

PET-Organoclay Nanocomposites using Grafted Polymer Brushes

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ABSTRACT

Polymer nanocomposites exhibit complex structural behavior due to physical and possibly also chemical interactions between individual components (polymer, clay, compatibilizer), which can be detected by rheology. From the commercial point of view, layered silicates (clays) are the most interesting nanoparticles for the reinforcement of polymers. In this contribution, polyethyleneterephthalate-clay (PET-clay) nanocomposites with different dispersion grades have been prepared and changes in physical network have been analyzed by oscillatory rheological parameters. As new type of the filler the clay functionalized with grafted polymer brushes was used. Grafted brush modified clay is a type of clay nanofiller that has been surface-modified with polymer brushes, which are long chains of polymer molecules attached to the surface of the clay. In general, this modification enhances the compatibility between the clay and the polymer matrix and improves the mechanical and rheological properties of the resulting nanocomposite material.

INTRODUCTION

Clay/polyethylene terephthalate (PET) nanocomposites are a type of hybrid material that combines the properties of clay nanoparticles with PET polymer¹. The fabrication process of clay/PET nanocomposites typically involves melt blending, which is a technique used to disperse the clay nanoparticles within the PET polymer matrix².

The first step in the fabrication process is to prepare the clay nanoparticles. This is typically done by intercalating the clay with an organic compound, which allows the clay layers to be separated and made more compatible with the polymer matrix. The intercalated clay is then mixed with PET polymer in a melt blending process, which involves heating the mixture to a temperature above the melting point of the PET polymer.

During the melt blending process, the clay nanoparticles are dispersed within the PET polymer matrix. The rheological properties of the resulting nanocomposite material depend on the degree of clay dispersion, as well as the clay content and the processing conditions.

The addition of clay nanoparticles to PET polymer can improve the mechanical properties of the resulting nanocomposite material, such as its tensile strength and stiffness. However, the addition of clay nanoparticles can also affect the rheological properties of the material, such as its viscosity and flow behavior.

Studies have shown that the addition of small amounts of clay nanoparticles can increase the viscosity of the PET polymer melt, while larger amounts of clay can lead to a decrease in viscosity. The addition of clay nanoparticles can also affect the shear-thinning behavior of the material, which is important for its processability.

In summary, the fabrication process and rheological properties of PET-clay nanocomposites are closely interrelated. The proper selection of processing conditions and the careful optimization of clay content are crucial for achieving the desired properties of the resulting material.

In our work we propose to use “traditional” and new type of the organoclay nanofillers for fabrication of the PET-clay composite materials. As new type of the fillers we used the clay functionalized with grafted polymer brushes. Grafted brush modified clay is a type of clay nanofillers that has been surface-modified with polymer brushes, which are long chains of polymer molecules attached to the surface of the clay. In general, this modification enhances the compatibility between the clay and the polymer matrix and improves the mechanical and rheological properties of the resulting nanocomposite material.

The application of grafted brush modified clay in the fabrication of PET-clay nanocomposites offers several advantages over traditional clay nanofillers. For example, the grafted brush modification increases the dispersibility of the clay in the polymer matrix, resulting in a more homogeneous and stable nanocomposite material. Additionally, the grafted brush modification can provide specific functional groups on the surface of the clay, which can be used for various applications such as flame retardancy or antimicrobial properties. The rheological properties of the grafted brush modified clay/PET nanocomposites can also be improved due to the enhanced compatibility between the clay and the polymer matrix. The grafted brush modification can reduce the viscosity of the PET polymer melt and improve the shear-thinning behavior of the nanocomposite material, which can improve its processability²

Overall, the use of grafted brush modified clay in the fabrication of PET-clay nanocomposites offers a promising approach for improving the mechanical and rheological properties of the resulting material, and for tailoring its properties for specific applications.

MATERIALS

The used clay mineral Cloisite Na⁺ (Na), was supplied by BYK-Chemie Ltd., Wesel, Germany. This natural clay was used as basis for synthesized materials with grafted polymer brushes (PBMA, PBA) on the surface.²

Colour-sorted recycled poly(ethylene)terephthalate (PET_R), was used as matrix.⁴

1.1. Preparation

1.1.1. Synthesis of samples

Grafting of polymer brushes is carried out in two stages (**Fig. 1.**):

1. Modification of clay fillers. 1 g of clay nanoparticles in the form of a powder is placed in 100 ml of distilled water, with constant stirring, a freshly prepared solution containing 1 g of APTES in 100 ml of distilled water is added. Intensive mixing is carried out for 30 minutes at room temperature.

