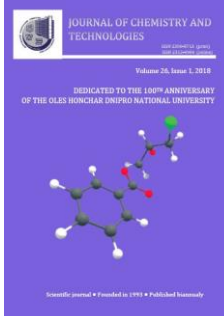




Journal of Chemistry and Technologies

pISSN 2306-871X (Print), ISSN 2313-4984 (Online)

journal homepage: <http://chemistry.dnu.dp.ua>



UDC 541.04

OBTAINING TECHNOLOGY FOR NANOCOMPOSITES BASED ON POLYAMIDE-6 AND ORGANOMODIFIED MONTMORILLONITE

Kostyantyn M. Sukhyy*, Elena A. Belyanovskaya, Mikhaylo P. Sukhyy, Vitaliy I. Tomilo,
Roman D. Lytovchenko

State Higher Education Institution 'Ukrainian State University of Chemical Engineering', Gagarine av. 8, Dnipro,
49005, Ukraine

Received 07 January 2018; revised 11 January 2018; accepted 05 February 2018

Abstract

The obtaining technology of nanocomposites based on polyamide-6 and organomodified montmorillonite is developed. The technological parameters of extrusion and injection molding, and their influence on the formation of nanoscale inorganic phase of the polyamide are investigated. Morphology and thermal behavior of polyamide-6, composites based on polyamide-6 and modified montmorillonite are studied by WAXS, XRD, DTA and DSC data. Morphology and thermal behavior of polyamide-6 and composites based on polyamide-6 and modified montmorillonite are shown to be in a strong juxtaposition. New γ -phase formation is revealed in composite polyamide-6 - 1-2 % of modified montmorillonite in contrast with polyamide-6 and mechanical mixtures of polyamide-6 and montmorillonite. Optimal concentrations of modified montmorillonite in the composites stated as 1 - 2 % are shown to correspond with composites improved properties as compared to initial polyamide-6. It is explained by increasing crystallinity degree, which resulted from acting of modified montmorillonite particles as nucleation heterogenetic agents.

Keywords: extrusion; montmorillonite; delamination; nanocomposites; crystallinity degree.

ТЕХНОЛОГІЯ ОТРИМАННЯ НАНОКОМПОЗИТІВ НА ОСНОВІ ПОЛІАМІДА-6 ТА ОРГАНОМОДИФІКОВАНОГО МОНТМОРИЛОНІТА

Костянтин М. Сухий*, Олена А. Беляновська, Михайло П. Сухий, Віталій І. Томіло,
Роман Д. Литовченко

ДВНЗ «Український державний хіміко-технологічний університет», пр. Гагаріна 8, Дніпро, 49005,
Україна

Анотація

Розроблено технологію отримання нанокompозитів на основі поліаміду-6 та органомодифікованого монтморилоніту. Досліджено технологічні параметри екструзії та лиття під тиском та їх вплив на формування нанодисперсної неорганічної фази поліаміду. Морфологія та термічна поведінка поліаміду-6, композитів на основі поліаміду-6 та модифікованого монтморилоніту вивчені за допомогою WAXS, XRD, DTA та DSC. Показана якісна відмінність морфології та термічної поведінки поліаміду-6 та композитів на основі поліаміду-6 і модифікованого монтморилоніту. В складі поліаміду-6 - 1-2% модифікованого монтморилоніту в порівнянні з поліамідом-6 та механічними сумішами поліаміду-6 та монтморилоніту виявлено нове утворення γ -фази. Показано, що оптимальні концентрації модифікованого монтморилоніту в композитах, які вказані як 1-2%, відповідають поліпшеним властивостям композитів у порівнянні з вихідним поліамідом-6. Це пояснюється збільшенням ступеня кристалінності, що виникає внаслідок дії модифікованих монтморилонітних частинок як зародкових гетерогенних агентів.

Ключові слова: екструзія; монтморилоніт; деламінація; нанокompозити; ступінь кристалінності.

* Corresponding author: tel: (050)4801116; e-mail:ksukhyy@gmail.com

© 2018 Oles Honchar Dnipro National University

doi: 10.15421/081802

ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ НАНОКОМПОЗИТОВ НА ОСНОВЕ ПОЛИАМИДА-6 И ОРГАНОМОДИФИЦИРОВАННОГО МОНТМОРИЛЛОНИТА

Константин М. Сухой*, Елена А. Беляновская, Михаил П. Сухой, Виталий И. Томило, Роман Д. Литовченко
ГВУЗ «Украинский государственный химико-технологический университет», пр. Гагарина 8, Днепро, 49005, Украина

Аннотация

Разработана технология получения нанокomпозитов на основе полиамида-6 и органоимодифицированного монтмориллонита. Исследованы технологические параметры экструзии и литья под давлением и их влияние на формирование нанодисперсных неорганической фазы полиамида. Морфология и термическое поведение полиамида-6, композитов на основе полиамида-6 и модифицированного монтмориллонита изучены с помощью WAXS, XRD, DTA и DSC. Показано качественное различие морфологии и термического поведения полиамида-6 и композитов на основе полиамида-6 и модифицированного монтмориллонита. В составе полиамида-6 – 1-2% модифицированного монтмориллонита по сравнению с полиамидом-6 и механическими смесями полиамида-6 и монтмориллонита обнаружено новое образование γ -фазы. Показано, что оптимальные концентрации модифицированного монтмориллонита в композитах, которые составляют 1-2%, соответствуют улучшенным свойствам композитов по сравнению с исходным полиамидом-6. Это объясняется увеличением степени кристалличности, возникающем вследствие действия модифицированных частиц монтмориллонита как зародышевых гетерогенных агентов.

Ключевые слова: экструзия; монтмориллонит; деламинация; нанокomпозиты; степень кристалличности.

Introduction

Modern trends for development and applying of polymeric materials concern with search for rational solutions to give a new properties to bulk polymers [1-3]. Design of polymeric nanocomposites based on engineering polymers is a relevant objective.

Physical and mechanical characteristics are determinant factors when changes accompanied transitions from macro- to nanostructure investigated [4-6]. When nanocomposites based on various polymeric matrixes, substantial increasing of physical and mechanical properties of composites is sufficiently observed as a natural and predicted result with relatively little concentration of clay mineral. Such changes of polymeric composites properties are peculiar to macro-nanostructure transition [7-9].

Layered silicates as nanoscale heterophase have a high demand for obtaining of polymeric nanocomposites [10]. Layered silicates, in particular montmorillonite, have a specific matrix structure causing their unique properties [11; 12]. For example, montmorillonite primary crystal elements (layers) can be expanded in water media. This process allows for sizable organic cation intercalation into interlamellar space resulted from replacements of metal cations. Subsequently, such modified layered silicates can be delaminated up to elementary nanosized layers during overlaying with polymeric matrix.

