

Thermo-rheological properties and miscibility of linear low-density polyethylene-silsesquioxane nanocomposites

Mateusz Barczewski,¹ Tomasz Sterzyński,¹ Michał Dutkiewicz²

¹Polymer Processing Division, Institute of Materials Technology, Poznań University of Technology, 61-138 Poznań, Poland

²Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, 60-780 Poznan, Poland

Correspondence to: M. Barczewski (E-mail: mateusz.barczewski@put.poznan.pl)

ABSTRACT: The influence of octakis(n-hexadecyldimethylsiloxy)octasilsesquioxane (hdPOSS) on rheological and thermal properties of linear low-density polyethylene was investigated. Rheological evaluations realized by two different measuring techniques (rotational and extensional rheometry) allowed to obtain a wide range of information concerning an influence of silsesquioxanes on rheological properties of polymeric matrix. The studies were complemented with Differential Scanning Calorimetry measurements. In order to evaluate the miscibility of thermoplastic matrix and hybrid organic-inorganic nanosized filler, rheological investigations, Dynamic Mechanical Thermal Analysis and Scanning Electron Microscopy were applied. Simultaneously, based on the rheological and thermal investigations, the mechanism of interactions between polymeric matrix and silsesquioxanes was considered. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42825.

KEYWORDS: composites; nanostructured polymers; polyolefins; rheology; thermal properties

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INTRODUCTION

Modification of polymers with silsesquioxanes received a considerable interest among researchers nowadays. An influence of POSS additives on thermal, rheological, mechanical, and structural properties of thermoplastics and curable polymeric materials has been investigated.^{1–10} In case of polyolefins, it is proved that small amounts of POSS, less than 1 wt %, rarely lead to significant changes in polymer properties.^{11,12} The problem of miscibility and interactions between silsesquioxanes and polymeric matrix was widely studied.^{13–15} Moreover, difficulties in dispersion of silsesquioxanes in thermoplastic nanocomposites forces to apply reactive blending.^{12,16,17} The influence of silsesquioxanes on polyethylene rheological and thermal behavior has been considered in several articles.^{15,18–24} Different rheological behaviors depending on functional silsesquioxane groups were observed. Hato *et al.* showed that the addition of octamethyl-POSS into LLDPE matrix led to an increase in molten state viscosity.¹⁸ Similar results were presented by Huang *et al.* who applied rheological measurements and defined octavinyl-silsesquioxane (in concentrations up to 6 wt %) as miscible with low-density polyethylene.²² In the study presented by Joshi, the impact of octamethyl-silsesquioxanes on HDPE was described.²⁰ A decrease of the complex viscosity in case of low POSS amounts (up to 0.5 wt %) and an increase in this value for HDPE samples that contained more than 1 wt % were found. It was also proved that a small amount of POSS acted

as lubricant, however in case of concentrations exceeding 5 wt % of POSS the blends became immiscible.²⁰ The rheological behavior of linear polyethylenes that contained silsesquioxanes with short aliphatic groups was well described. However, an explanation of an influence of long-branched silsesquioxanes on polyethylene properties is still deficient.

The aim of this study was to investigate the influence of octakis(n-hexadecyldimethylsiloxy)octasilsesquioxane (hdPOSS) on rheological and thermal properties of linear low-density polyethylene. The idea of long chain branched hdPOSS addition was based on the assumption stating that the incorporation of branched small particles or highly branched polyethylenes into metallocene or butene-copolymer LLDPE might have led to improved processability, *i.e.* a suppression of sharkskin instability during extrusion processes. This results from dissipative effect caused by the presence of LDPE long chain branches (LCB).^{25–30} Therefore, an application of silsesquioxane nanofillers which may act as self-assembling LCB source is well founded. Two different mechanisms of an interaction between POSS nanoparticles and LLDPE macromolecular chains may be proposed. In the first case, well-dispersed POSS nanoparticles act as a source of long chains branches. This in turn, may lead to an increase in polyethylene processability (suppression of surface melt flow instabilities in case of extrusion process) and may be noticeable as the strain hardening effect observed during extensional rheological measurements.

