layers, and melt mixing, although simple and convenient, does not yield exfoliated nanocomposites. Thus, new concepts and approaches are needed to utilize fully the potentials of nanofillers and to prepare materials with special properties for functional applications, which tolerate even the higher price of nanocomposites. Nanofillers can form different interactions and have enormously large surface area and surface energy, which allow them to adsorb various compounds, i.e. they can be used as adsorbing materials in water treatment[17], carriers for different active agents e.g. in antimicrobial coatings[18], or in the controlled release of poorly soluble compounds[19].

Based on a thorough literature survey and the conclusions above, we decided to start experiments with the synthetic silicate, laponite and with halloysite nanotubes (HNT), instead of montmorillonite because they have larger potential in functional applications. First, we characterized the properties of laponite in detail, and then investigated two different methods for its surface modification and the effect of the modification on its properties. The possible application of HNT as enzyme carrier was investigated in another project. This thesis summarizes the most important scientific results of the research done, its main conclusions and further outlook.

2 Materials and methods

2.1 Materials

Four different silicates were selected for our experiments. Sodium montmorillonite (NaMt, cation exchange capacity, CEC: 1.16 meq/g), Laponite XLG (CEC: 0.55 meq/g), Laponite XLS (CEC: no data) were purchased from Byk Additives and Instruments. The halloysite (HNT) used as support was the New Zealand CC Ultrafine H filler obtained from Imerys Ceramics.

[17] González B, da Silva TH, Ciuffi KJ, Vicente MA, Trujillano R, Rives V, et al., *Microporous Mesoporous Mat.*, **253**:112-122, (2017)

[18] Tornuk F, Sagdic O, Hancer M, Yetim H. *Food Res. Int.*, **107**:337-345, (2018)

[19] Hári J, Sárközi M, Földes E, Pukánszky B. *Polym. Degrad. Stab.*, **147**:229-236, (2018)

The chloride salt of methylene blue (MB) trihydrate was applied for the determination of the specific surface area of the silicates. The surface of Laponite XLG was modified with ethoxytrimethyl silane (ETMS) on the edges while with methyl methacrylate (MMA) on the faces after an ion exchange reaction with [2-(acryloil-oxy)-ethyl]-trimethylammonium chloride (AETAC).

The enzymatic degradation of polylactic acid and poly-ε-caprolactone was performed in the presence of lipase from *Candida rugosa*, Amano Lipase PS from *Burkholderia cepacia* or a Proteinase K from *Tritirachium album*.

2.2 Characterization

The concentration of methylene blue, Bradford reagent and the product of the enzymatic degradation of the polymers was determined based on UV-Vis spectroscopy measurements. Fourier transform infrared spectroscopy (FTIR) was used for the chemical characterization of the modified silicate. Fillers were characterized by thermogravimetric analysis (TGA) to measure their water content and the amount of the organic material adsorbed on their surface.

Gallery distance and the layer structure of the silicate were investigated by X-ray diffraction (XRD) measurements. The possible formation of a silicate network in silicate suspension was checked by rotational viscosimetry. Differential scanning calorimetry (DSC) was used for the determination of the glass transition temperature of the coupled polymer. The morphology of the composites was investigated with scanning electron microscopy (SEM).