After modification, ungrafted silane molecules are removed by washing the obtained substance several times with water and subsequent centrifugation. After that, the obtained substrate interacts with a multifunctional initiator based on a peroxide-containing oligoperoxide with chloride groups. For this, 100 ml of a 1% solution of the initiator in anhydrous dioxane is mixed with the amino-functionalized substrate. Stir intensively for 24 hours.

2. Graft polymerization of polymer brushes. The surface initiated by the initiator was placed in a metal cylinder with a stirring system, then filled with a 0.1 M solution of the

corresponding monomer in methanol. Samples are polymerized at a temperature of 90°C for 24 hours with constant stirring. After the polymerization time, the samples are removed and washed with ethanol and water.

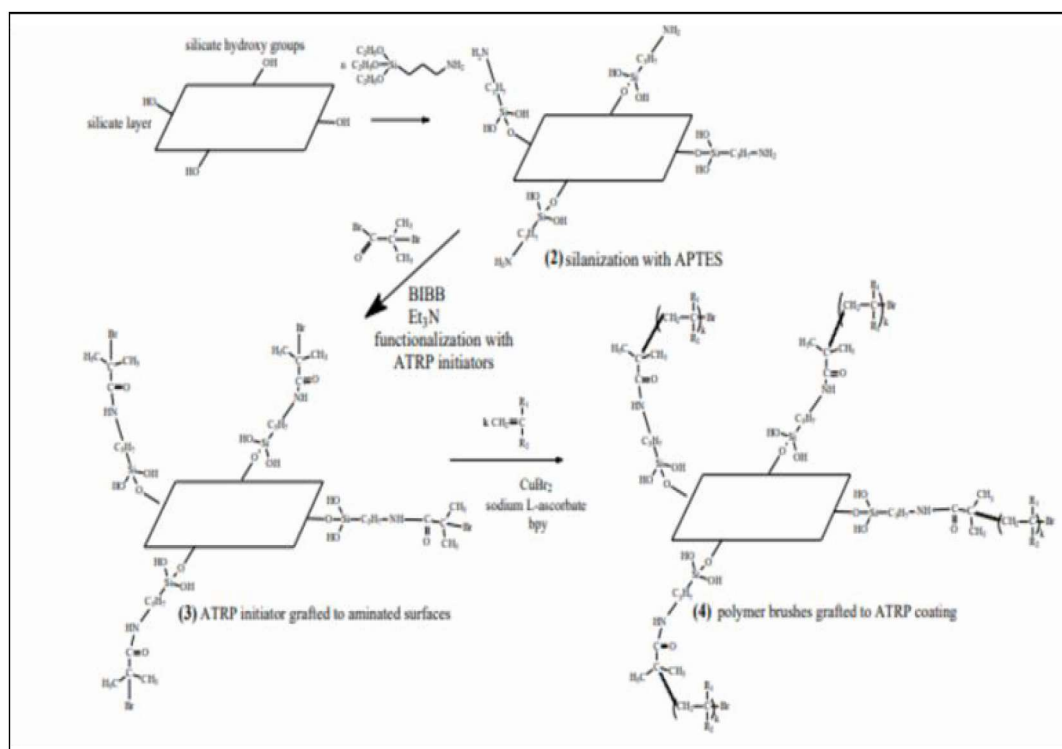


FIGURE 1: Functionalization of the surface of clay nanoparticles (1) by amino groups of APTES molecules (2), subsequent grafting of a multifunctional graft polymerization initiator (MFI) (3) and polymerization of monomers initiated by peroxide groups of MFI (MFI), resulting in the formation of polymer

METHODS

To analyze the samples used such methods as: Infrared spectroscopy (FTIR spectra), Thermogravimetric analysis (TGA), Dynamic Scanning Calorimetry (DSC), Rotational rheometry.⁵

Mixtures & samples have been prepared using laboratory compounder MiniLab II Haake Rheomex CTW5 in combination with Haake MiniJet Pro (Thermo Fisher Scientific, Germany). Performance of five different compositions (pure PET_R matrix, 5 wt% of different clay minerals in PET_R) have been compared. Rheological properties in the shear flow were studied using a Physica MCR 502 rheometer (Anton Paar Ltd., Graz, Austria) with the cone-plate geometry of 25 mm diameter and measuring gap of 43 μm.⁴

RESULTS

In our previous paper¹ was described a study on the rheological properties of clay/PET nanocomposites using a novel analysis approach. The study has investigated the effects of various factors on the rheological behavior of the nanocomposites, such as the type of

organoclay nanofiller, processing conditions, and the extent of PET degradation during recycling.⁶

This approach was developed now, where for fabrication of the clay/PET composites were used “traditional” organoclay nanofillers as well as clay nanofillers functionalized with grafted polymer brushes.