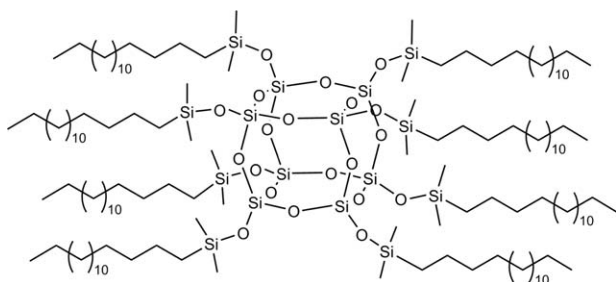


Figure 1. Octakis(n-hexadecyldimethylsiloxy)octasilsesquioxane, hdPOSS.

In the second case, incompatibility of hdPOSS particles with polyethylene matrix occurs because of formation of hdPOSS agglomerates in LLDPE matrix where clusters of nanoparticles may act as low efficiency slip agents.

EXPERIMENTAL

Material

The investigations were performed using commercial linear low-density polyethylene LLDPE SABIC 118 NJ, with MFI = 1 g/10 min (190°C, 2.16 kg) from the Sabic (Riyadh, Saudi Arabia). The selected LLDPE butane copolymer is characterized by a low modification level and narrow molecular weight distribution.

Octakis(n-hexadecyldimethylsiloxy)octasilsesquioxane, abbreviated as hdPOSS, was synthesized by the Centre for Advanced Technologies AMU (Poznań, Poland). The thermal stability of silsesquioxane was verified with thermogravimetric analysis (TGA), using a Netzsch TG 209 F1 Libra apparatus, operating at standard polyethylene processing temperatures, i.e. in the range between 170°C and 230°C. The chemical formula of POSS used in the studies is presented in Figure 1. The comprehensive structure studies realized by Azis *et al.* showed that despite the n-alkyl-substituted polyhedral oligomeric silsesquioxanes that contained longer than $n = 14$ alkyl groups appeared to be crystalline, although it was unable to grow large crystals.^{14,31}

Sample Preparation

The LLDPE pellets were milled into powder with a Tria high-speed grinder. Prior to processing the nanofiller was dried in vacuum for 2 h at 120°C. The polymeric powder was mixed with hdPOSS in a rotary mixer Retsch GM 200 for 3 min with a rotation speed of 3000 rpm. The homogenization of the premixed blends with different hdPOSS concentrations (0.5–10 wt %) was realized by molten state extrusion, using a Zamak co-rotating twin screw extruder operated at 190°C and 100 rpm. The screws geometry was configured for processing of polyolefins. The extruded rod was then pelletized in a water bath. The samples used for extensional rheological measurements were compression molded, between two PTFE film sheets, using a hydraulic press at 180°C for 5 minutes. A fixed thickness of samples was achieved by using a steel frame of 0.9 mm. The samples for SEM microphotography were shaped at the same conditions as described above but without the steel frame, the polymeric film thickness was about 5 μm .

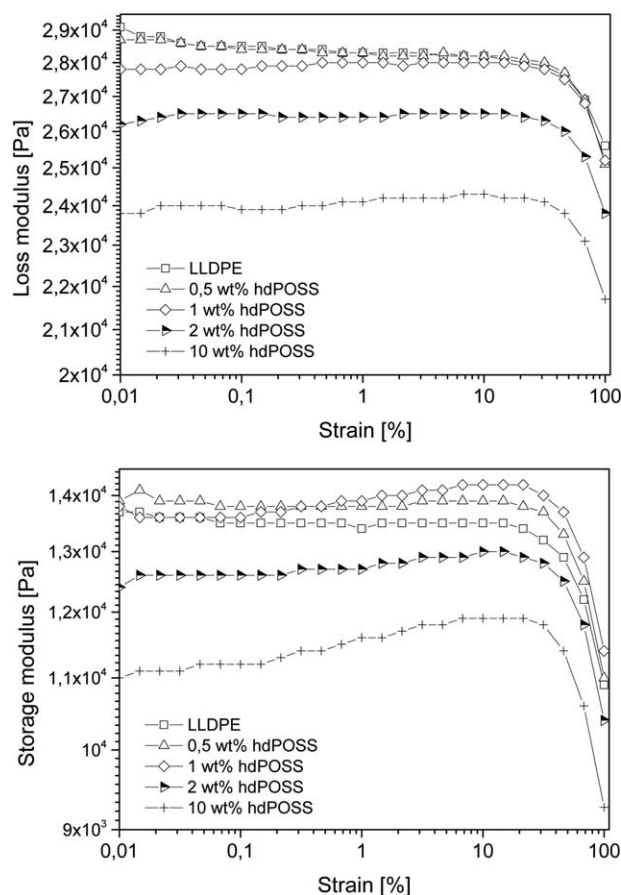


Figure 2. Strain dependence of storage and loss modulus for pure LLDPE and LLDPE-hdPOSS nanocomposites (190°C), obtained during rheological measurements.