3 Results

3.1 Comparison of different methods for the determination of the specific surface area of layered silicates

Nitrogen adsorption and methylene blue adsorption are the most frequently applied methods for the determination of the specific surface area of smectites. As the measured values very often differs from the values yielded from the geometry of the silicate layers, we aimed to resolve the apparent contradiction. The specific surface area of three layered silicates was determined by three different approaches and good agreement was observed between experimental and theoretical values for some of the results, while considerable discrepancies in other cases. Surface area resulting from the geometry of the platelets and that determined by the adsorption of methylene blue are larger than values obtained by the nitrogen adsorption. This is not very surprising since the penetration of nitrogen molecules into the gallery space of the dry silicate is quite limited. It is worth to note that some correlation can be seen between the penetration of nitrogen molecules and the regularity of gallery structure. The results of the methylene blue adsorption measurements also did not match the values of the calculations in every cases. If adsorption occurs through attractive ionic forces and methylene blue molecules are arranged parallel to the silicate layers in a monomolecular coverage, the agreement between surface areas calculated from the geometry of the plates and those determined by the adsorption of methylene blue agree well with each other. The specific surface area of a silicate with relatively small size (laponite) and cation exchange capacity (CEC = 0.55 meq/g) was smaller than expected because of the dependence of the adsorbed amount of methylene blue molecules on pH. The addition of methylene blue solution decreases pH considerably leading to particles with positive charge, as shown by zeta potential measurements, to smaller methylene blue adsorption and small apparent specific surface area. The modification of the clay or the control of pH by a buffer solve the problem, and real values for surface areas are obtained which agree well with geometric calculations. At large ion exchange capacity (sodium montrmorillonite, CEC = 1.16 meq/g), the molecules adsorb in a tilted orientation and not parallel to the surface. Tilted orientation results in larger than monomolecular coverage and

the specific surface area calculated from methylene blue adsorption is considerably larger than the real surface area.

3.2 Edge modification

The planar surface of the silicates is negative while the edges of the silicate discs are positively charged in water. The so called house-of-card structure forms as the result of electrostatic interactions between the negatively charged lateral surface of the plates and the positively charged edges. This structure leads to the special behavior of layered silicates in aqueous medium e.g. to non-Newtonian viscosity. The presence of the structure was confirmed also in layered silicate nanocomposites by several researchers and was found to be disadvantageous for the processing of the material. We aimed to prevent the network formation of the silicate by the modification of the edges with a monoalkoxy silane compound (ethoxy-trimethyl-silane, ETMS). The edges of a synthetic layered silicate, laponite, were successfully modified with ETMS. The occurrence of the reaction was confirmed with various methods and surface coverage was determined. The determination of the bonded amount of silane by FTIR analysis must be carried out with care, since side reactions take place during modification. Although the expected dimerization of the silane did not occur, it hydrolyzed during treatment systematically changing the amount of bonded silane determined from the FTIR absorption of oxygen containing groups. Only vibrations related to the absorption of the –$SiCH_3$ group can be used for quantitative analysis. XRD measurements proved that the silane is bonded onto the surface of the silicate and it does not enter the gallery space. According to the FTIR measurements, approximately 50 mg silane is bonded to 1 g silicate corresponding to almost complete surface coverage. The results of the measurements were supported by model calculations and extremely good agreement was found between the calculated and measured values. Surface modification did not hinder the formation of a house-of-card structure showing that silanol groups does not play a role in the process (Fig. 1). An explanation was offered based on the release of hydroxide ions from the –MgOH moiety of the silicate. Covalent modification of the edges of layered silicates may facilitate exfoliation or help functionalization, but does not prevent

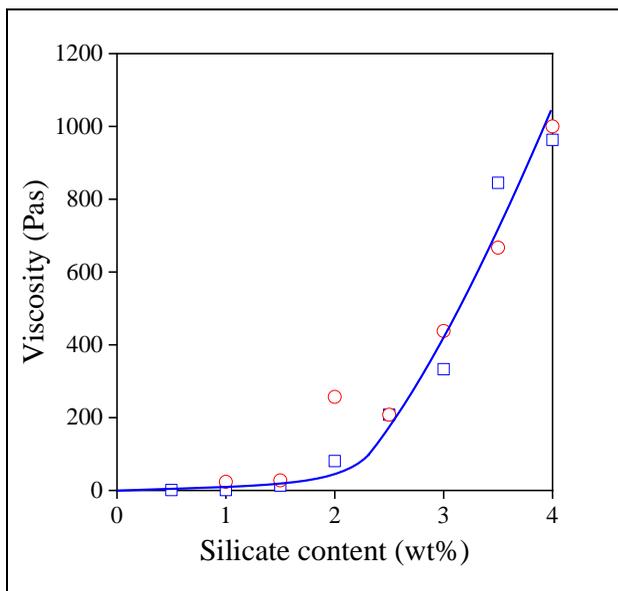network formation and cannot be used for the control of rheological properties.

