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The synthesis and investigation of structure – properties relationship in polyoxymethylene (POM) / montmorillonite (MMT) nanocomposites.

Otrzymywanie i badanie zależności struktura – właściwości nanokompozytów polioksymetylen (POM) / montmorylonit (MMT).

Keywords: polyoxymethylene, montmorillonite, nanocomposites, mechanical properties, thermo-oxidative degradation,

Słowa kluczowe: polioksymetylen, montmorylonit, nanokompozyty polimerowe, właściwości mechaniczne, degradacja termooksydacyjna,

Abstract

Polymer composites are important commercial materials with good mechanical and thermal properties dependent on interface interaction and aspect ratio of fillers. In recent years, polymer-nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. Nanocomposites are a new class of composites with small contents of nanoscale size fillers and excellent properties. In this work the results of kinetic analysis of thermooxidative degradation of POM/MMT nanocomposites modified with ammonium and imidazolium salts were presented. The influence of onium salt on kinetic parameters of degradation process was studied. Simulations of isothermal decompositions in oxidative atmosphere allowed to compare the rate of nanocomposites' decomposition in 265°C. The changes in thermal properties were explained in terms of limited oxygen diffusion into material. In case of the imidazolium salt the deterioration of thermal stability can be bounded with extensive production of volatile compounds via autocatalytic process produced by degradation products of organomodifier. The heat distortion temperature (HDT) and hardness of nanocomposites were found to increase as compared with neat POM, regardless of the type of onium salt applied for MMT modification. The WAXD diffractograms confirmed the intercalation and/or exfoliation of aluminum silicate layers dispersed in POM matrix. Nanocomposites of polyoxymethylene (POM) and organo-modified montmorillonite containing quaternary amines exhibited improved tensile strength and modulus as well as increased elongation at break. Both mechanical and thermal properties of nanocomposites varied depending on type of ammonium surfactant used for organomodification of MMT. The addition of imidazolium salt caused some detrimental effect on the mechanical properties of these systems.

Kompozyty polimerowe są ważnymi komercyjnymi materiałami o polepszonych właściwościach mechanicznych i cieplnych, zależnych od oddziaływań międzyfazowych oraz współczynnika kształtu napelnaczy. W ostatnich latach materiały kompozytowe na osnowie polimeru modyfikowane przez dodatek nanocząstek przyciągnęły zainteresowanie dużej liczby ośrodków badawczych z powodu ich hybrydowych właściwości i często obserwowanego efektu synergistycznego. Dodatkowo poprawę właściwości w nanokompozytach polimerowych uzyskuje

się przy małych zawartościach napełniaczy. Dla uzyskanych nanokompozytów POM/MMT obserwowano wzrost twardości i temperatury mięknienia w porównaniu do naturalnego POM. Gęstość nanokompozytów nie ulegała zasadniczej zmianie, jak w przypadku klasycznych kompozytów napełnianych np. włóknem szklanym. Wykonane badania metodą szerokokątowej dyfrakcji rentgenowskiej pokazały zanik regularnej struktury warstw glinokrzemianu w nanokompozytach POM z dodatkiem soli imidazoliowej wskazujący na dobrą homogenizację nanododatku. W materiale zawierającym handlowy gatunek OMMT (Nanofil N3010) doszło do interkalacji polimeru pomiędzy warstwy MMT i zachowanie uporządkowanej struktury warstw glinokrzemianu. Przeprowadzono pomiary wytrzymałości na rozciąganie nanokompozytów z dodatkiem soli amoniowej oraz imidazoliowej. Nanokompozyty polioksymetyleny (POM) i montmorylonitu (MMT) organofilizowanego za pomocą związków powierzchniowo czynnych typu amin czwartorzędowych, wykazują zwiększoną wytrzymałość mechaniczną. Zaobserwowano, iż dodatek soli imidazoliowej niekorzystnie wpływa na niektóre właściwości mechaniczne tych systemów. Poprawa właściwości termicznych nanokompozytów w warunkach utleniających związana była z efektem barierowym, polegającym na ograniczeniu dyfuzji tlenu do wnętrza próbki przez zdyspergowane warstwy MMT. Pogorszenie stabilności termicznej w przypadku zastosowania soli imidazoliowej może być związane z efektem autokatalitycznym wywołanym obecnością produktów degradacji organicznego modyfikatora montmorylonitu wywołującego acydolizę polioksymetyleny. Zaprezentowano wyniki analizy kinetycznej degradacji nanokompozytów POM/OMMT modyfikowanych dodatkiem soli amoniowej i imidazoliowej w atmosferze powietrza. Następnie z wykorzystaniem metody regresji nieliniowej poszukiwano teoretyczny model reakcji o najlepszym dopasowaniu do wyników eksperymentalnych w pierwszym etapie degradacji.

