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Thermally more durable electromechanical films by POSS nanomodification

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Abstract. The thermal stability of polypropylene (PP) based cellular electromechanical films was improved by compounding PP with thermally more durable cyclo olefin copolymer (COC) and polyhedral oligomeric silsesquioxane (POSS) nanochemical. The cast films were biaxially oriented in laboratory scale and then expanded by a gas diffusion expansion method, which increased the pore size inside the cellular film structure and the thickness of the film. The cellular films were then electrostatically charged by a contact charging method and metallized by gold sputtering. The samples were aged at 85°C showing that the d_{33} signal decreased from the original value, but remained at high level; more than 120 pC/N even after two weeks of ageing.

Introduction

Cellular electromechanical films have been used especially for large area sensor applications, but also for robust and tailored sensors requiring high sensitivity [1-3]. These films based on polypropylene have been commercially available for quite some time already, but their thermal stability has limited their use in some more demanding applications [4]. When subjected to elevated temperatures the electromechanical coefficient is permanently reduced due to the loss of the stored electrostatic charge in the film. We have demonstrated that by utilizing polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals it has been possible to improve the thermal stability of the films based on polypropylene (PP) and/or cycloolefin copolymers (COC) [5]. The improvement in the thermal stability of the electrostatic charges seems to be much higher compared to the influence on the mechanical properties. The mechanisms behind the improved thermal stability is somewhat unclear, but one explanation is that the space charges are stored on the POSS chemical with deeper charge traps. In this paper we investigate the thermal stability of cellular electromechanical films based on compounds of PP and COC that are modified with POSS nanochemical.

When mixing PP and COC polymers the compound is thermally more stable and requires higher temperatures during processing when using higher content of COC. The type and content of the POSS chemical has an influence not only on the thermal stability of the film, but also on the successful processing of the cellular film. The POSS chemical is commercially available in micrometer-size crystal form. These crystals act as rupture nuclei during biaxial orientation and facilitate the forming of the cellular structure. Part of the POSS crystals are mechanically grinded to nano-sized powder by compounding. The nanosized fraction of the POSS chemical increase the effective surface area and increase the potential amount of the trapping sites for space charges. This work describes the optimization of the filmmaking, gas diffusion expansion, and electrostatic charging of the film in order to produce thermally more durable film with potential to be produced in industrial scale in the future.

Experimental

Materials. PP polymer was a commercial grade from Borealis Polymers. The COC polymer was also a commercial grade from TOPAS Advanced Polymers. POSS was a commercial grade from Hybrid Plastics Inc and was delivered as micron sized agglomerates, which prevented the nano dusting

during processing. The PP/COC/POSS nanocomposite included 55/36/9 wt% of these materials, respectively.

Nanocomposite preparation. PP/COC/POSS nanocomposite films were prepared by thermoplastic compounding with Berstorff ZE25x48D, cast film extrusion with Brabender and biaxial sheet stretching with Bruckner Karo IV.

Gas diffusion expansion (GDE). The film samples were expanded using high-pressure and temperature treatment. The gas was first forced into the film at room temperature at high pressure. Then the pressure was rapidly reduced and the film was put to an oven at higher temperature at ambient pressure. This permanently expanded the film due to the high gas pressure inside the film, which caused viscous expansion deformation of the plastic at high temperature. Nitrogen gas was used in the experiments. The average thickness of the PP/COC/POSS sample films was 42 μm before the GDE and 74 μm after the GDE.

Electrostatic charging. The film samples were electrostatically charged by a contact charge method with constant current mode using Eltex KNH64 high-voltage generator.

Sample preparation and d_{33} measurements. Circular samples of 30 mm in diameter were metallized on both sides by gold sputtering. The sheet stretched films and the samples can be seen in Figure 1. The constant force of 3 N was applied on the sample and then the pressure was changed sinusoidally with an amplitude of 11.5 N and a frequency of 2 Hz. The electromechanical d_{33} [pC/N] coefficient was determined from the applied force and from the charge generated from the sample. The charge was amplified using a charge amplifier, which enabled to read the signal from an oscilloscope. Each d_{33} results of a PP/COC/POSS based compound is an average result of three samples, which each were measured from three locations on both sides of the film. The d_{33} for the reference material was measured only from one sample.

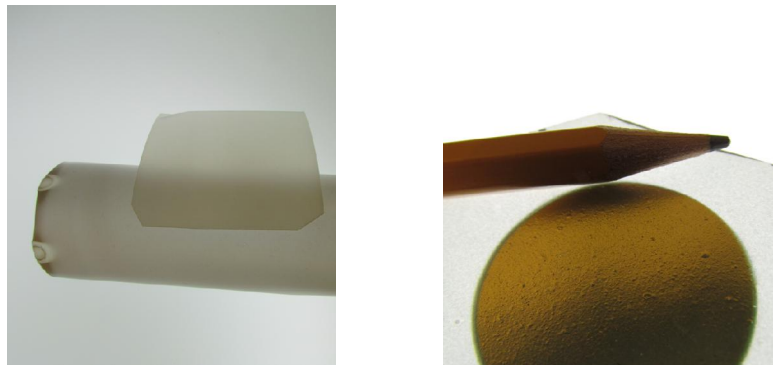


Fig.1 Sheet stretched PP/COC/POSS films (on left) and gold sputtered sample (on right).

Results and Discussions

Film structure. The preferred structure of the cellular electromechanical film consists of closed voids (bubbles) that are lense-like in shape due to the biaxial orientation of the film. According to the experimental test the preferred thickness of the voids is a few micrometers, but the required charging field [6] has yet not been fully explained by Paschen's law [7]. The reference film based on PP includes CaCO_3 , which act as rupture nuclei during the biaxial orientation. In the thermally more stable PP/COC compounds POSS nanochemical was used instead. The microgranulates of the POSS material were broken into finer particles down to nanometer size during thermoplastic processing. Therefore the POSS particles can be seen in a wide size range from micro to nanometers (Figure 2).