Figure 1   *Development of a house-of-card structure independently of the surface modification of the silicate. Symbols: (□) 0 mmol, (○) 1 mmol ETMS/g silicate.*

3.3 Coupling of PMMA onto the surface of laponite

Our goal was to attach polymer molecules onto the surface of laponite which later can be used as reinforcement in polymer nanocomposites. According to our hypothesis, the long coupled polymer chains can entangle the polymer matrix in melt state compounding. It is expected that the entanglement of the polymer matrix and the coupled polymer can reduce the interaction decreasing effect of the surface treatment between the polymer and the filler. Long poly(methyl methacrylate) (PMMA) chains were successfully attached to the surface of laponite layers through [2-(acryloil-oxy)-ethyl]-trimethylammonium

chloride (AETAC) linker. Grafting was carried out in water and the molecular weight of the grafted polymer was between 40 and 110 kDa. The amount of PMMA attached to the silicate and the length of the polymer depended on the extent of ion exchange and on the amount of methylmethacrylate (MMA) added. Thermogravimetric measurements carried out before and after extraction proved that most of the polymer was attached to the surface of the silicate. The layer distance of the silicate increased as the result of grafting (Fig. 2).
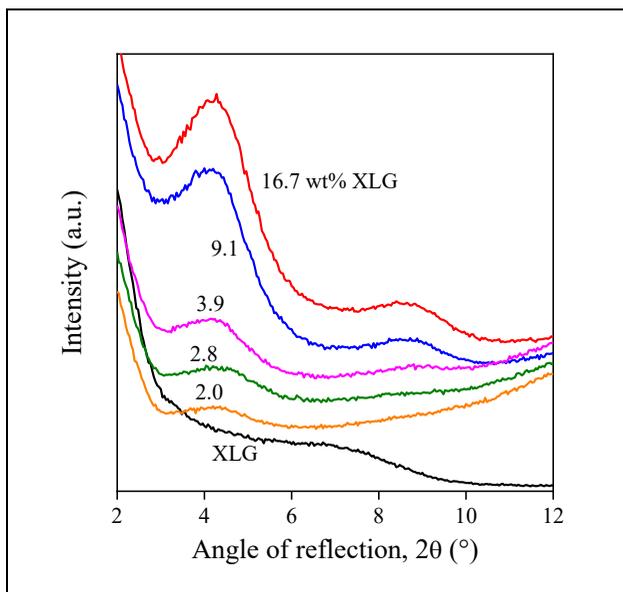

Figure 2 *XRD traces recorded on laponite modified with different amounts of polymer. Effect of XLG content on gallery structure.*

Model calculations proved that a part of the polymer is outside the galleries. The polymer chains located inside the galleries are oriented parallel to the surface and two chains are found inside each gallery. The very high surface energy of the silicate results in this parallel arrangement and the resulting strong interactions decrease the mobility of the chains. The glass transition temperature of the polymer increases while

the change in specific heat decreases with decreasing amount of PMMA and also with decreasing chain length. Improvement in the properties of composites reinforced with a layered silicate, which has PMMA attached to its surface, can be expected only in the case of long grafted chains.