1. Introduction

Polymer nanocomposites are materials composed of two phases – organic polymer (continuous phase) and inorganic filler (dispersed phase), obtained mostly as a result of the modification of traditional polymeric materials by dispersing nanoparticulate fillers. As a polymer matrix both thermoplastic and thermosetting polymers can be used. Depending on the properties of polymer and layered silicates three types of nanocomposites can be obtained (Fig. 1):

- conventional nanocomposites,
- intercalated nanocomposites,
- exfoliated nanocomposites.

Unfortunately, the nanoscale dispersion of filler in polymer matrix is usually very difficult to achieve, due to the high surface activity of a nanofillers and its tendency for agglomeration. In order to improve the dispersion of nanofillers different treatments of filler are applied. Most popular method of surface modification of MMT is cation exchange reaction, where inorganic cations from interlayer space are displaced by organic ones, eg. ammonium or phosphonium cations.

There are four principal methods for producing polymer – layered silicate nanocomposites:

- intercalation of polymer or prepolymer from solution,
- in situ intercalative polymerization,
- melt intercalation,
- template synthesis (sol-gel technology).

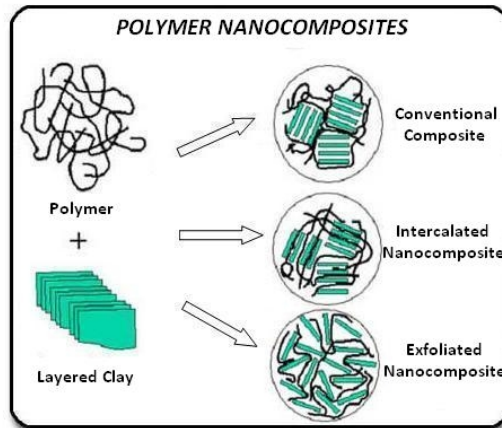


Figure 1. Schematically illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites [1,2].

2. Tasks

The aims of this study were:

- Melt mixing of polyoxymethylene (POM) with montmorillonite (MMT) using laboratory twin-screw extruder;
- Study on the effects of nanofillers on physical (hardness and density), mechanical (tensile strength) and thermal (the heat distortion temperature and thermal stability) properties of POM / MMT nanocomposites;
- Determination of the effect of nanofillers on the kinetic parameters and mechanism of thermal oxidative degradation of polyoxymethylene and its compositions;
- Investigation of the effect of ammonium and imidazolium salt on the properties of POM nanocomposites.

3. Experimental part

Preparation of the material and test samples:

- Preparation of POM / MMT nanocomposites by homogenization in melt using a twin screw extruder - HAAKE Reomex OS PTW 16 with screw diameter 16 mm and L/D ratio 25 (Fig. 2a). The processing parameters were: temperatures of the barrel zones - 175, 190, 190, 200 i 200°C, the screws speed – 100 rpm. The selected weight contents of nanofillers were used: 1, 3 and 5%.
- Obtaining injection bars of POM / MMT nanocomposites in the laboratory pneumatic injection molding machine - ZAMAK WT-12 ZMK/102/09 (Fig. 2b) at the temperatures of barrel and mould 200°C and 80°C respectively.