Physical and mechanical properties are affected by the next factors: size and shape of filler particles, filler particles orientation and

their relative positions in the matrix, filling ratio, filler-binder interaction, polymeric matrix characteristics [13-15].

Numerous reports describing the preparation and characterization of polymer-based clay involved reinforcing a polymer with modified clay (ceramic type filler) verify a considerable improving the degree of homogeneity and adhesion between the organic (polymer) and inorganic (clay) components when reactive organoclay applied [16; 17]. It results in greatly enhanced properties of the hybrid materials, i.e. mechanical [18-20], thermal [21; 22] and barrier [17; 23; 24].

Also, consideration must be given to extrusion and pressure casting technical parameters influence over physical and mechanical properties when products obtained.

Experimental

Polyamide-6 (PA-6) and montmorillonite modified with polyionene are used to obtain nanocomposites. Montmorillonite modification includes the next steps elutriation of montmorillonite fraction; preparing of 1 % bentonite water dispersion; desilting of dispersion during 1 hour followed by separation of montmorillonite dispersion; separation and drying of precipitate; preparing of 1 % montmorillonite suspension, desilting during 1 hour and decantation of high disperse fraction; immixture with water at ratio 1 : 100, disilting during 1 hour and decantation of high disperse fraction. Elutriation is repeated 3-4 time.

Moisture removal from polyamide-6 is carried out by drying at 60 °C during 4 hours. Then modified montmorillonite is mechanically inmixed with polymer. Obtained mixture is loaded into bunker of screw-disk extruder ED-2.2 (screw rotary speed is 50–250 revolutions per minute, screw diameter is 45 mm, length-diameter ratio is 8, disk diameter is 120 mm, disk backlash is from 3 to 88 mm).

Composite extrusion is carried out at definite extruder screw rotary speeds and modified montmorillonite-polymer ratio.

Extrudate is disintegrated in the rotor breaking machine ShR-100. Obtained granulate is dried at 60 °C during 2 hours.

Standard samples to study are obtained by pressure casting on injection-molding machine «Kuasy 25-32» in optimal temperature range for each of polymers.

Research is conducted in the next directions:

1. to study thermomechanical effect influence during screw-disk extrusion over layered montmorillonite structure delamination extent;

2. to determined the possible range for polymeric matrix propertied characteristics resulted from organomodified montmorillonite introduction;

3. to develop the mathematic model for screw-disk extrusion that describes viscoelastic polymers properties and allows determining the operating parameters affected thermomechanical transformations of layered silicates in polymeric matrix and to extrapolate processing regimes of intended properties products obtained in laboratory conditions up to equipment with determined output.

Results and discussion

Rheological equations of non-Newtonian fluid state applied in commonly used mathematic models of screw-disk extrusion processes are not fit to behavior of polymer melt by delaminated layered silicates. Consequently, White-Metzner characteristic equation of highly elastic fluid should be applied because of it describes polymer composites rebound properties, generation of direct stresses Bisenberg effect. Constructive peculiarities and extrusion carrying conditions allow applying the following simplification: material movement in the extruder disk space is plain, forcible, constant flow of continual viscoelastic fluid between two disks in isothermal conditions.

Sliding component is calculated by [25]:

$$\tau_{12} = K \cdot (W \cdot r / B)^{1+1/n} \quad (1)$$

where K is a consistency index,
 B is a distance between disk and case;
 W is disk rotary speed;
 r is disk radius.

Direct stresses are determined according to [14]:

$$\tau_{22} = (K^2 / G \cdot n) \cdot (1 / (1 + n)) \cdot (W \cdot R / B)^{2n} \quad (2)$$

where R is disk radius.

Volume flow rate is calculated as:

$$Q = \left(\frac{\pi \cdot r^3}{64} \right) \cdot \left(\frac{n}{3n-1} \right) \cdot \left(\frac{W \cdot r}{B} \right)^2 \cdot \left(\frac{H}{4G \cdot n} \right)^{1/n} \cdot \left(\frac{2r}{L} \right)^{1/n} \quad (3)$$

Where L is screw length.

Hold-up time of polymer melt in the space of intensive thermomechanical influence is determined by:

$$t = \frac{2\pi \cdot B}{Q} \cdot \int_r^R r dr = \frac{\pi \cdot B \cdot R^2}{Q} \cdot \left(1 + \frac{r^2}{R^2} \right) \quad (4)$$

Mathematic model of screw-disk extrusion allows determining the following flow parameters polymer composite melt in the disk unit: deformation rate distribution in gap disk section, composite hold-up time in intensive thermomechanical influence area, motion trajectory of composite flow, sliding and normal component of stress deformation tensor. These parameters allow for calculation power characteristics of delamination processes.

Mathematic model is applied for calculation of optimal technological regimes and initial data for design of engineering equipment based on unobservable process parameters values which are invariant to device geometrical dimension, i.e. deformation rate, shear deformation and composite hold-up time in extruder disk space.

Operational conditions optimization during screw-disk extrusion is carried out by combination of mathematical and physical methods of model analysis. To perform the physical model analysis of material behavior during processing influence of operating parameters on material properties and characteristics of products manufactured with it are studied in laboratory conditions. The operational parameters for obtaining of superior-processing products are determined based on these data.

During process physical modeling influence of operating parameters of processing on inorganic nanophase during extrusion process is studied on screw-disk extruder ED-2.2.

Influence efficiency is estimated by change in rheological properties of material melt when various thermospeed rates used for change in viscosity indicates material transformation.

Melt deformation of polymer matrix and organomodified layered silicates are known to be accompanied with transformations correlated by layered structure destruction and nanophase formation in polymer matrix. It results in significant changing in obtained composite physical-and-mechanical properties as compared to initial polymer matrix. It causes of applying of delamination factor as crucial criteria for extrusion process quality.

Influence of total shear deformation and nanocomposite hold-up time under intensive

thermomechanical treatment on polymer inorganic nanocomposites is studied when processing temperature or shear velocity varied in a wide range. The relationships between tensile strength or impact strength of organomodified montmorillonite composites PA-6+2% and shear deformation in the disk space and extrusion temperature are given on Fig. 1 and Fig. 2.

The relationships tensile strength and impact strength of unmodified montmorillonite composites PA-6+2% vs. shear deformation in the disk space and extrusion temperature are given on Fig. 3 and Fig. 4.

Characteristics of studied composites based on PA-6 after processing with screw-disk extrusion are given in the Table 1 when optimal operational parameters applied.