Measurements

Oscillatory Rheological Measurements. Investigations were carried using an Anton Paar MCR 501 rotational rheometer, with 25 mm diameter parallel plates under the oscillatory mode. The experiments were conducted at 190°C. A frequency sweep for experiments was set at 5% and was determined during preliminary investigations (the strain amplitude during sweep experiments) and in case of all samples located in linear-viscoelastic region (LVE).

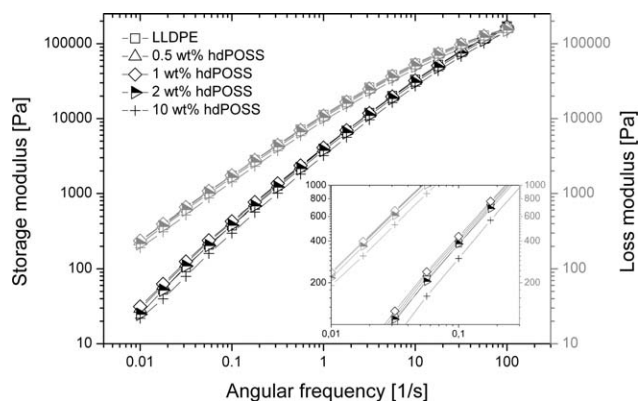


Figure 3. Frequency dependence of storage and loss modulus for pure LLDPE and LLDPE-hdPOSS nanocomposites (190°C, $\gamma = 5\%$), obtained during rheological measurements.

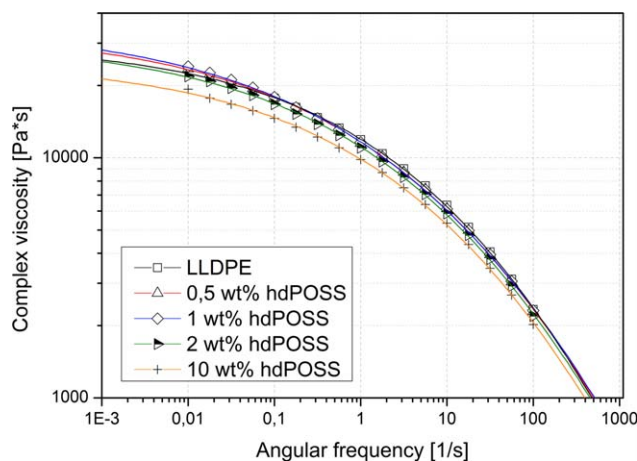


Figure 4. Complex viscosity of pure LLDPE and LLDPE-hdPOSS nanocomposites at 190°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Extensional Rheological Measurements. Extensional rheological measurements were carried out using a SER Universal Testing Platform (Xpansion Instruments) mounted on an Anton Paar MCR 501 host system. Measurements were realized according to methodology described by Sentmanat *et al.*^{32–34} The samples were stretched with Hencky strain rates in the range between 0.1 and 10 s⁻¹.

Scanning Electron Microscopy. To observe the dispersion level of POSS nanoparticles in polymeric matrix, a scanning electron microscope (SEM), model Vega 5135MM, produced by the TESCAN (Czech Republic) was used. The structure of LLDPE-hdPOSS nanocomposites was investigated by Back Scattered Electron signal (BSE) and Secondary Electron signal (SE) with an accelerating voltage of 15 kV followed by mapping of silicon distribution.

Dynamic Mechanical Thermal Analysis. Dynamic Mechanical Thermal Analysis (DMTA) test was performed using Anton Paar MCR 501 rheometer equipped with a torsion DMTA measuring tool. Investigations were carried out with a constant frequency of 1 Hz and a strain of 0.01%. All samples were cooled down to -140°C and heated up to 110°C with a temperature ramp of 2°C/min.