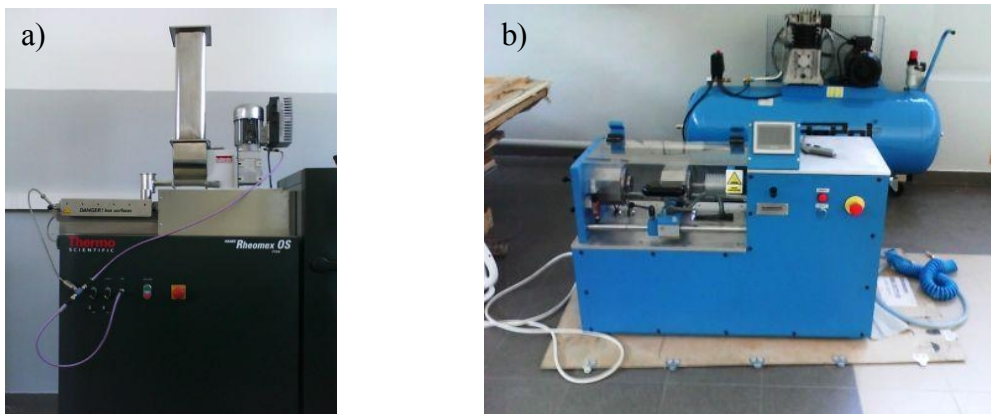


Figure 2. Illustration of: a) a twin screw extruder - HAAKE Reomex OS PTW 16; b) laboratory pneumatic injection molding machine - ZAMAK WT-12 ZMK/102/09.

Methods

X-ray diffraction experiments were carried out on a Philips X-Pert diffractometer, with graphite monochromator placed in the front of detector - $\lambda_{\text{Cu}} = 1.5418 \text{ \AA}$. Thermogravimetric analysis was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample weight - $\sim 5 \text{ mg}$, atmosphere - argon, open $\alpha\text{-Al}_2\text{O}_3$ pan. The heat distortion temperature was measured according to Vicat method.

4. Results

The Wide X-ray diffraction studies performed for the nanocomposites containing montmorillonite with ammonium compounds showed changes in the structure of layered silicates due to intercalation of polymer in the gallery spaces occurring in the extruder. The imidazolium containing nanofillers underwent complete exfoliation in POM since the diffraction peaks corresponding to the regular structure of MMT was not recorded on the WAXD spectra of POM/ImidS nanocomposites. (Figs. 3a, 3b).

An increased heat distortion temperature was observed for POM modified by both types of nanofiller - with ammonium and imidazolium salts (Table 1). For compositions of POM/Nanofil N3010 temperature increased for about 3.3°C with respect to the pure polyoxymethylene, and for the composition of POM/ImidS the increase was about 7.2°C . This results can be explained in terms of the improved mechanical properties at high temperatures due to strengthening of polymer by highly anisometric nanoparticles. The restriction of thermal movement of individual molecules and whole polymer segments due to interfacial interactions should also be considered as a probable phenomena operating in raised temperatures. Higher effect was observed in imidazolium-containing nanocomposites probably due to higher degree of MMT dispersion (exfoliation) and developed interfacial surface.

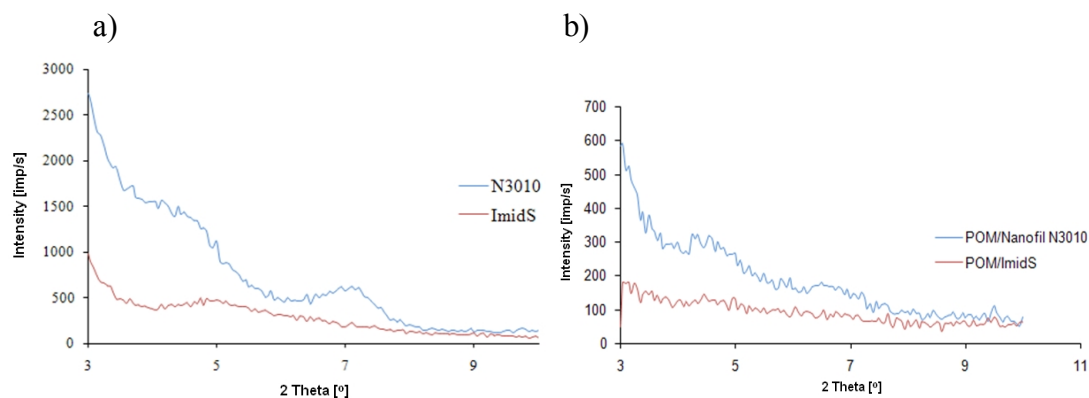


Figure 3. Illustration of: a) WAXD diffractogram Nanofil N3010 and montmorillonite modified with an imidazolium salt; b) WAXD diffraction pattern of nanocomposite POM/Imids and POM/Nanofil N3010.

Table 1 Test results of the heat distortion temperature measurement according to Vicat method.