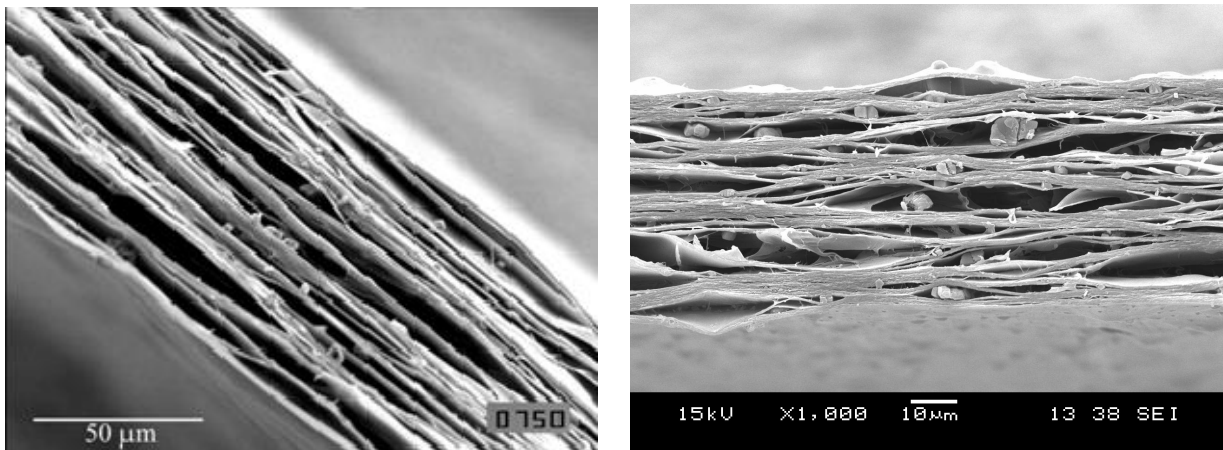


Fig.2 SEM micrographs of the film cross section. Reference PP/CaCO₃-based electromechanical reference film (on left) and PP/COC/POSS nanocomposites (on right).

Electromechanical d_{33} coefficient and ageing. The charged and metallized films were aged for at least two weeks at 85°C in order to study the thermal stability of the electromechanical d_{33} coefficient. The PP/COC/POSS nanocomposite clearly showed better relative thermal stability compared to the reference PP film. The relative reduction of d_{33} was only 44% for the nanocomposite after four days of ageing at 85°C, while the reduction was 57% in the reference film. The absolute d_{33} value was initially higher in the reference film with 335 pC/N compared to 211 pC/N in PP/COC/POSS film. After ageing for more than eight days the absolute d_{33} value of the reference film dropped to lower level compared to the PP/COC/POSS film. The ageing curves at 85°C can be seen in Figure 3.

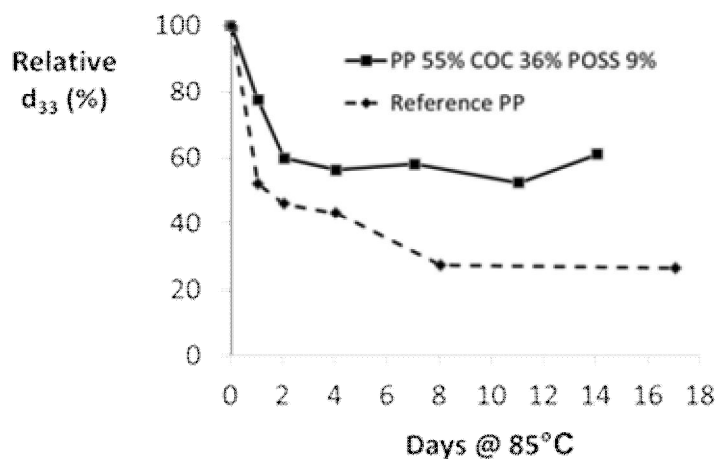


Fig.3. The relative d_{33} at 85°C (on left) and the absolute d_{33} value (on right) as a function of time.

The d_{33} signal seems to increase at some points during ageing in the PP/COC/POSS samples. The reason is most likely the relaxation processes where the deformation caused to the film by the biaxial stretching and by the GDE are slowly relaxed and cause small changes to the film structure.

Since the electromechanical operation of the cellular film is based on space charges that create a permanent electric field inside the film, the value of the d_{33} constant depends on the space charge density and on the stiffness of the film. A polymer suitable for higher temperatures like COC is harder compared to PP and therefore mixing PP and COC together gives a compound that has higher Young's modulus than pure PP. As a result the thermally more durable films tend to have in principle smaller d_{33} coefficients due to their higher Young's modulus. The benefits can be found only when the film is used at high temperature.

Summary

It was challenging to make an optimally structured porous film, but already a moderately porous film with closed porous structure (cellular) gave high electromechanical d_{33} response when the film was expanded with gas diffusion expansion method after biaxial orientation. The GDE method increased the film thickness on the average about 76% from 42 μm to 74 μm thus making it more ideal for the electrostatic charging and partial discharge processes. The film making was optimized by selecting PP and COC polymer grades so that they had an adequate match in thermoplastic melt processing behavior. The PP/COC/POSS composites proved to offer a thermally more stable alternative at 85°C compared to purely PP-based film that was used as a reference. With the PP/COC/POSS based cellular electromechanical films the main challenge was the reproducibility of the optimal cellular structure during the laboratory scale film making. In the future online film making in industrial scale could offer a possibility for better film quality compared to the batch type laboratory processing.

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