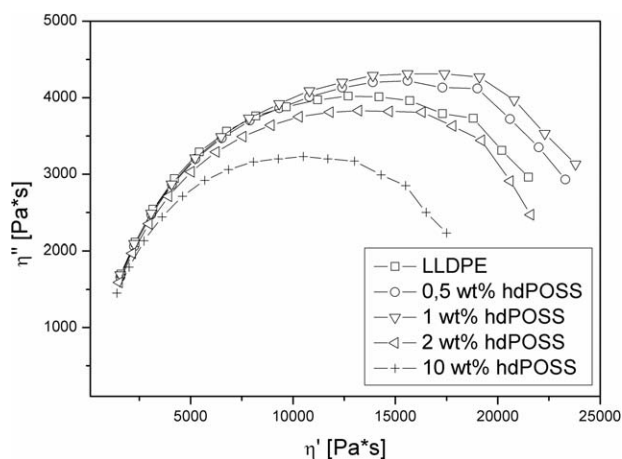


Figure 5. Cole–Cole plots of LLDPE and LLDPE nanocomposites.

Differential Scanning Calorimetry. Differential Scanning Calorimetry (DSC) experiment was performed using a Netzsch DSC 204 F1 Phoenix® with aluminum crucibles and approximately 5 mg samples under nitrogen atmosphere. All samples were heated up to 200°C and held in a molten state for 5 min, followed by cooling down to 20°C with heating and cooling rates equal to 10°C/min. This heating–cooling procedure was conducted twice to evaluate the thermal properties from the second melting DSC run and to obtain broad information about modification of LLDPE with hdPOSS.

RESULTS AND DISCUSSION

Oscillatory Rheological Measurements

Rheological investigations were focused on evaluation of the LVE region for LLDPE and LLDPE nanocomposites. In Figure 2, the storage (G') and loss (G'') modulus were presented as a function of the strain for LLDPE and its nanocomposites. Newtonian plateau in the strain range between 0.01% and 20% might have been observed. For all the investigated materials the onset of nonlinear viscoelastic behavior appeared almost at the same strain value. Therefore, it can be stated that no strain-sensitive rigid structures in the investigated nanocomposites occurred. Hato *et al.* revealed that this effect was caused by a strong phase separation between silsesquioxanes and polyethylene.¹⁸ In case of 10 wt % hdPOSS addition, nonlinear behavior in the range of 0.01 and 5% in storage modulus vs. strain plot occurred. This indicated strong plasticizing effect of amorphous silsesquioxane domains in polyethylene matrix.

An absence of physical or chemical bonds between LLDPE macromolecules and hdPOSS nanoparticles was indicated by dominant viscous behavior obtained during oscillatory dynamic rheological investigations (Figure 3). A similar tendency was observed for the storage and loss modulus vs. angular frequency curves. In both cases a slight decrease in the G' and G'' values with an addition of hdPOSS nanoparticles into LLDPE matrix was noted.

The complex viscosity as a function of angular frequency was also analyzed (Figure 4). It should be noticed that a viscosity drop was not observed for the samples that contained less than

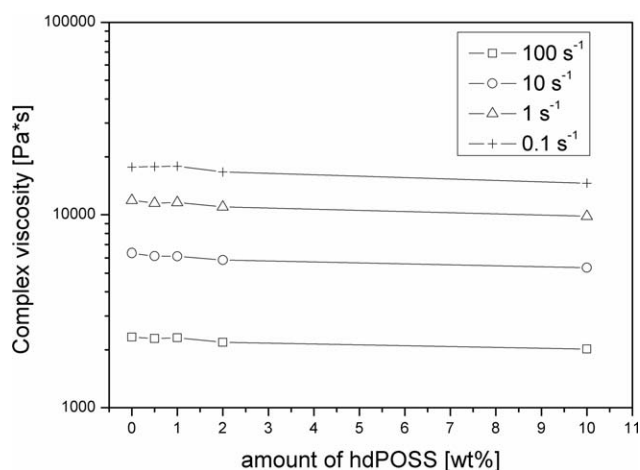


Figure 6. Dependence of hdPOSS amount on the complex viscosity.