Sample	Heat Distortion Temperature [°C]
POM	155,0
POM/Nanofil N3010 3%	158,3
POM/ImidS 3%	162,2

The results of hardness tests show that even a small addition nanofillers increases hardness of the material. The change of hardness depended on the type of salt used for the filler modification and the amount of filler. The best results were obtained for the filler modified by imidazolium salt. The addition of 3wt% of OMMT into the POM increased its hardness by approximately 10.44% (Table 2).

Table 2 Hardness of POM and POM/MMT nanocomposites.

Sample	Hardness [MPa]	Increase in hardness [%]
POM T200	97,7	-
POM/Nanofil N3010 1%	98,1	0,41
POM/Nanofil N3010 3%	98,5	0,82
POM/Nanofil N3010 5%	102,9	5,32
POM/ImidS 3%	107,9	10,44

The addition Nanofil did not cause significant changes in the density of the material, while the density of the nanocomposite modified with imidazolium salt increased slightly. This effect is advantageous in terms of potential application of POM/MMT nanocomposites in automotive industry. It is worth to mention that conventional composites have significantly increased density,

as compared to neat polymers, which contribute to increase of the total weight of final product. In automotive industry this leads to higher fuel consumption. Nanocomposites, on the other side, offer improved mechanical and thermal properties maintaining low specific weight.

The kinetic analysis of the degradation process of all tested nanocomposites was conducted according to Friedman method. It has shown the increase of the activation energy of nanocomposite degradation at small values of degree of conversion with respect to neat polymer (Figure 4a, 4b, 4c). Moreover, the isoconversional lines of nanocomposites had higher slope than the experimental points, which suggested the contribution of autocatalytic reactions in the degradation process.

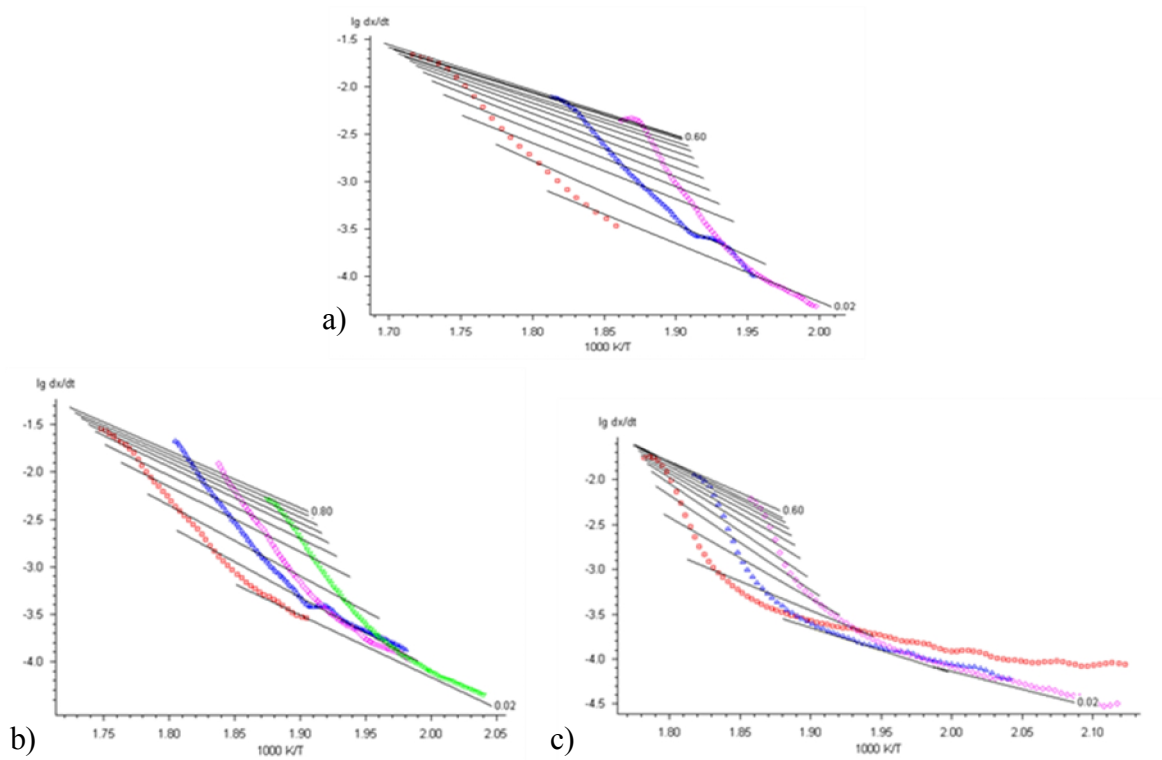
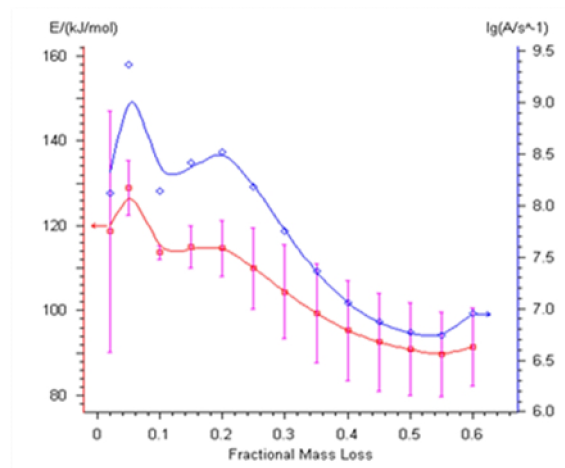