3.4 Enzymatic degradation of PLA/CNC nanocomposites

Polylactic acid (PLA) is used in increasing quantities mostly for packaging and in biomedical applications because of its advantageous properties. It is produced from renewable raw material and biodegradble. However, PLA has some drawbacks as well, it is very sensitive to water during processing, brittle, crystallizes very slowly, and its physical ageing is relatively fast, which further decreases its fracture resistance. Cooperating with a research group from Shanghai, we added crytallalline nanocellulose (CNC) to PLA for improving its properties. We studied the effect of the addition of the nanofiller to the biodegradability of PLA. Preliminary experiments showed that the lipase from *Candida rugosa* does not catalyze the degradation of PLA, but Proteinase K is very efficient. The lactic acid forming during the reaction is a relatively strong acid, changes the pH of the degradation medium that leads to the denaturation of the enzyme. Denaturation occurs below $pH = 6.5$, thus either the degradation solution must be changed regularly or a buffer with sufficient capacity must be used as medium. Besides pH, the ion concentration of the solution also influences the rate of degradation; smaller ionic strength is more advantageous. The cellulose nanocrystals used for the reinforcement of PLA increase the rate of degradation (Fig. 3) and the samples disintegrate very rapidly. Because the samples lose their integrity, an alternative method is needed to follow degradation. This can be done by the determination of the amount of lactic acid forming during degradation. Complex formation with iron(III) chloride hexahydrate and UV-Vis spectroscopy proved to be a very appropriate method for the purpose. A model was applied for the quantitative analysis of the kinetics of degradation and denaturation, which takes into account and describes both processes well. The model and the obtained parameters can be used for the design of experiments and the prediction of the degradation of aliphatic polyesters as well as their blends and composites.
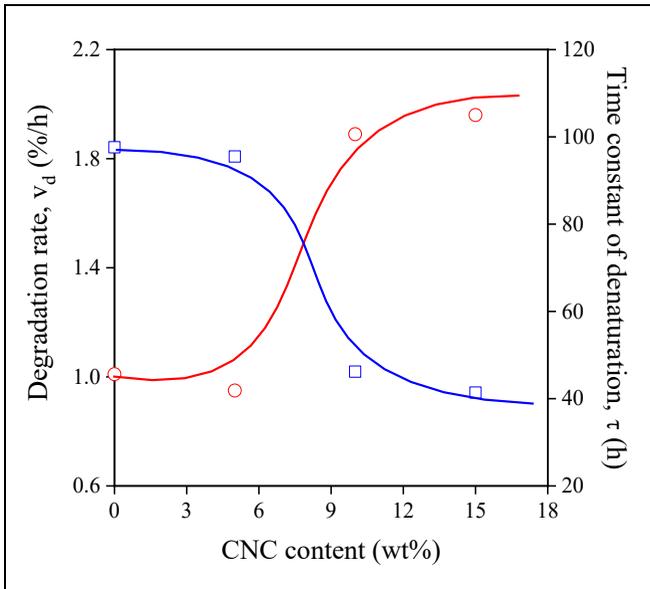
Figure 3 *Effect of CNC content on the rate of degradation and the time constant of denaturation during the enzymatic degradation of PLA/CNC nanocomposites. Symbols: (○) rate of degradation, v_d; (□) time constant of denaturation, τ.*

3.5 Enzymatic degradation of PCL/HNT composites

Besides PLA, other polyesters (e.g.: poly-ε-caprolactone, PCL) can also be relevant in biomedical applications. Controlled degradation at physiological conditions is required from some products made of PCL (e.g.: artificial scaffolds). However, PCL can be degraded only by enzymes under physiological conditions. Enzymes attached to a carrier were dispersed in the polymer matrix to achieve controlled degradation. Lipase from *Burkholderia cepacia* was successfully adsorbed on the surface of halloysite nanotubes, and the resulting coated tubes were incorporated into poly-ε-caprolactone. The measurement of the activity of the enzyme adsorbed on the surface of the support in different amounts proved that the enzyme remains active even after adsorption;

in fact, larger activities were measured for the immobilized enzyme than for the original enzyme preparation. The enzyme immobilized on halloysite nanotubes degraded PCL efficiently (Fig. 4), the rate of degradation depended on the amount of enzyme adsorbed. The kinetics of degradation was described quantitatively with an appropriate model accounting for the two determining steps of the process, i.e. for degradation and the denaturation of the enzyme. The determination of time constants allows the adjustment of degradation rate. This is the first time that the enzyme catalyzing degradation is incorporated into the polymer, and not into the degradation medium, thus allowing the preparation of resorbable scaffolds with controlled lifetime.