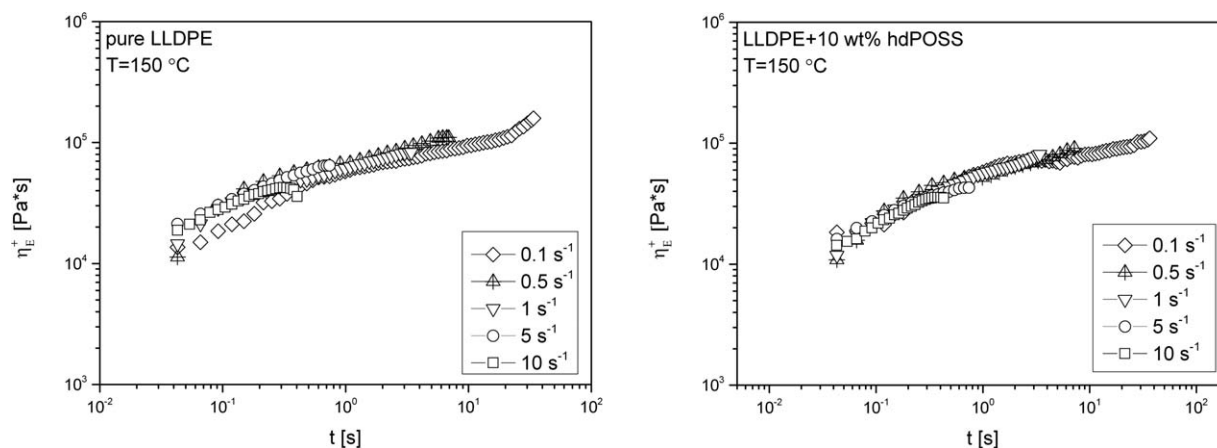


Figure 7. Extensional rheological curves obtained for pure LLDPE and LLDPE that contained 10 wt % of hdPOSS.

or equal to 2 wt % of hdPOSS, hence significant viscosity changes were observed for the highest hdPOSS concentration applied. This phenomenon was unlike the one already described in literature for silsesquioxanes with short aliphatic functional groups.¹⁹ On the contrary, despite the agglomerated short chain nanoparticles might have been a steric hindrance limiting the mobility of polyethylene chains, it was supposed that the immiscible agglomerates of long chain branched silsesquioxanes acted as low molecular weight lubricants, as it was observed.

Miscibility of LLDPE with hdPOSS in a molten state was investigated by interpretation of rheological data according to Zhou and

Kwak.^{12,35} First rheological interpretation of miscibility was based on interpretation of Cole–Cole plots (Figure 5). A smooth semi-circle shape of plotted curves suggest good compatibility of two-phase blend in molten state. Lack of the curves with changed shape may be acknowledgment of overall good LLDPE-based nanocomposites homogeneity. Zhou *et al.* discuss the effect of octavinyl silsesquioxane on rheological behavior of iPP.¹² In proposed interpretation they suggest that lowered position of modified polymer Cole–Cole curve was caused by the lubricating behavior of silsesquioxanes. In our studies the higher placement of the Cole–Cole curves of polyethylene samples containing 0.5 and 1 wt % of hdPOSS may be an effect of long chain branched