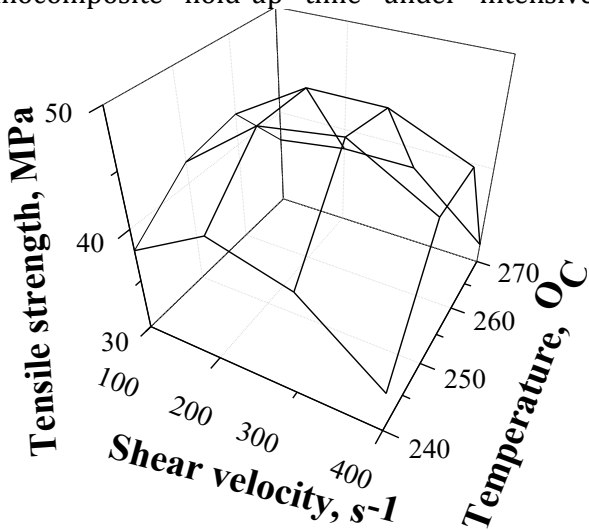


Fig. 1. 3D plot of tensile strength vs. extrusion temperature and shear velocity of composite PA-6+2 % organomodified montmorillonite

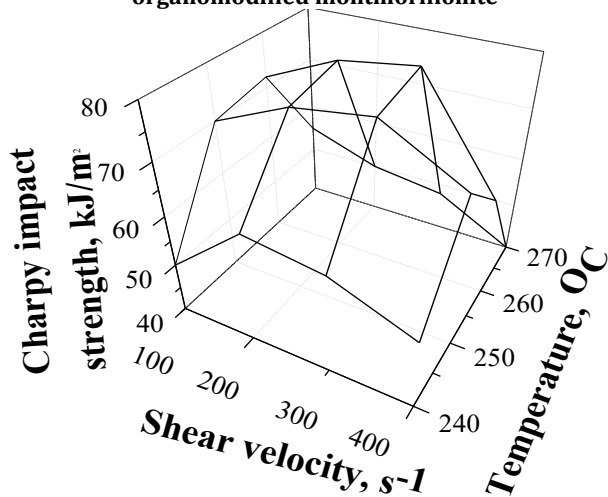


Fig. 2. 3D plot of impact strength vs. extrusion temperature and shear velocity of composite PA-6+2 % organomodified montmorillonite

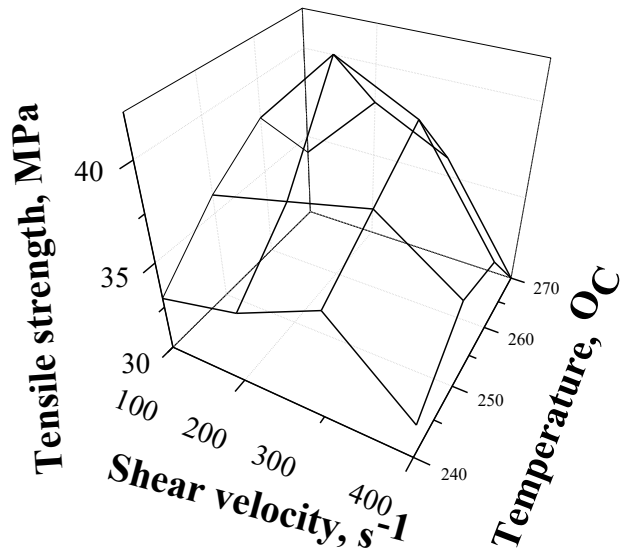


Fig. 3. 3D plot of tensile strength vs. extrusion temperature and shear velocity of composite PA-6+2 % unmodified montmorillonite

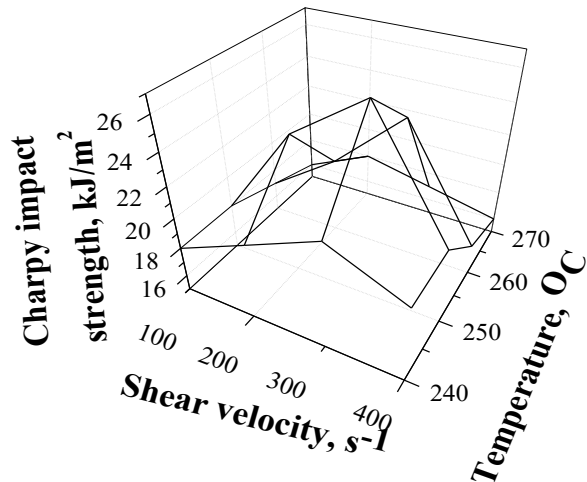


Fig. 4. 3D plot of impact strength vs. extrusion temperature and shear velocity of composite PA-6+2 % unmodified montmorillonite

Table 1

Characteristic	Physical-mechanical properties of polyamide-6					
	Montmorillonite content, % wt.			Content of montmorillonite modified by polyionene, % wt.		
	0	1	2	5	1	2
Tensile strength, MPa	31	40	37	33	46	47
Charpy impact strength (with notch), kJ/m ²	32	28	24	21	68	76
Extension coefficient, %	29	22	18	10	35	35

Initial polyamide physicomachanical properties are essentially independent of extrusion operational parameters. Variation range of physicomachanical parameters is 10–15 %. Evidently, external behavior of tensile strength is resulted from change in polymer molecular mass in flexing area. Physicomachanical properties variation of polyamide filled with unmodified montmorillonite is typical for trivial filled polymer system, i.e. impact strength drops when tensile strength increased.

Well-defined dependence between structure and tensiles is observed. When 1 % of initial montmorillonite added into polyamide, tensile strength is observed to be increased by about 30 % of magnitude, impact strength and linear strain being decreased by 11 % and 23 % of magnitude, respectively. As content of the initial montmorillonite in polyamide increased to 2 %, tensile strength is observed to be increased by 19 %, decreasing of impact strength and linear strain is 24 and 36 %.

When montmorillonite content in montmorillonite occurred to be 5 %, tensile strength increasing is stated to be much less apparent, it being 6 %. Impact strength and extension coefficient are registered to reveal substantial decrease down to 32 % and 62 % of magnitude, respectively. So, non-expediency of montmorillonite concentration in composites polyamide-6 – montmorillonite higher than 2 % is becoming apparent. Obviously, change in processing regime (variation of sliding tensions in extrusion area) does not result in destruction of crystal structure of unmodified montmorillonite.

Physicomachanical properties of composite based on polyamide-6 are taken to the next level by applying modified montmorillonite. This is resulted from montmorillonite structure destruction and formation of nano-sized discrete phase in polymer matrix, it being accompanied by

a 2–3 order of magnitude increase of montmorillonite-polymer-matrix interaction surface and formation of interfacial transition layers which determine strength characteristics of the whole polymer composition. Because of great of magnitude surface energy of individual montmorillonite plates' interaction between montmorillonite nanoparticles (lamenes) and polymer matrix chain is reinforced, it being resulted in formation of qualitatively new composition structure and accompanied with by increasing of strength characteristics.

