MORPHOLOGY, MECHANICAL PROPERTIES AND PROCESSABILITY OF POLY(ETHYLENE TEREPHTHALATE) MODIFIED BY POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

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Abstract

The presented research results are a summary of the work carried out under the project on the application attempts to use POSS additives as modifiers of poly(ethylene terephthalate). The carried out works included preparation processing and properties measurements of obtained nanocomposites. The heptaizobutylo (vinyl) silsesquioxane was introduced into the polymer matrix by hot mixing in two concentrations 0.5% and 1% wt. Samples necessary to conduct further investigations were made by injection molding. The prepared material properties were evaluated in the several tests: static tension measurement, DMTA and DSC analysis, SEM observations. Calorimetric measurements were performed to follow the differences in the kinetics of crystallization. Rheological measurements were carried out using a rotational rheometer to evaluate the processability of the nanocomposite. The research was supplemented by the acetaldehyde emission test. Studies have shown a tendency to aggregation of used nanoadditive, despite his very low concentrations, SEM-EDS analysis revealed the presence of numerous clusters of used POSS compound. The most visible effect of POSS addition was observed in the level of crystallinity of the polymer, where the nucleation process was reported. This happens in the absence of significant changes in mechanical properties.

1. Introduction

The properties of polymer nanocomposites have been repeatedly widely described. The nanoadditives can be used to replace fibrous structures such as carbon nanotubes, fillers plate and spherical including numerous varieties of silicas as well as metal oxides. Numerous changes in the mechanical properties and performance are caused very significant field interaction between nanometric filler and polymer matrix. The key issue the case of nanofillers effectiveness is the proper selection of the mixing process, which affects all composite materials, but in this case mixing of the material at the nano scale

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determines the occurrence or not any changes in material properties. Poly (ethylene terephthalate) as a material is mainly used in the packaging industry. However, many of its advantages such as dimensional stability and high resistance to scratching mean that the polymer can be used as a structural polymer. The most important factor determining the mechanical properties of PET resin is the crystalline phase morphology. During the processing operations the increase in the proportion of the crystalline phase is generally carried out by raising the temperature of processing equipment in the cooling zone, which cause the grown of poly(ethylene terephthalate) spherulites. Since this method increases the energy consumption and extends the production cycle, therefore more promising for application appear to be a phenomenon of nucleation, which is one of the main investigated processes in this work.

2. Experimental

2.1. Materials

Monovinyl-silsesquioxane was synthesized *via* the hydrolytic condensation of incompletely condensed trisilanolisobutyl POSS with $ViSiCl_3$. This synthetic methodology is well-documented for the synthesis of monofunctional-silsesquioxanes (Fig. 1). We applied the modified procedure described by Abbenhuis *et al.* and were able to get an analytically pure compound with an isolated yield of 92%.

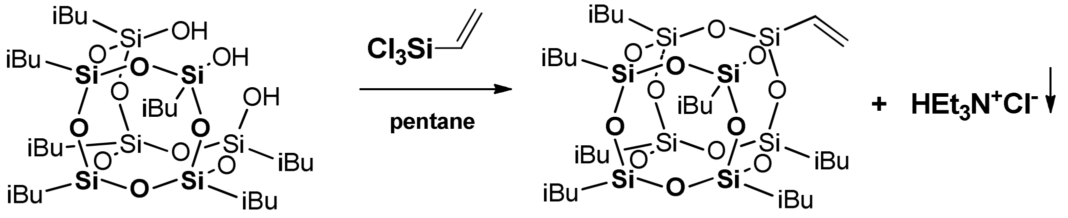

Figure 1. Reaction path for synthesis of 1-vinyl-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane.

2.2. Nanocomposite preparation

The composite mixture was prepared by hot melt mixing process during the extrusion process. Both materials were drying for 6 hours at the temperature of 100°C. The dry-blend mixture was prepared in the rotating barrel mixer. The extrusion process was carried out on the twin screw machine (ZAMAK EH16D). Material was quenched and pelletized. The prepared pellets were used in rheological tests and DSC measurements. The second step of sample preparation was the injection moulding. Previously prepared composite was dried for another 6 hours and then shaped to standard geometries. The temperature profile of the injection moulding process was: zone 1= 240°C, zone 2=250°C, zone 3=260°C and the nozzle=270°C, mould temperature was 40°C. The used machine was ENGEL ES 80 HLS, the mould cavity allows to obtain a sample dimensions for static tension test and DMA analysis.