In our former works⁵, a method for fabrication of grafted brush-coatings using graft polymerization “from the surface” of multifunctional peroxide or ATRP initiators, grafted to a native surface functionalized with (3-aminopropyl) triethoxysilane (APTES), was developed. This strategy was extended in this work where CloisiteNa⁺ fillers were functionalized in three steps process: functionalization with APTES, fabrication of the initiating coatings onto CloisiteNa⁺/APTES; and finally fabrication of the grafted poly(butyl methacrylate) - PBMA or poly(butyl acrylate) - PBA brushes. The first step involved chemical functionalization of the “native” CloisiteNa⁺ fillers via covalent bonding of APTES and following grafting multifunctional peroxide initiator to amino groups of the attached APTES taking advantage of the interaction between amino groups of APTES coatings and pyromellitic chloroanhydride fragments in multifunctional peroxide molecules. The second step involved the grafting polymerization of the BMA or BA initiated “from the surface” of functionalized CloisiteNa⁺ fillers.

The functionalization process and properties of modified CloisiteNa⁺ were studied by FT-IR, TGA and DSC methods. The resulting “traditional” and functionalized CloisiteNa⁺ was used as fillers to fabricate polyethylene terephthalate nanocomposites and tune the rheological properties of “pure” polyethylene terephthalate (PET).¹

2.1. Rheological properties (rotational rheometer)

The nanocomposites dispersion grade and effect of matrix molar mass on final morphology can be evaluated using analysis of viscosity curve (shear-thinning effect) in combination with information obtained from the storage modulus curve (G' secondary plateau)⁴. In Fig. 1, Fig. 2, magnitudes of complex viscosity as well as storage modulus in dependency on angular frequency are plotted. As can be seen from **Fig.2**, the CPN systems prepared with PBA, Diethoxymethyl silane, PBMA, Oligoperoxide and Cloisite Na⁺ with PET-R. Matrix nanocomposite with prepared samples showed typical liquid viscoelastic behavior. CPN Cloisite Na⁺ (industrial sample), showed shear-thinning behavior only in a very short range of low frequencies. Concerning the range of high frequencies, the complex viscosity of CPN systems using Na⁺ was higher than that of PBA, Diethoxymethyl silane, PBMA, Oligoperoxide matrix, which reflects strong degradation reactions occurring during the processing.⁶