It should be noted that viscosity of the samples obtained at processing temperatures 240 – 250 °C is higher of magnitude as compared to initial raw ones.

When temperature increased above 260 °C, viscosity is observed to be decreased down to values below initial PA-6 viscosity.

Strength is varied only slightly when temperature increased to 260–270 °C. Nevertheless, samples obtained at 260 °C exhibit a little more large magnitudes.

Investigation of properties of composites processed at shear velocities 100–400 s⁻¹ determined with extruder construction possibility and temperature processing 250 °C revealed the following peculiarities. In the melts of the composites filled with 2 % of organomodified montmorillonite at the shear velocities 100 and 200 s⁻¹ effective viscosity is shown to increase to 32 and 25 % as compared to initial polyamide viscosity. The maximal strength is registered for composites processed at the shear velocity 200 s⁻¹.

When shear velocity increased to 300 s⁻¹, melt viscosity is decreased to about 40 % of magnitude, relaxation spectrum curve shift to lower relaxation time being observed. This phenomenon was not registered earlier. Change in delamination rates is revealed to result in some degradation of physicomachanical properties.

Samples processed at shear velocity 400 s⁻¹ exhibit effective viscosity sharp decrease of half scale. Simultaneously, tensile strength sharp decrease is revealed. These data confirm the destruction processes proceeding.

When short-term processing regime influence on rheological properties of composites based on polyamide studied at 260 °C, monotone decrease of melt viscosity is noted as shear rate increased in extruder disk area. Strength characteristics are observed to be significantly worse. Consequently, temperature increasing over than 250 °C is

founded to adversely affect material properties and accelerate destructive processes.

Investigation results raise the wide possibility for regulation of rheological and physicomechanical properties of composites based on PA-6 and montmorillonite due to change in parameters of thermomechanical influence on delamination processes of montmorillonite layered structure.

Both substantial improvement of products based on PA-6 and 2% organomodified montmorillonite at the processing temperature of 250 °C and shear rates 200–300 s⁻¹ and properties deterioration under a different set of conditions are observed. These are resulted from change in molecular mass and PA-6 distribution on molecular mass during extrusion with organomodified montmorillonite. These changes have an effect on rheological properties of material melt.

So, when even 1% of modified montmorillonite introduced into polyamide, tensile strength is appeared to increase by 50% of magnitude as compared to initial montmorillonite. Impact strength and extension coefficient are increased by 114% and 22%, respectively. When modified montmorillonite concentration in polyamide increased from 1% to 2%, tensile strength and extension coefficient are registered to change little. By contrast, impact strength is raised by 140% and occurs to be 76 kJ/m² as compared to 32 kJ/m² for initial polyamide. Composition enrichment with modified montmorillonite up to 5% results in extension coefficient decreasing by 40%, tensile strength and impact strength being increased only by 12% and 61%. So, concentration of 2 wt.% of montmorillonite modified with polyionene is optimal for composition based on polyionene-6.

The similar tendency of improving of physical and mechanical properties is observed for compositions based on polystyrol, but it being less detectable. For example, at the concentrations of modified montmorillonite of 1 and 2% in the polystyrol tensile strength is increased by 21% and 28%. Impact strength is grown by 12% and 27%, and extension coefficient being increased by 192% and 212%. It should be noted that stretching of the samples of the composition polystyrol – 2% modified with polyionene montmorillonite is accompanied by even neck-down which confirms the

substantial changes in structure. Increasing of modified montmorillonite concentration in polystyrol to 5% is accompanied by decreasing of impact strength by 23% and extension coefficient by 9%. The polystyrol composite tensile strength is almost unaffected.

Obtained data confirm adequate processing parameters resulting in substantial increasing of mechanical properties of products based on polymer nanocomposites.

These effects could be explained by two main reasons. First, in the disk gap shear velocities of 10² – 10⁴ s⁻¹ could be realized during various time intervals. It results in nanoaggregates fission into separate elements with free radicals those allows to produce new bonds. Second, these elementary nanoparticles are equidistributed in throughout polymer matrix developing more branching contact surface between nanoparticles and polymer melt.

Results of physicomechanical trials of composites and structural investigations indicate nanostructure formation in the polymer composites.

Montmorillonite layered structure delamination speed rate criteria values and physicomechanical properties have been analyzed. The data obtained during tests of samples of composites processed with various operational regimes were compared. Estimation criterion can be proposed for physicochemical transformations occurred in composite during change in thermomechanical influence. The optimal regime for polymer nanocomposites processing with applied extruder for obtaining products with improved physicomechanical characteristics is determined as processing temperature 250–260 °C, disk speed rate 100–110 rev. per min., that provide with shear speed 200–300 s⁻¹ and hold-up time in disk area 8–9 s, total shear deformation 7500–8500.

Based on mathematic model of screw-disk extrusion input data to project apparatus with capacity of 500 kg/h and operational parameters of processing of nanocomposites based on polyamide and organomodified montmorillonites in products with desired properties were calculated.

To determine optimal operational parameters of pressure casting composites mechanical and thermophysical properties vs. casting temperature characteristics were studied. These results are given in the [Table 2](#).

Table 2
Characteristics of nanocomposites based on polyamide-6 as a function of pressure casting temperature (concentration of montmorillonite modified with polyionene 2 %)

Characteristic	Dosage area temperature, °C				
	240	250	260	270	280
Impact strength, kJ/m ²	73	74	76	74	73
Tensile strength, MPa	45	45	47	46	43
Extension coefficient, %	32	33	35	35	33

Maximal value of impact strength of nanocomposite based on polyamide-6 is observed at 260 °C. So, this particular temperature promotes to formation of the most permanent composite structure. Impact strength is observed to increase from 73 kJ/m² at 240 °C to 76 kJ/m² at 260 °C and then to decrease to 73 kJ/m² at 280 °C. Tensile strength occur to increase from 45 MPa at 240 °C to 47 MPa at 260 °C, and then it being decreased to 43 MPa at 280 °C.

Extension coefficient is slowly increased from 32 % at 240 °C to 35 % at 260 °C, and it being decreased to 33 % at 280 °C. So, processing temperature slightly affects extension coefficient. Only in some instances it occur to be substantial increased when temperature rises from 240 °C to 270 °C, it decreases to 33 % at 280 °C.

Consequently, composite optimal processing temperature is determined to be 260°C. Material obtained at that temperature have the best properties as compared to composites obtained at other temperatures, i.e. high tensile strain at break is 34%; maximal tensile strength is 47 MPa and maximal impact strength is 76 kJ/m².

Regularities of properties of composites based on polyamide-6 vs. pressure hold-up time are given in the [Table 3](#).