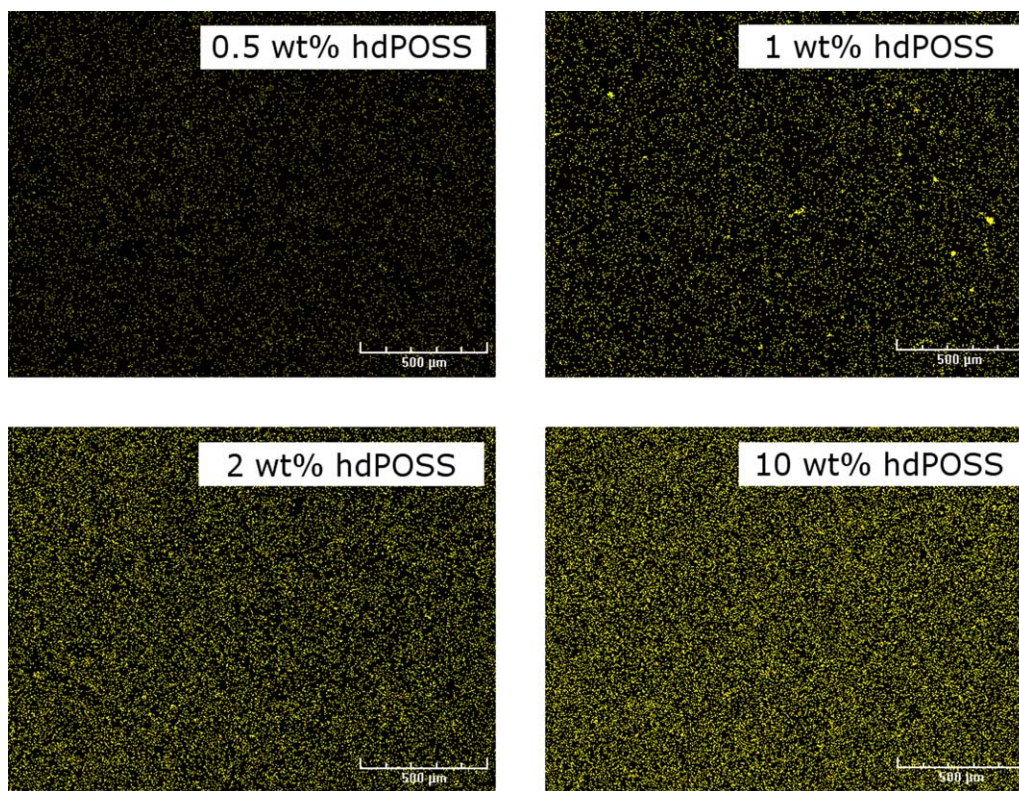


Figure 8. Distribution of hdPOSS in LLDPE matrix based on SEM microphotographs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

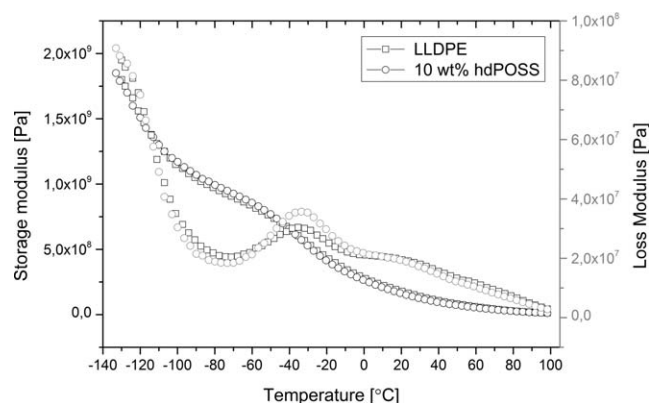


Figure 9. Storage and loss modulus of LLDPE and LLDPE-10 wt % hdPOSS samples presented as a function of temperature, obtained during DMTA measurements.

silsequioxane presence. hdPOSS containing long alkyl chains, well dispersed in polymeric matrix, became steric hindrance for backbone long polymer chains movements. This effect was intensified with increasing amount of hdPOSS (from 0.5 to 1 wt %). In case of higher hdPOSS amounts (2 and 10 wt %), silsequioxanes reveal higher tendency to create agglomerates that became to act as lubricants causing lowering of Cole–Cole plots. What should be mentioned is a fact that tendency observed for semicircle Cole–Cole plots location changes was similar to the rheological behavior presented in Figure 4.

Figure 6 shows the dependence of hdPOSS content on complex viscosity. Four curves represent η^* values recorded at different shear rates. Linear shape of presented rheological results and A SLIGHT hdPOSS amount dependence on η^* may be also interpreted as a result of a good dispersion of hdPOSS in polyethylene melt. Moreover, no significant negative deviation from simple rule of mixtures may also attribute that LLDPE and hdPOSS are miscible in molten state. It should be noticed that both components even in molten state are miscible and allow to obtain good dispersion, may become thermodynamically immiscible in solid state.