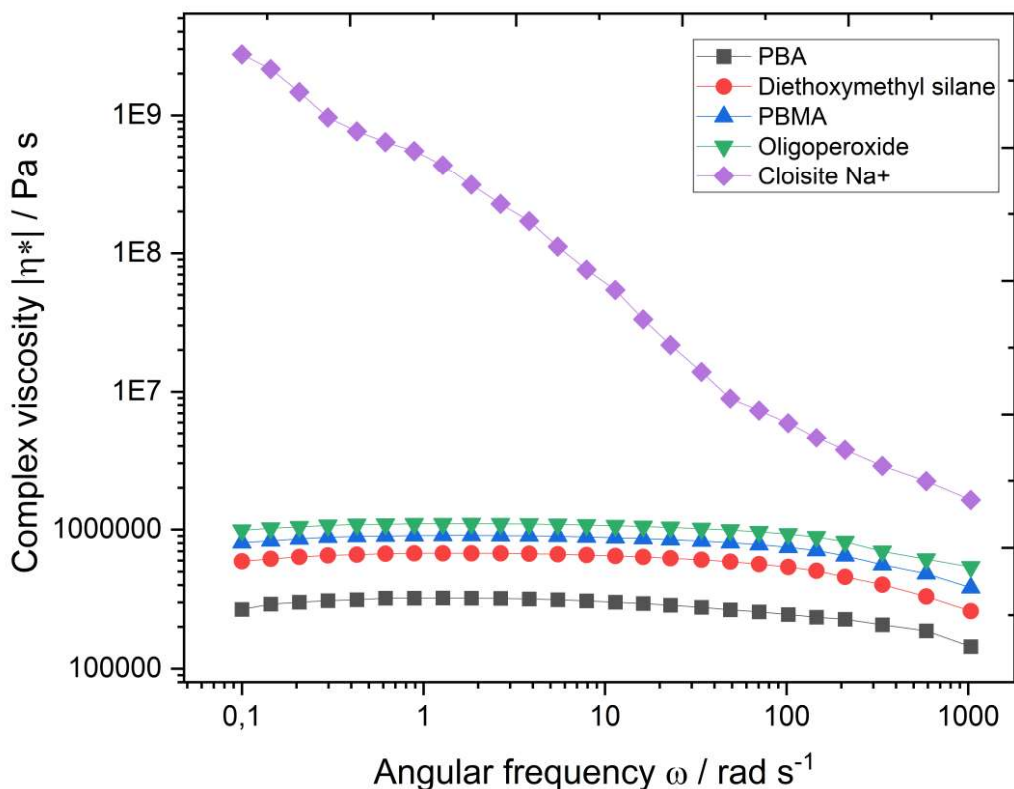


FIGURE 2: Complex viscosity of nanocomposites.

For CPN systems with high dispersion grade, the dependence of $G'(\omega)$ becomes almost invariable at low frequencies. Such “secondary” plateau indicates the formation of a network structure (“rubber-like” behavior) reflecting the exfoliation of clay layers in CPN.⁴ As can be seen in **Fig. 3**, CPN systems prepared with Cloisite Na⁺ showed “rubber-like” behavior i.e. high dispersion grade, while matrix as well as CPN nanocomposite with prepared samples exhibited typical viscoelastic behavior.

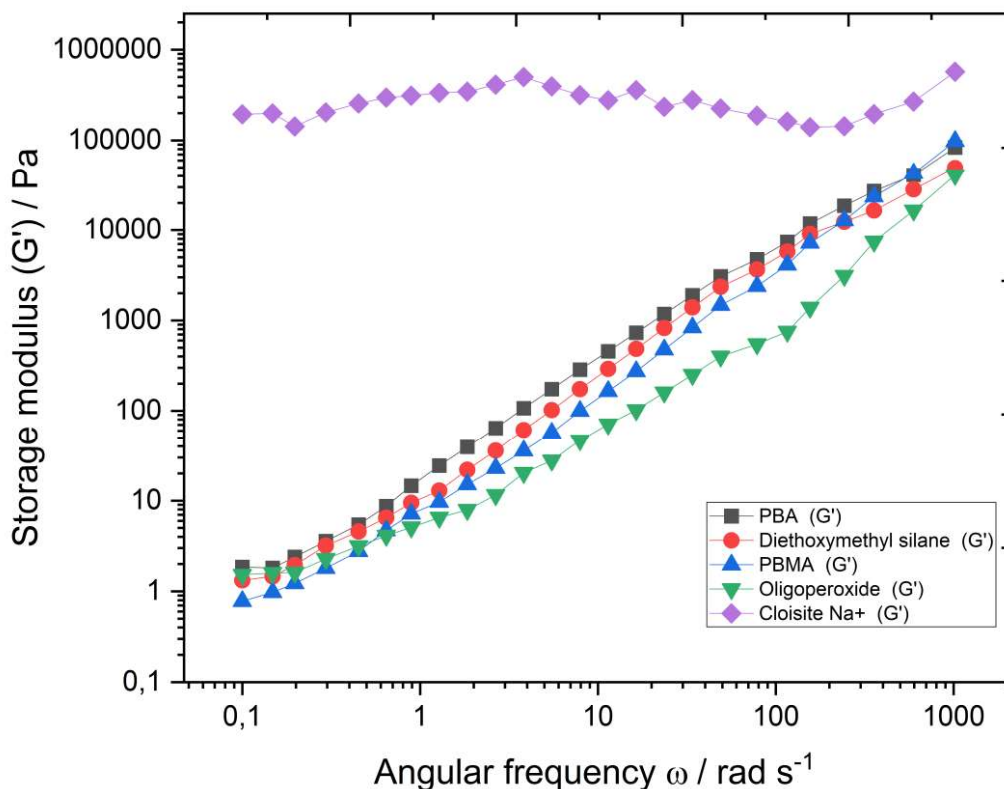


FIGURE 3: Storage modulus of nanocomposites.