Table 3
Regularities of properties of composites based on polyamide-6 vs. pressure hold-up time

Properties	Pressure hold-up time, s			
	5	10	20	40
Impact strength, kJ/m ²	73	74	76	76
Tensile strength, MPa	45	45	46	46
Extension coefficient, %	35	34	34	34

According to data given in the [Table 3](#), pressure hold-up time is confirmed to affect on physicomechanical properties of the composites in a different ways. Composite impact strength is observed to increase from 73 kJ/m² to 76 kJ/m² when pressure hold-up time increased from 5 s to 40 s. It results from more overdense and ordered structure.

Tensile strength of nanocomposites based on polyamide-6 is riched the maximal level of

47 MPa at pressure hold-up time 20 s. At hold-up time 5 s tensile strength is 45 MPa, at 10 and 40 s it being 45 and 46 MPa. So, it is stated that the more hold-up time, the sturdier the composite. Nevertheless, at high hold-up time (40 s) the strength appears to decrease.

The composite tensile strain at break is almost independent from hold-up time, and only when hold-up time increased from 5 s to 10 s, tensile strain occur to decrease from 35.0 % to 34.0 %.

So, hold-up time of 20 s is selected. In these conditions the composite with high mechanical properties is produced.

Extrusion parameters for nanocomposite production were optimized by the following parameters, i.e. screw rotary speed, disk backlash value, temperature in the dosage area. For polyamide-6 such parameters are stated to be optimal: screw rotary speed 150 rpm, disk backlash value 4 mm, temperature in the dosage area 260 °C.

Heat stability of the obtained nanocomposites has been analyzed as compared to initial polyamide-6. Thermogravimetric curves of composites with optimal concentration of montmorillonite (2 %) are given on [Fig. 5](#). Mass loss curves analysis of polyamide composites is indicative of change in nature of destruction process. Heat stability is changed unsubstancially, but temperature of half mass loss occur to increase to 120 °C for polyamide with modified montmorillonite. Heat stability of the composite with unmodified montmorillonite appeared to increase by 20 °C as compared to initial polyamide. Moreover, two processes are observed to proceed during the destruction of the composite with modified montmorillonite. In temperature range 380–550 °C mass decreases slowly, and after 550 °C mass reduction occur to be an avalance-type with higher rate as compared to initial polyamide.

Increase of thermostability of examined polyamide nanocomposites results from changes in barrier properties. Montmorillonite nanosized particles with a thickness of 1.5 nm and both length and width of a few μm inhibit the oxygen molecules diffusion and as a consequence of catalytical polymer destruction.

Wide-angle X-ray scattering (WAXS) profiles of the composites obtained during extrusion as compared to WAXS profiles of the mechanical mixtures of polymer powders with 2 % of modified montmorillonite are given on the [Fig. 6](#) and [Fig. 7](#).

In partially-crystalline polyamide-6 substantial structural changes were observed. In the low-angle range for nanocomposite based on PA-6 typical of modified montmorillonite peak was not observed (Fig. 6), it being registered on WAXS profile of mechanical mixture of PA-6 and 2 % modified montmorillonite. So, this gives evidence of destruction of modified montmorillonite layered structure and nanosized inorganic phase in PA-6.

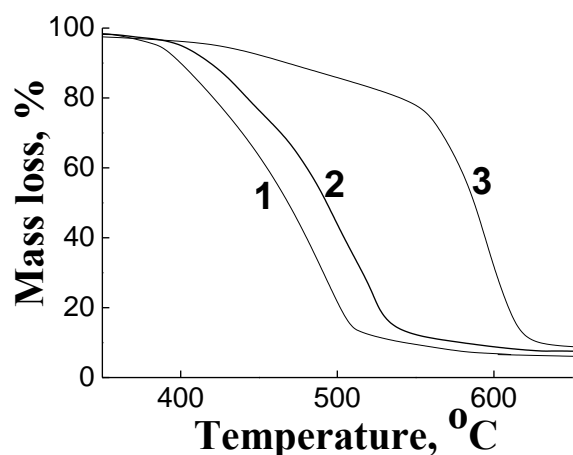


Fig. 5. Mass loss curves of the polyamide-6 (1), the composite polyamide-6 - 2 wt.% of unmodified polyamide (2) and the composite polyamide-6 - 2 wt.% of modified polyamide (3)

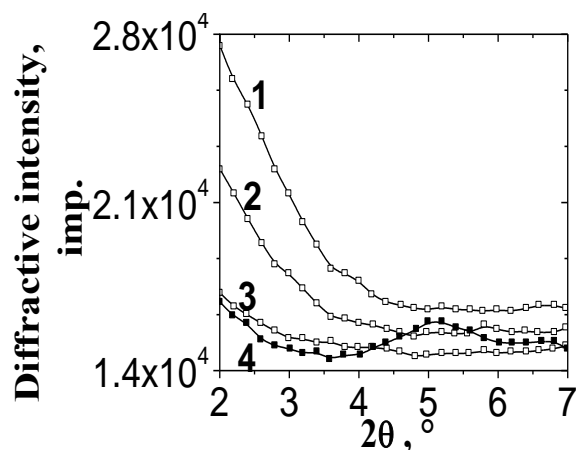


Fig. 6. WAXS profiles of initial PA-6 (3), nanocomposite with 1 (2) and 2 wt.% of modified montmorillonite (1) as compared to mechanical mixture with 2 wt.% of modified montmorillonite (4)

X-Ray diffraction patterns of initial PA-6 and compositions based on PA-6 and 1, 2, 5% of modified montmorillonite are given on the Fig. 7.

Two stable crystalline modification are possible for PA-6. They are identified as α - and γ -phases. On X-Ray diffraction pattern of α -phase of PA-6 (Fig. 7) two intensive maxima were observed at $2\theta \approx 200$ ($d=0.44$ nm) and $2\theta \approx 250$ ($d=0.37$ nm). On the γ -phase X-Ray diffraction

pattern occur to be only one peak at $2\theta=210$ ($d=0.41$ nm) (Fig. 7).

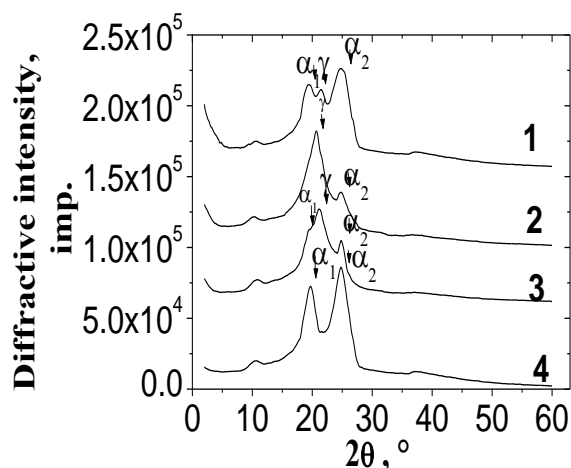


Fig. 7. X-Ray diffraction patterns of PA-6 (4); compositions PA-6 - 1 % (3), PA-6 - 2 % (2), and PA-6 - 5 % (1) of modified montmorillonite

Typical peculiarities of α -phase are hydrogen bonds formation between molecules «oriented» in various directions and shift of associates on 3/14 of identity period. Wherein, conformation of the molecules becomes entirely straightened. For γ -phase hydrogen bonds formation between parallel chains «oriented» in the same direction is distinctive. It results in slightly contracted form of macromolecules and as a consequence to decrease of identity parameters as compared to α -phase.