2.3. Material characterization

The crystallization behavior of pure and modified PET resin was evaluated using the differential scanning calorimeter (Netzsch DSC 204 F1 Phoenix). Two temperature programs were used to investigate materials properties. The first one was conducted with low cooling rate, second measurement program was carried out with high cooling rate. In both cases the first stage of melting was performed with the heating rate of 10 K/min up to 270°C. Then crystallization was carried out with two different cooling rates of 10 K/min and 40 K/min. The second melting stage was performed to evaluate the difference in crystallization behavior, condition were the same for both heating stages

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(10 K/min, 270°C). The samples used for the DSC analysis were collected from injection moulded samples (1mm thick), each specimen from the same part of the dumb-bell sample. The weight of investigated samples was 4-5 mg.

In order to determine the glass transition temperature T_g, storage modulus G’, and tangens δ the DMA tests were conducted. The analysis was performed using the Anton Paar MCR 301 rheometer attached with the torsion clamps for solid rectangular samples. The measurements were performed for samples dimension 50x5x1 mm. The test was performed in the range of 25°C - 150°C, the strain was set to 0,01%, the constant frequency was 1 Hz, the heating rate of the measurement was 2 °C/min.

The structure observations were performed using the SEM technique, where the EDS mapping were used for more complex analysis of the miscibility and homogeneity of the mixture.

3. Results

The first heating signals are not responded to a meaningful difference in the crystallographic structure of the tested materials, mainly due to the amorphous nature of the structure obtained during the injection molding of samples. The only observation concerns the steady decreasing trend of temperature associated with the occurrence of the beginning of the cold crystallization. The difference are not passing the error limit of the method, however, further analysis after controlled crystallization conditions confirms that changes with increasing content of POSS additive. In order to show the changes of materials crystalline structure, the prepared measurement program consisted of two cycles of cooling and heating. During the first cycle, the cooling and heating rate was equal, and states at 10K/min. In the second cycle (Fig. 2) cooling step was carried out at 40 K/min, which was too performed to highlight any changes in the course of the crystallization process, the final stage of heating was conducted at the standard 10K/min.

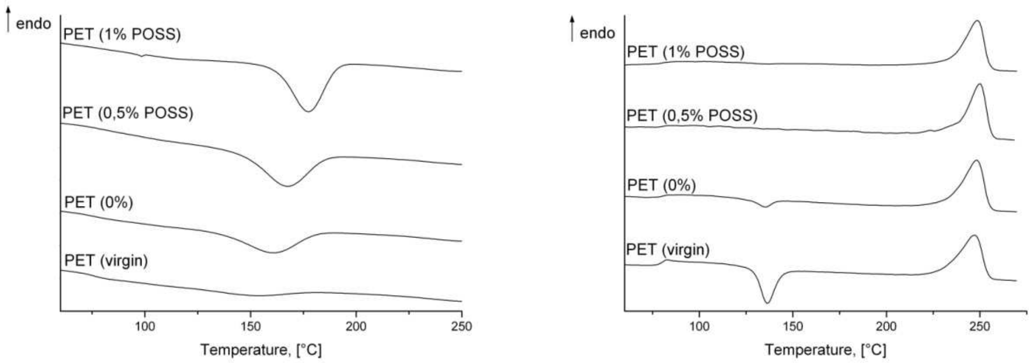

Figure 2. The 2nd cooling (left) and heating (right) segment, cooling rate was 40 K/min, heating rate 10 K/min.

In the described case, the addition of POSS influences the structure during the cooling stage causing partial nucleation. In the case of investigated materials this process has not resulted in a significant increase of the crystallinity which was caused by of the high cooling rate during injection molding, but in the case of extrusion technology when the gradient of cooling rate is smaller, the nucleation effect may be seen more significant causing the increase of the crystalline phase in the final product.

The presented in the Fig. 3 storage modulus thermograms are representing POSS modified samples and reference material with the same thermal history and virgin one. Considering the very similar course of G’ changes in mechanical properties of injection molding samples are small, for reference samples identical. The reinforcing effect of POSS additive turns out to be negligible at such a low concentrations.

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The similar conclusions apply to the course of tan δ, where main factors, the area under curve and the value of peak maximum are comparable in the range of glass transition for all investigated materials.