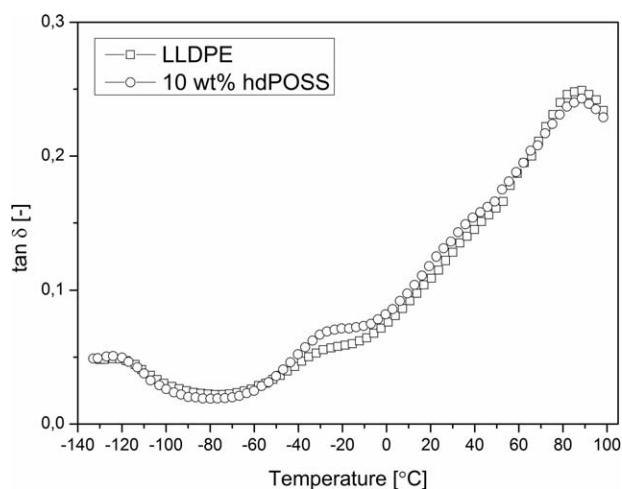


Figure 10. Loss factor ($\tan \delta$) of LLDPE and LLDPE-10 wt % hdPOSS samples presented as a function of temperature, obtained during DMTA measurements.

Extensional Rheological Measurements

Results of extensional rheological measurements are presented in a form of tensile stress growth coefficient vs. time plots (Figure 7). Pure LLDPE and LLDPE that contained 10 wt % of hdPOSS were examined at 150°C with Hencky strain rates in the range between 0.1 and 10 s^{-1} and subjected to further analysis. It can be concluded that no significant changes were observed. Courses of the curves obtained for both investigated samples were similar and collapsed in the range between 0.4 and 36 s for applied Hencky strain rates. For the LLDPE sample at $\dot{\epsilon}_H = 0.1 s^{-1}$, a low strain hardening effect could have been observed. The collapse for all considered samples was noted at similar time.

Scanning Electron Microscopy

Morphological analysis were performed using SEM to identify miscibility and silsequioxane dispersion in polyethylene matrix and exclude the presence of macroscopic agglomerates of hybrid nanosized additive. The converted SEM microphotographs showing maps of silicon distribution are presented in Figure 8. Insufficient nanoparticle distribution in polymeric matrix could have been observed for all considered samples, in particular the addition of 1 wt % of hdPOSS caused an appearance of highly visible aggregates. For samples containing 2 and 10 wt % of hdPOSS more uniform structure may be observed. hdPOSS agglomerates became smaller and well dispersed in polyethylene matrix, which allow them to act as lubricants for LLDPE.

Dynamic Mechanical Thermal Analysis

In order to evaluate miscibility of LLDPE and hdPOSS DMTA experiment was performed. DMTA results present changes in storage (G'), loss modulus (G''), and loss factor ($\tan \delta$) as a function of temperature for pure LLDPE and LLDPE-hdPOSS nanocomposite containing 10 wt % of nanofiller are presented in Figures 9 and 10. Linear polyethylenes usually reveal three

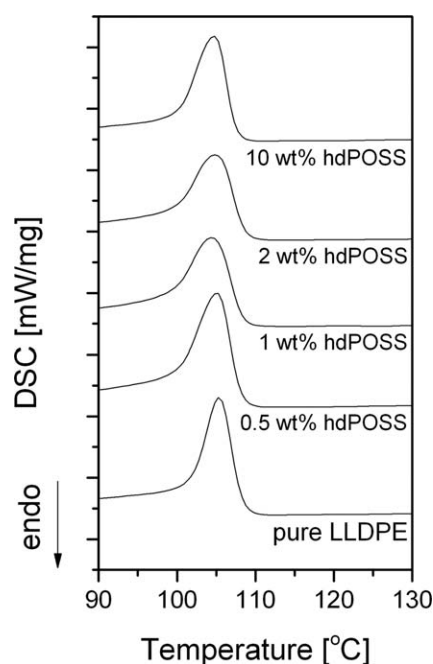


Figure 11. DSC crystallization curves of pure LLDPE and LLDPE-hdPOSS nanocomposites.

Table I. Thermal Parameters of Pure LLDPE and LLDPE-hdPOSS Nanocomposites Obtained during DSC Investigations

| Sample | T_{CP} (°C) | T_{CO} (°C) | T_M (°C) | ΔH_m (J/g) | X_c (%) |
|-------------------------|---------------|---------------|------------|--------------------|-----------|
| LLDPE | 105.4 | 108.3 | 123.9 | 120.8 | 41.9 |
| LLDPE + 0.5 wt % hdPOSS | 105.1 | 108.1 | 122.5 | 121.9 | 42.5 |
| LLDPE + 1 wt % hdPOSS | 104.4 | 108.2 | 123.7 | 113.2 | 39.7 |
| LLDPE + 2 wt % hdPOSS | 104.9 | 108.6 | 123.3 | 109.9 | 38.9 |
| LLDPE + 10 wt % hdPOSS | 104.7 | 107.5 | 122.4 | 101.5 | 39.2 |