α -Modification of crystalline lattice is indicative for initial PA-6. For nanocomposites based on PA-6 and modified montmorillonite new γ -phase is observed to be formed. When 1 % and 2 % of modified montmorillonite added in PA-6, diffractive intensity of α -phase peaks is appeared to decrease in combination with registration of a new peak in the range of the angles $2\theta = 21^\circ$ which is typical for PA-6 crystalline γ -phase. As concentration of modified montmorillonite increased to 5 %, crystalline γ -phase content in the composite occurs to be negligible.

Obviously, delamination of crystalline structure of modified montmorillonite is accompanied with change in composites crystallization regimes and new crystalline γ -phase formation by heterogenetic mechanism of nucleation.

Occurrence of crystalline γ -phase in the studied nanocomposites is confirmed by differential scanning calorimetric data. DSC-curves of initial PA-6 and studied nanocomposites are given at the Fig. 8.

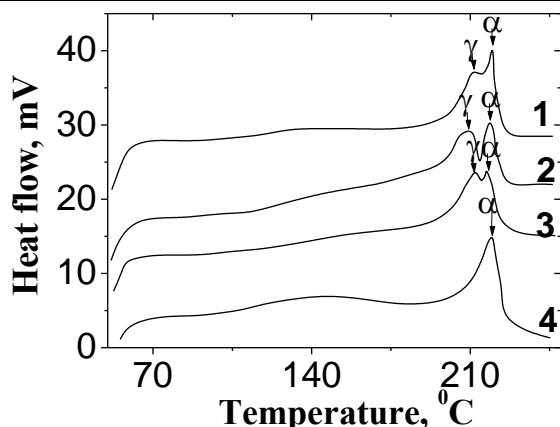


Fig. 8. DSC-curves of initial PA-6 (4), nanocomposites PA-6 - 1% (3), PA-6 - 2% (2), PA-6 - 5% (1) of modified montmorillonite

For initial polyamide only one melting peak corresponded to melting of crystalline α -phase of PA-6 is registered at 220 °C. For nanocomposites occurrence of two melting peak is typical. The high-temperature peak at 220 °C corresponds to melting of crystalline α -form, the low-temperature one at 210–215 °C being resulted from melting of PA-6 crystalline γ -form. Maximal intensity of melting peak γ -phase is observed for nanocomposite with 2 % of modified montmorillonite, it being absolutely correlated with WAXS data. Inasmuch as occurrence of both α - and γ -phases is observed, averaged value of 190 J/g is chosen as melting enthalpy.

Crystallinity degree of the samples vs. modified montmorillonite content in the composites based on PA-6 is given on the Fig. 9. Crystallinity degree of the nanocomposites is higher as compared to initial PA-6, i.e. particles of modified montmorillonite act as nucleation heterogenetic agents.

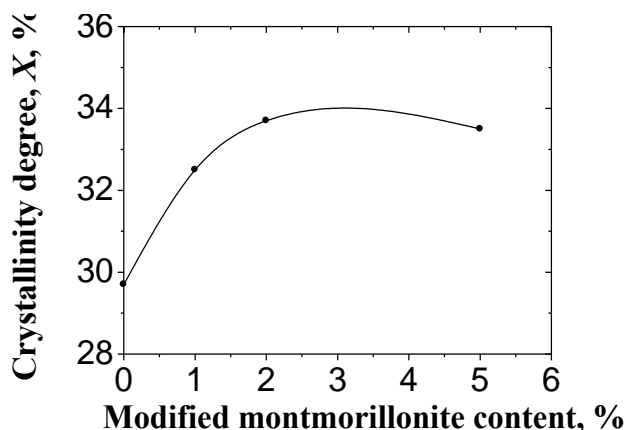


Fig. 9. Crystallinity degree of the samples vs. modified montmorillonite content in the composites based on PA-6

Conclusions

Nanocomposites based on polyamide-6 and montmorillonite modified with polyionene have been obtained with screw-disk extrusion. Mathematic model described viscoelastic polymers properties was developed. It was shown that the operating parameters are determined as a consequence of thermomechanical transformations of layered silicates in polymeric matrix and extrapolate processing regimes of intended properties products obtained in laboratory conditions up to high-scale equipment.

Distinction-in-kind of morphology and thermal behavior of PA-6, composites based on modified montmorillonite was shown by WAXS, XRD, DTA and DSC data. Destruction of modified montmorillonite layered structure and nanosized inorganic phase in polyamide-6 was confirmed.

These processes are explained by formation of crystalline γ -phase of polyamide in the presence of 1–2 % of modified polyamide in contrast with initial polyamide-6 and mechanical mixtures of polyamide and montmorillonite. Optimal concentrations of modified montmorillonite in the composites were stated to be 1–2 %. It was established by increasing crystallinity degree, that being explained by acting of modified montmorillonite particles as nucleation heterogenetic agents.

The technology of nanocomposites based on polyamide-6 and organo-montmorillonite was developed. The technological parameters of extrusion and injection molding, and their influence on the formation of nanoscale inorganic phase of the polyamide were investigated.

Acknowledgments

This work was supported by Ministry of Education and Science of Ukraine (grant number 0116U001489).

Bibliography

- [1] Utracki L. A. Clay-containing polymeric nanocomposites/ L. A. Utracki. - Shawbury, Shrewsbury, Shropshire: Smithers Rapra Publishing, SY4 4NR, UK. - 2004. - 785 p.
- [2] High performance extrusion blown starch/polyvinyl alcohol/clay nanocomposite films / W. Wang, H. Zhang, R. Jia [et al.] // Food Hydrocolloids, - 2018. - Vol. 79. - P. 534–543.
- [3] Polyaniline/clay nanocomposites. A comparative approach on the doping acid and the clay spacing technique / C. M. De León-Almazan, I. A. Estrada-Moreno, U. Páramo-García, J. L. Rivera-Armenta // Synthetic Metals. - 2018. - Vol. 236. - P. 61–67.
- [4] Chen Ch. Epoxy layered-silicate nanocomposites /