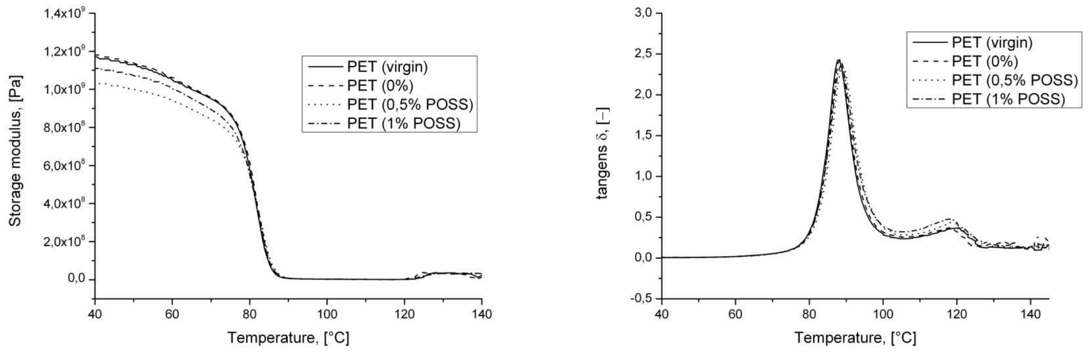

Figure 3. The storage modulus (left) and tangens δ thermograms.

The SEM analysis was performed to confirm the expected tendency for nanoparticles agglomeration. This phenomenon was observed previously in many other research works. The POSS particles with relatively short function groups (butyl, vinyl) create a large aggregation. This problem occurs for the composites with the minimum concentration of 1% of weight (Fig. 4).

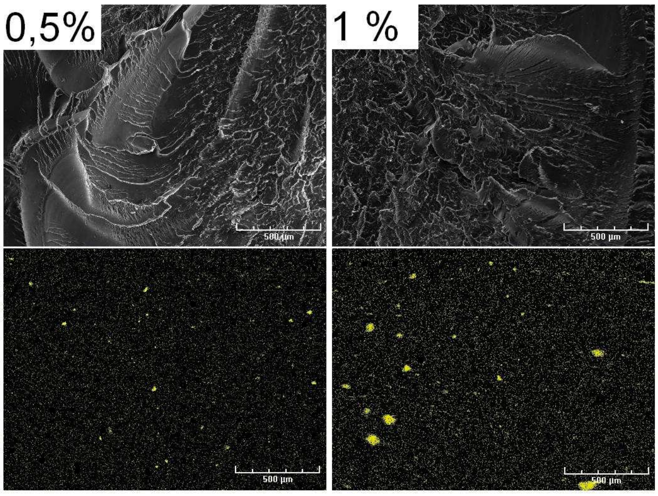

Figure 4. SEM-EDS micrographs of injection moulded samples.

The transparency of injection molded samples (Fig. 5) confirmed the overall tendency to haze for all nano composites. In the particular situation this opaque is associated with two phenomena occurring at the same time. First one is related with the poor dispersion of POSS nano fillers, which tendency to aggregation was confirmed by SEM analysis. If the POSS cages can’t be dispersed into nano scale particles, then the larger aggregates starts to scatter the light and reduce the clarity of molded sample. The second relationship is affiliated with the crystallite size, which for the PET resin is the primary factor determining the transparency. The nucleation effect of nano filler could lead to faster formation of the crystallites and its growth to bigger sizes. The final diameter of crystallite was greater than wavelength of visible light and finally leads to more hazy structure.

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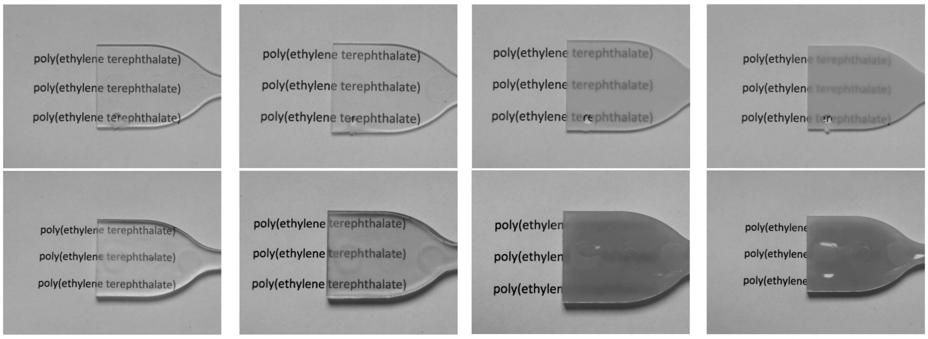

PET (virgin) PET (0%) PET (0,5% POSS) PET (1% POSS)

Figure 5. Injection molded samples transparency, thickness 1mm (top) and 3mm (bottom).

3. Conclusions

The use of POSS additives in processing of poly(ethylene terephthalate) seems to be an effective method for modification of polymer structure, especially regarding changes in the crystalline structure of the final product. The processing method due to the tendency to agglomeration need to be revised. However the obtained results achieved at very low nanofiller content prompt further research into commercial application.

Acknowledgments

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