a) no enzyme
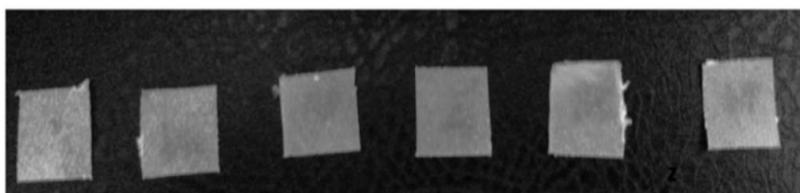
| 24 h | 168 h | 216 h | 576 h | 792 h | 1080 h |

b) 3.8 U/g enzyme activity
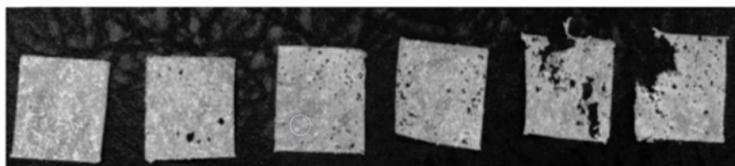
| 24 h | 168 h | 216 h | 576 h | 792 h | 1080 h |

Figure 4 *PCL films prepared only with HNT remain intact (a). Deterioration of PCL films containing the supported enzyme with the activity of 3.8 U/g (b).*

4 New scientific results

1. During the revision of the known methylene blue adsorption meth-od used for the determination of the specific surface area of com-pletely delaminated layered silicate we pointed out for the first time that several factors might bias the value obtained. Changing pH decreases the determined surface area, while large ion ex-change capacity and tilted orientation of the molecules yields a larger area than the theoretical value. [P1]

2. We successfully modified the edges of layered silicate particles with a monofunctional silane compound in order to prevent the network formation of the silicate. Contrary to expectations, the goal was not achieved and the network formed. We pointed out for the first time that the network formation of trioctahedral smectites is caused by the release of hydroxyl ions from the –MgOH moiety of the silicate while silanol groups do not play a role in the pro-cess. [P2]

3. We attached long PMMA chains to the surface of a completely exfoliated layered silicate, laponite, in homogeneous water solu-tion. The length of the chains was controlled successfully by the proper selection of the composition of the reaction medium. [P3, Chapter 5]

4. We could prove with appropriate measurements and model calcu-lations that the PMMA chains attached to the surface of laponite are oriented parallel to the surface, and two chains are located in each gallery space. Adsorption and parallel orientation decreases the mobility of the attached chains. [Chapter 5]

5. We prepared poly(lactic acid)/crystalline nanocellulose composites and determined their enzymatic degradation in the presence of Pro-teinase K. We pointed out the first time that the rate of degradation depends very much not only on pH, but also on the ionic strength of the degradation medium. [P4]

6. We adsorbed an enzyme onto the surface of halloysite nanotubes and incorporated the tubes into a polycaprolactone matrix. The adsorbed enzyme degraded PCL efficiently and the rate of degradation could be controlled by the amount of enzyme attached to the surface of the nanotubes. This is the first time that the enzyme catalyzing degradation is incorporated into the polymer and not into the degradation medium which opens the route for the preparation of medical devices with controlled lifetime. [P5]

7. We successfully developed a kinetic model for the description of the enzymatic degradation of aliphatic polyesters in a long time scale. We proved the general validity of the approach not only for neat aliphatic polyesters, but also for heterogeneous materials. [P4, P5]

5 Possible applications

At current prices only special and functional applications justify the use of nanocomposites. Nanofillers can form different interactions and have enormously large surface area and large surface energy, which allow them to adsorb compounds, i.e. they can be used as carriers for different active agents. Aliphatic polyesters are promising polymer for biomedical application but their degradation in physiological conditions are limited. The rate of their degradation can be increased by enzymes while with the help of a carrier the increased degradation rate also can be controlled that is necessary in the case of resorbable scaffolds.