- Ch. Chen, M. Khobaib, D. Curliss // *Progress in Organic Coatings*. – 2003. – Vol. 47. – P. 376–383.
- [5] Effect of compatibilizer on morphology, rheology and properties of SEBS/clay nanocomposites / X. Li, J. Yang, X. Zhou [et al.] // *Polymer Testing*. – 2018. – Vol. 67. – P. 435–440.
- [6] Zare Y. Multistep modeling of Young's modulus in polymer/clay nanocomposites assuming the intercalation/exfoliation of clay layers and the interphase between polymer matrix and nanoparticles / Y. Zare, K. Y. Rhee // *Composites Part A: Appl. Sci. and Manufacturing*. – 2017. – Vol. 102. – P. 137–144.
- [7] Zhong Y. Synthesis and rheological properties of polystyrene/layered silicate nanocomposites / Y. Zhong, Z. Zhu, S. Wang // *Polymer*. – 2005. – Vol. 46. – P. 3006–3013.
- [8] Semi-automated quantification of the microstructure of PLA/clay nanocomposites to improve the prediction of the elastic modulus / M. Iturrondobeitia, J. Ibarretxe, A. Okariz [et al.] // *Polymer Testing*. – 2018. – Vol. 66. – P. 280–291.
- [9] A technical review on epoxy-clay nanocomposites: Structure, properties, and their applications in fiber reinforced composites / O. Zabihi, M. Ahmadi, S. Nikafshar [et al.] // *Composites Part B: Engineering*, 2018. – Vol. 135. – P. 1–24.
- [10] Kotal M. Polymer nanocomposites from modified clays: Recent advances and challenges / M. Kotal, A. K. Bhowmick // *Progress in Polymer Sci.* – 2015. – Vol. 51. – P. 127–187.
- [11] Resonance energy transfer between dye molecules in hybrid films of a layered silicate, including the effect of dye concentration thereon / S. Belušáková, R. Sola-Llano, I. Lopez Arbeloa [et al.] // *Appl. Clay Sci.* – 2018. – Vol. 155. – P. 57–64.
- [12] Volzone C. High Temperature Structural Modifications of Intercalated Montmorillonite Clay Mineral with OH-Al Polymers / C. Volzone, L. B. Garrido // *Procedia Materials Sci.* – 2012. – Vol. 1. – P. 164–171.
- [13] Influence of processing conditions on the optical and crystallographic properties of injection molded polyamide-6 and polyamide-6/montmorillonite nanocomposites / A. Yebra-Rodriguez, P. Alvarez-Lloret, C. A. Cardell, B. Rodriguez-Navarro // *Appl. Clay Sci.* – 2011. – Vol. 51. – P. 414–418.
- [14] Faghihi K. Preparation and characterization of new polyamide/montmorillonite nanocomposites containing azo moiety in the main chain / K. Faghihi, M. Taher, M. Hajibeygi // *Arab. J. Chem.* – 2016. – Vol. 9. – P. S1496–S1502.
- [15] Influence of clay mineral structure and polyamide polarity on the structural and morphological properties of clay polypropylene/polyamide nanocomposites / Q. Beuguel, J. Ville, J. Crepin-Leblond [et al.] // *Appl. Clay Sci.* – 2017. – Vol. 135. – P. 253–259.
- [16] Zulfiqar S. Synthesis and Characterization of Aromatic-Aliphatic Polyamide Nanocomposite Films Incorporating a Thermally Stable Organoclay / S. Zulfiqar, M. I. Sarwar // *Nanoscale Res. Lett.* – 2009. – Vol. 4. – P. 391–399.
- [17] Barrier properties of polyamide 12/montmorillonite nanocomposites: Effect of clay structure and mixing conditions / N. Follain, B. Alexandre, C. Chappay [et al.] // *Composites Sci. and Technol.* – 2016. – Vol. 136. – P. 18–28.
- [18] Wang Z. Hybrid organic-inorganic nanocomposites: exfoliation of magadiite nanolayers in an elastomeric epoxy polymer / Z. Wang, T. J. Pinnavaia // *Chem. Mater.* – 1998. – Vol. 10. – P. 1820 – 1826.
- [19] Burnside S. D. Synthesis and properties of new poly (dimethylsiloxane) nanocomposites / S. D. Burnside, E. P. Giannelis // *Chem. Mater.* – 1995. – Vol. 7. – P. 1597–1600.
- [20] Alexandre M. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials / M. Alexandre, P. Dubois // *Mater. Sci. Eng.* – 2000. – Vol. 28. – P. 1–63.
- [21] Thermal and mechanical properties of SEBS-g-MA based inorganic composite materials / S. Zulfiqar, Z. Ahmad, M. Ishaq [et al.] // *J. Mater. Sci.* – 2007. – Vol. 42. – P. 93–100.
- [22] New nanocomposite materials based on plasticized poly (L-lactide) and organo-modified montmorillonites: thermal and morphological study / M. A. Paul, M. Alexandre, P. Degée [et al.] // *Polymer*. – 2003. – Vol. 44. – P. 443–450.
- [23] Messersmith P. B. Synthesis and characterization of layered silicate-epoxy nanocomposites / P. B. Messersmith, E. P. Giannelis // *Chem. Mater.* – 1994. – Vol. 6. – P. 1719–1725.
- [24] Rao Y. Q. Barrier properties and structure of liquid crystalline epoxy and its nanocomposites / Y. Q. Rao, A. Liu, K. O'Connell // *Polymer*. – 2018. – Vol. 142. – P. 109–118.
- [25] Uthirakumar P. Exfoliated high-impact polystyrene/MMT nanocomposites prepared using anchored cationic radical initiator-MMT hybrid / P. Uthirakumar, Y. Hahn, K. Nahm // *European Polymer J.* – 2005. – Vol. 35. – P. 987–995.

References

- [1] Utracki, L. A. (2004). *Clay-containing polymeric nanocomposites*. Smithers Rapra Publishing, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK.
- [2] Wang, W., Zhang, H., Jia, R., Dai Ya., Dong, H., Hou, H., Guo, Q. (2018). High performance extrusion blown starch/polyvinyl alcohol/clay nanocomposite films *Food Hydrocolloids*, 79, 534–543. <https://doi.org/10.1016/j.foodhyd.2017.12.013>
- [3] De León-Almazan, C. M., Estrada-Moreno, I. A., Páramo-García, U., Rivera-Armenta, J. L. (2018). Polyaniline/clay nanocomposites. A comparative approach on the doping acid and the clay spacing technique. *Synthetic Metals*, 236, 61–67. <https://doi.org/10.1016/j.synthmet.2018.01.006>
- [4] Chen, Ch., Khobaib, M., Curliss, D. (2003). Epoxy layered-silicate nanocomposites, *Progress in Organic Coatings*, 47, 376–383. [https://doi.org/10.1016/S0300-9440\(03\)00130-9](https://doi.org/10.1016/S0300-9440(03)00130-9)
- [5] Li, X., Yang, J., Zhou, X., Wei, Q., Li, J., Biwei, Q., Wunderlich, K., Wang, X. (2018). Effect of compatibilizer on morphology, rheology and properties of SEBS/clay nanocomposites. *Polymer Testing*, 67, 435–440 <https://doi.org/10.1016/j.polymertesting.2018.03.037>
- [6] Zare, Y., Rhee, K. Y. (2017). Multistep modeling of Young's modulus in polymer/clay nanocomposites assuming the intercalation/exfoliation of clay layers and the interphase between polymer matrix and nanoparticles. *Composites Part A: Appl. Sci. and Manufacturing*, 102, 137–144. <https://doi.org/10.1016/j.compositesa.2017.08.004>
- [7] Zhong, Y., Zhu, Z., Wang, S. (2005). Synthesis and rheological properties of polystyrene/layered silicate