According to **Fig. 4**, the samples produced by the new method have lower values of the loss modulus (G''), which indicates that these samples have a better processability compared to the sample Cloisite Na⁺. For all samples, the loss modulus (G'') is higher than the storage modulus (G') - the materials are susceptible to segregation. In this case, effects such as subsidence (re-agglomeration of clay particles) can be expected. On the other hand, it displays a predominantly viscous behaviour and is therefore not a stable structure.

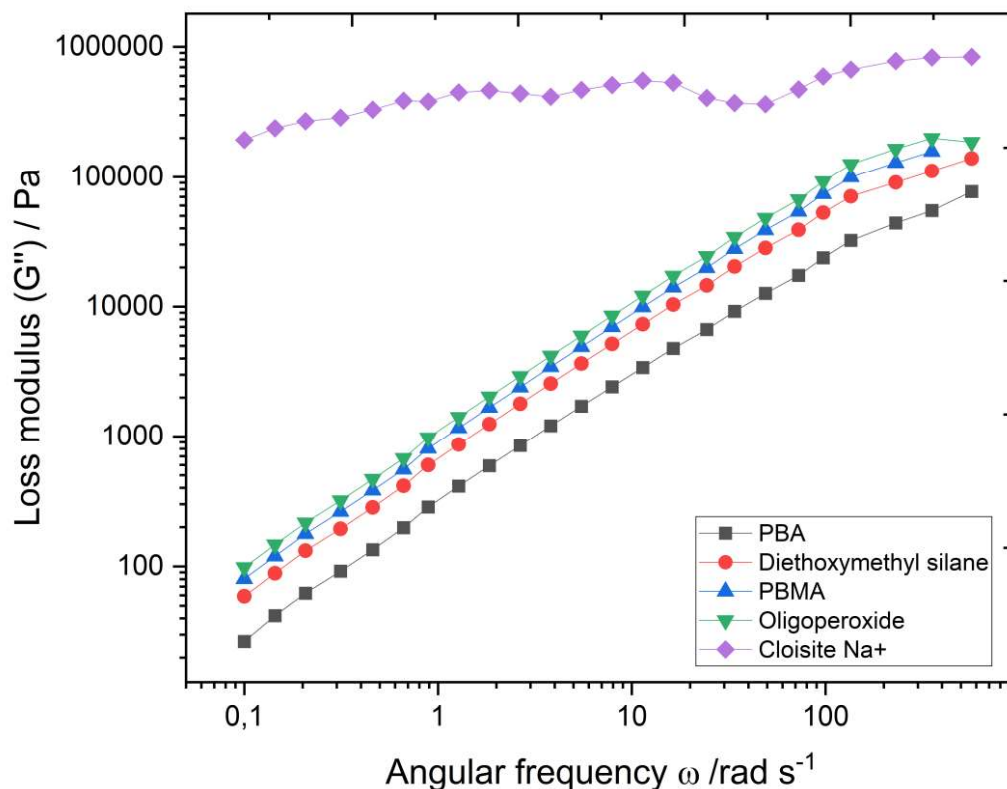


FIGURE 4. Loss modulus of nanocomposites.

CONCLUSIONS

As material development of PET-organoclay based nanocomposites faces high complexity (balance between reinforcement coming from rigid particles and degradation coming from side reactions), this way seems to be interesting for speeding up industrial applications of PET-clay systems.^{3,4,6}

The contribution describes the fabrication process and properties of PET-organoclay nanocomposites, which are a hybrid material that combines the properties of clay nanoparticles with PET polymer. The nanocomposites were prepared by melt blending the functionalized clay with PET polymer, which involves heating the mixture to a temperature above the melting point of the PET polymer. The addition of clay nanofillers to PET polymer can improve the mechanical properties of the resulting material, but can also affect the rheological properties such as its viscosity and visco-elasticity. The use of grafted brush modified clay in the fabrication of PET-clay nanocomposites offers several advantages over traditional clay nanofillers, such as enhanced compatibility between the clay and the polymer matrix, and improved mechanical and rheological properties. The study has investigated the effects of various factors on the rheological behavior of the nanocomposites and could provide insight into the mechanical and processing properties of clay/PET nanocomposites for various applications.¹

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