Figure 4. The results of kinetic analysis of the degradation process in air atmosphere using Friedman method: a) POM; b) POM/OMMT nanocomposite modified with ammonium salt; c) POM/OMMT nanocomposites modified with imidazolium salt.

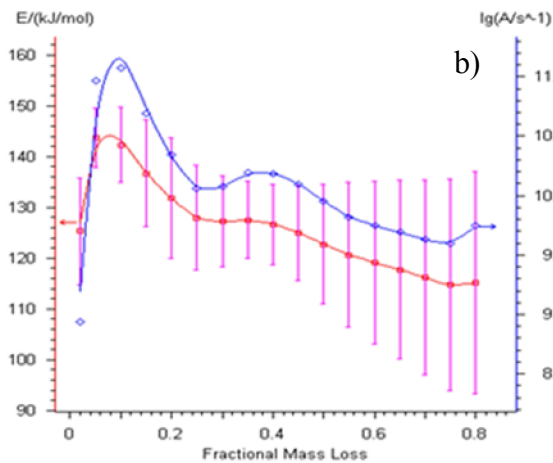
Interestingly nanocomposite sample modified with imidazolium salt had a much lower value of activation energy in the initial stage of thermooxidative degradation process as compared with pure POM. This explains the deterioration on thermal stability of POM/ImidS nanocomposites possibly due to initiation of decomposition by imidazolium compound or products of its decompositions at lower temperatures (Fig. 5a, 5b, 5c).

A successive modeling of degradation process in the beginning stage was carried out using the nonlinear regression method and kinetic parameters calculated in the Friedman analysis. The

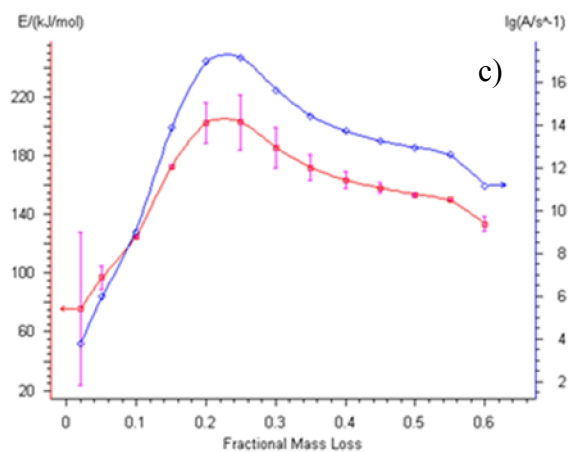
mathematical model of degradation reactions with the best fit to the series of experimental points of all tested samples was in the form of two-stage process: the main reaction and the subsequent reaction (Figure 6). Interestingly, the introduction of naofiller caused change in the geometry of diffusion field from 3 dimensional to 1 dimensional. This may reflect the restricted path for diffusion of low molecular weight products of degradation entrapped between the MMT layers and confirm the barrier mechanism of polymer stabilization by nanofillers.



a)



b)



c)

Figure 5. The dependence of apparent activation energy (E) and the exponential factor (A), the relative weight loss determined by Friedman to the process of thermal oxidative degradation of: a) Polyoxymethylene; b) POM/OMMT nonocomposite modified with ammonium salt; c) POM/OMMT nanocomposites modified with imidazolium salt.