- nanocomposites. *Polymer*, 46, 3006–3013. <https://doi.org/10.1016/j.polymer.2005.02.014>
- [8] Iturrondobeitia, M., Ibarretxe, J., Okariz, A., Jimbert, P., Fernandez-Martinez, R., Guraya, T. (2018). Semi-automated quantification of the microstructure of PLA/clay nanocomposites to improve the prediction of the elastic modulus. *Polymer Testing*, 66, 280–291. <https://doi.org/10.1016/j.polymertesting.2018.01.015>
- [9] Zabihi, O., Ahmadi, M., Nikafshar, S., Preyeswary, K. Ch., Naebe, M. (2018). A technical review on epoxy-clay nanocomposites: Structure, properties, and their applications in fiber reinforced composites. *Composites Part B: Engineering*, 135, 1–24. <https://doi.org/10.1016/j.compositesb.2017.09.066>
- [10] Kotal, M., Bhowmick, A. K. (2015). Polymer nanocomposites from modified clays: Recent advances and challenges. *Progress in Polymer Sci.*, 51, 127–187. <https://doi.org/10.1016/j.progpolymsci.2015.10.001>
- [11] Belušáková, S., Sola-Llano, R., Lopez Arbeloa, I., Martínez-Martínez, V., Bujdák, J. (2018). Resonance energy transfer between dye molecules in hybrid films of a layered silicate, including the effect of dye concentration thereon. *Appl. Clay Sci.*, 155, 57–64. <https://doi.org/10.1016/j.clay.2018.01.001>
- [12] Volzone, C., Garrido, L. B. (2012). High Temperature Structural Modifications of Intercalated Montmorillonite Clay Mineral with OH-Al Polymers. *Procedia Materials Sci.*, 1, 164–171. <https://doi.org/10.1016/j.mspro.2012.06.022>
- [13] Yebra-Rodríguez, A., Alvarez-Lloret, P., Cardell, C. A., Rodríguez-Navarro, B. (2011). Influence of processing conditions on the optical and crystallographic properties of injection molded polyamide-6 and polyamide-6/montmorillonite nanocomposites. *Appl. Clay Sci.*, 51, 414–418. <https://doi.org/10.1016/j.clay.2010.12.031>
- [14] Faghihi, K., Taher, M., Hajibeygi, M. (2016). Preparation and characterization of new polyamide / montmorillonite nanocomposites containing azo moiety in the main chain. *Arab. J. Chem.*, 9, S1496–S1502. <https://doi.org/10.1016/j.arabic.2012.03.010>
- [15] Beuguel, Q., Ville, J., Crepin-Leblond, J., Mederic, P., Aubry, T. (2017). Influence of clay mineral structure and polyamide polarity on the structural and morphological properties of clay polypropylene / polyamide nanocomposites. *Appl. Clay Sci.*, 135, 253–259. <https://doi.org/10.1016/j.clay.2016.09.034>
- [16] Zulfiqar, S., Sarwar, M. I. (2009). Synthesis and Characterization of Aromatic-Aliphatic Polyamide Nanocomposite Films Incorporating a Thermally Stable Organoclay. *Nanoscale Res. Lett.*, 4, 391–399. <https://doi.org/10.1007/s11671-009-9258-1>
- [17] Follain, N., Alexandre, B., Chappey, C., Colasse, L., Médéric, P., Marais, S. (2016). Barrier properties of polyamide 12/montmorillonite nanocomposites: Effect of clay structure and mixing conditions. *Composites Sci. and Technol.*, 136, 18–28. <https://doi.org/10.1016/j.compscitech.2016.09.023>
- [18] Wang, Z., Pinnavaia, T. J. (1998). Hybrid organic-inorganic nanocomposites: exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. *Chem. Mater.*, 10, 1820–1826. <https://doi.org/10.1021/cm970784o>
- [19] Burnside, S.D., Giannelis, E. P. (1995). Synthesis and properties of new poly (dimethylsiloxane) nanocomposites. *Chem. Mater.*, 7, 1597–1600. <https://doi.org/10.1021/cm00057a001>
- [20] Alexandre, M., Dubois, P. (2000). Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater. Sci. Eng.*, 28, 1–63. [https://doi.org/10.1016/S0927-796X\(00\)00012-7](https://doi.org/10.1016/S0927-796X(00)00012-7)
- [21] Zulfiqar, S., Ahmad, Z., Ishaq, M., Saeed, S., Sarwar, M. I. (2007). Thermal and mechanical properties of SEBS-g-MA based inorganic composite materials. *J. Mater. Sci.*, 42, 93–100. <https://doi.org/10.1007/s10853-006-1082-8>
- [22] Paul, M. A., Alexandre, M., Degée, P., Henrist, C., Rulmont, A., Dubois, P. (2003). New nanocomposite materials based on plasticized poly (L-lactide) and organo-modified montmorillonites: thermal and morphological study. *Polymer*, 44, 443–450. [https://doi.org/10.1016/S0032-3861\(02\)00778-4](https://doi.org/10.1016/S0032-3861(02)00778-4)
- [23] Messersmith, P. B., Giannelis, E. P. (1994). Synthesis and characterization of layered silicate-epoxy nanocomposites. *Chem. Mater.*, 6, 1719–1725. <http://dx.doi.org/10.1021/cm00046a026>
- [24] Rao, Y. Q., Liu, A., O'Connell, K. (2018). Barrier properties and structure of liquid crystalline epoxy and its nanocomposites. *Polymer*, 142, 109–118. <https://doi.org/10.1016/j.polymer.2018.03.027>
- [25] Uthirakumar, P., Hahn, Y., Nahm, K. (2005). Exfoliated high-impact polystyrene/MMT nanocomposites prepared using anchored cationic radical initiator–MMT hybrid. *European Polymer J.*, 35, 987–995. <https://doi.org/10.1016/j.eurpolymj.2005.01.017>