6 Publications

6.1 The thesis is based on the following papers
    (IF: impact factor, IC: independent citations)

1. N. Hegyesi, RT. Vad, B. Pukánszky, Determination of the specific surface area of layered silicates by methylene blue adsorption: The role of structure, pH and layer charge, *Appl. Clay Sci.*, 146 (2017) 50-55. DOI: 10.1016/j.clay.2017.05.007 (IF = 3.641; IC: 19)

2. N. Hegyesi, N. Simon, B. Pukánszky, Silane modification of layered silicates and the mechanism of network formation from exfoliated layers, *Appl. Clay Sci.*, 171 (2019) 74-81. DOI: 10.1016/j.clay.2019.01.023 (IF = 3.890; IC: 2)

3. N. Hegyesi, B. Pukánszky, Poli(metil-metakrilát) rögzítése ionosan rétegszilikátok felületén nanokompozit töltőanyagként való alkalmazásra, *Műanyag és Gumi*, 51 (2014) 476-480. (IF: -; IC: 0)

4. N. Hegyesi, Y. Zhang, A. Kohári, P. Polyák, X. Sui, B. Pukánszky, Enzymatic degradation of PLA/cellulose nanocrystal composites, *Ind. Crops Prod.*, 141 (2019) 111799. DOI: 10.1016/j.indcrop.2019.111799 (IF = 4.191; IC: 0)

5. N. Hegyesi, E. Hodosi, P. Polyák, G. Faludi, D. Balogh-Weiser, B. Pukánszky, Controlled degradation of poly-ε-caprolactone for resorbable scaffolds; *Colloids Surf. B, Biointerfaces*, 186 (2020) 110678. DOI: 10.1016/j.colsurfb.2019.110678 (IF = 3.973; IC: -)

6.2 Manuscripts

6. N. Hegyesi, Sz. Pongrácz, RT. Vad, B. Pukánszky, Coupling of PMMA to the surface of a layered silicate by intercalative polymerization: processes, structure and properties, *submitted*

6.3 Other publications

7. X. Li, N. Hegyesi, Y. Zhang, Z. Mao, X. Feng, B. Wang, B. Pukánszky, X. Sui, Poly(lactic acid)/lignin blends prepared with the Pickering emulsion template method, *Eur. Polym. J.*, 110 (2019) 378-384. DOI: 10.1016/j.eurpolymj.2018.12.001 (IF2018 = 3.621; IC: 7)

8. A. Selim, A.J. Toth, E. Haaz, D. Fozer, A. Szanyi, N. Hegyesi, P. Mizsey, Preparation and characterization of PVA/GA/Laponite membranes to enhance pervaporation desalination performance, *Sep. Purif. Technol.*, 221 (2019) 201-210. DOI: 10.1016/j.seppur.2019.03.084 (IF = 5.107; IC: 4)

9. B. Gyarmati, N. Hegyesi, B. Pukánszky, A. Szilágyi, A colourimetric method for the determination of the degree of chemical cross-linking in aspartic acid-based polymer gels, *Express Polym. Lett.*, 9 (2015) 154-164. DOI: 10.3144/expresspolymlett.2015.16 (IF = 2.965; IC: 5)

6.4. Oral presentations (HN as presenting author)

1. E. Hodosi, N. Hegyesi, D. Weiser, B. Pukánszky, Controlled bulk degradation of poly -ε-caprolactone by the entrapment of lipase enzyme into Halloysite nanotubes *8th Workshop on Green Chemistry and Nanotechnologies in Polymer Chemistry.* **September 6-8, 2017**, Prague, Czech Republic

2. RT. Vad, N. Hegyesi, B. Pukánszky, Comparing of various methods for the determination of the specific surface area of layered silicate polymer fillers *BYPOS 2017.* **June 12-16, 2017,** Zemplinska Sirava, Slovakia

3. Cs. Balázs, N. Hegyesi, B. Pukánszky, Estimation of interfacial interactions in polymer/layered silicate composites *BYPOS 2016.* **March 15-19, 2016,** Ziar, Slovakia

4. N. Hegyesi, B. Pukánszky, Attachment of poly(methyl methacrylate) to laponite for the preparation of PMMA/layered silicate nanocomposites, *DVSPM 2015,* **May 11-13, 2015**, Gmunden, Austria