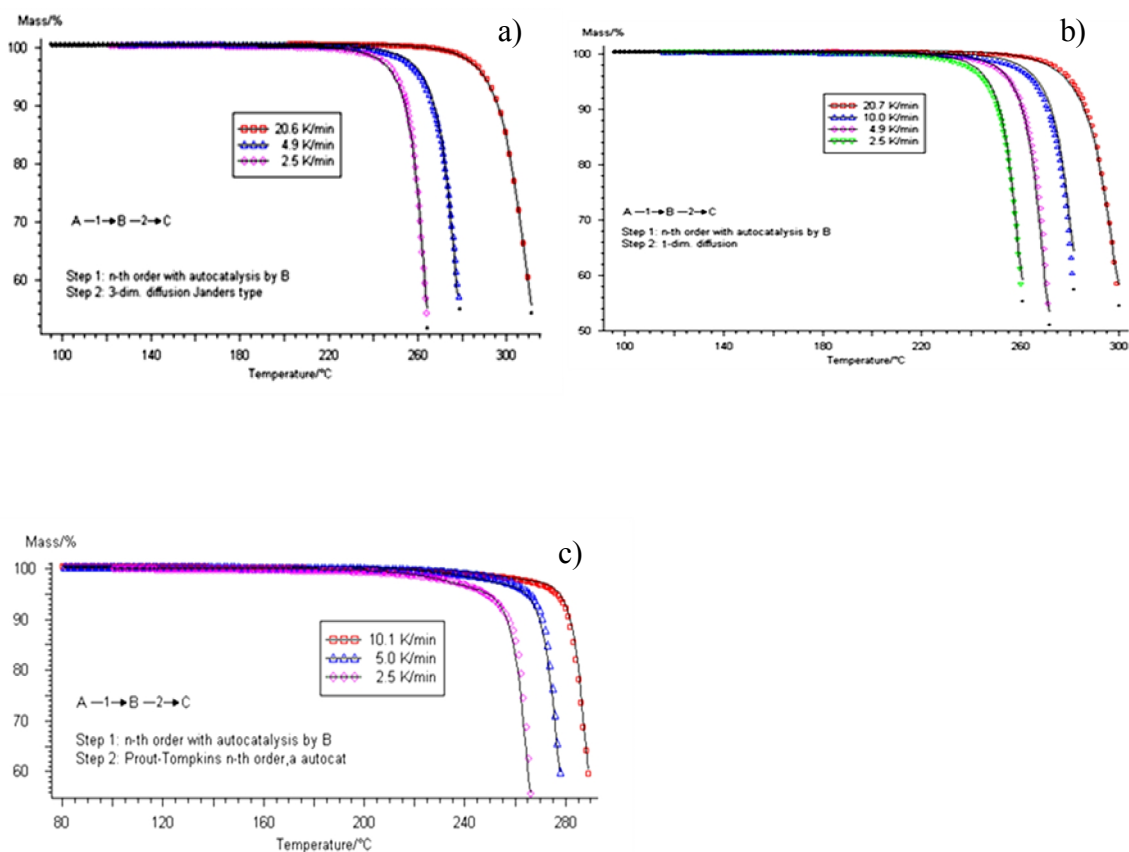


Figure 6. Results of non-linear regression analysis for the best fitting model of main reactions and subsequent reactions: a) Cn-D3 for sample POM; b) Cn-D1 for sample POM/OMMT modified with ammonium salt; c) Cn-Bna for sample POM/OMMT modified with imidazolium salt.

4. Conclusions

The WAXD studies have shown that the degree of dispersion depends on the type of organic modifier used for MMT modification. The ammonium surfactant rendered the regular structure of MMT layers in polymer while imidazolium surfactant enabled complete exfoliation of layered silicates. An increase in the melting temperature and hardness was observed due to addition of filler. Similar changes were achieved for nanocomposites containing the ammonium and imidazolium salt. Addition of Nanofil did not cause significant change in material's density, whereas the use of imidazolium modified clays caused slight increase in density. The kinetic analysis indicated that the mechanism of thermal oxidative degradation process in the first stage of mass loss of all tested samples were two-stage process – modeling for two consecutive reactions gave good correlation with the experimental data. The n-order reaction with autocatalytic effect

and diffusion controlled reaction were found to rule the degradation of nanocomposite materials. Research on the tensile strength under static deformation of all tested nanocomposites revealed that these materials are capable of handling the larger stresses.

5. Literature

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