ΔH_m 100% = 288 J/g.³⁹

transitions (γ , β , and α) that may be evaluated by DMTA experiment. The transition may be found at three temperature ranges: -150°C to -120°C for γ transition; -30°C to -10°C for β transition and 10 – 120°C for α transition. γ transition is related to the relaxation of very short sequences. β transition relates to the relaxation of the amorphous structures and branches which are a part of semicrystalline polymer. The broad α transition is because of a relaxation process related to the presence of crystalline regions involving longer chain segments.^{16,36,37} In contrary to the results presented by Hato *et al.* incorporation of hdPOSS did not cause any significant changes in G' , G'' , and $\tan \delta$.^{19,38} The G' curves for LLDPE and LLDPE-hdPOSS nanocomposite (Figure 9) are similar which may be interpreted as a lack of three-dimensional network-like structure of nanocomposite. Moreover, no difference in rubbery plateau between both materials was denoted. The values of G'' recorded for LLDPE-hdPOSS are slightly lower than those observed for pure LLDPE, except the region of β relaxation when nanocomposite sample reveals a distinct increase in comparison to LLDPE. This fact may be attributed to increased content of disordered amorphous phase resulting from the presence of hdPOSS agglomerates. However, it should be mentioned that the values of β transition temperature determined from G'' curves peaks were equal to -35.3°C for LLDPE and -31.9°C for LLDPE-hdPOSS nanocomposite. Figure 10 shows the loss factor ($\tan \delta$) curves for the LLDPE and nanocomposite containing 10 wt % of hdPOSS. The values of glass transition temperature (T_g) determined by loss factor were equal to -123°C for LLDPE and -125°C for LLDPE-hdPOSS nanocomposite. The lowered T_g and the increase of $\tan \delta$ values resulting from hdPOSS incorporation may be attributed to plasticizing effect of amorphous hdPOSS domains. Moreover, there was a lack of additional relaxation peak corresponding to melting of hdPOSS which is characteristic for phase separated blends.

Thermal Properties

Figure 11 shows nonisothermal crystallization DSC plots of pure LLDPE and LLDPE-hdPOSS samples during cooling at $10^\circ\text{C}/\text{min}$. Thermal parameters obtained during DSC investigations are summarized in Table I, where T_{CP} and T_{CO} are crystallization temperatures obtained from peak and onset, T_M is melting temperature, ΔH_m is the melting enthalpy and X_c is crystallinity degree. An increasing amount of hdPOSS led to a SLIGHT decrease in the crystallization temperature of LLDPE based nanocomposites. The addition of hdPOSS also resulted in significant changes in the melting enthalpy and crystallinity of the samples. The ΔH_m values decreased in a function of increasing hdPOSS content from 120.8 to 101.5 J/g,

while the crystallinity degree was reduced from 41.9%, for pure LLDPE, to 39.2%, for the sample that contained 10 wt % of hdPOSS. This effect may indicate that the LLDPE crystallization process was limited by the presence of hdPOSS aggregates. Despite crystalline nature of hdPOSS as it was mentioned before, its aggregates seem to be amorphous. Consequently, their increasing amount in LLDPE matrix caused a growth of amorphous phase in polyethylene in comparison to the nonfilled sample.

CONCLUSIONS

Based on a moderate influence of octakis(n-hexadecyldimethylsiloxy)octasilsesquioxane on modification of linear low-density polyethylene rheological properties, determined by extensional rheological experiments correlated with rotational tests, it may be stated that among two suggested mechanisms of interactions between polyethylene and silsesquioxanes, the second one took place in this case. The hdPOSS was not prone to self-assembly in polyethylene matrix between polymer chains and exhibited a strong tendency to agglomeration, which was confirmed by SEM investigations. Therefore, incompatible thermodynamically in solid state hdPOSS, dispersed in polyethylene matrix, acts as low efficiency slip agents. An increasing content of nanofiller decreased viscosity of polyethylene. Moreover, agglomerated hdPOSS domains had become amorphous what led to decrease in crystallinity level of LLDPE-hdPOSS nanocomposites and acted as plasticizer slightly influencing dynamic properties of linear low-density polyethylene.

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