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Functional Block Copolymers as Compatibilizers for Nanoclays in Polypropylene Nanocomposites

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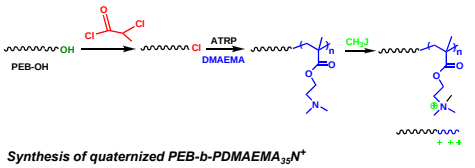
Introduction

Nanoclays (NCl) possess a significant ion exchange capacity. Wetting of their naturally hydrophilic surface by the matrix polymer is undoubtedly a prerequisite for nanocomposites (NC) formation. Usually the NCl surface is rendered compatible with organic molecules by an onium exchange of the Na^+ ions using hydrophobic surfactants like dimethyl dehydrogenated tallow ammonium ions.[1]

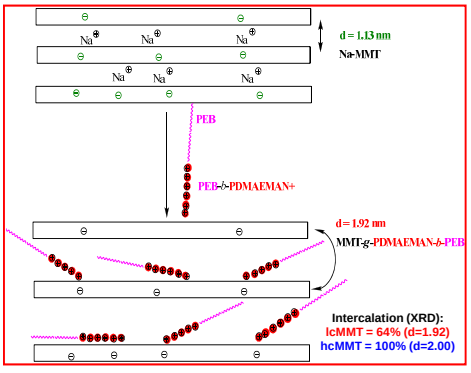
Design, synthesis & characterization of a compatibilizer for MMT - PP nanocomposites

With the aim of creating tough nanocomposits (NC) [1] based on polypropylene (PP) and nanoclay (NCl) in the framework of the 7th EU program NANOTOUGH we have designed amphiphilic block copolymers utilizing Atom Transfer Radical Polymerization (ATRP) [2]. They consist of a hydrophobic block of Kraton L-1203 from Kuraray Co., Japan with molecular weight 7000 and PDI=1.05 (compatible with PP), and a hydrophilic block of quaternized dimethylaminoethyl methacrylate, DMAEMA (capable to perform the Na^+ exchange):

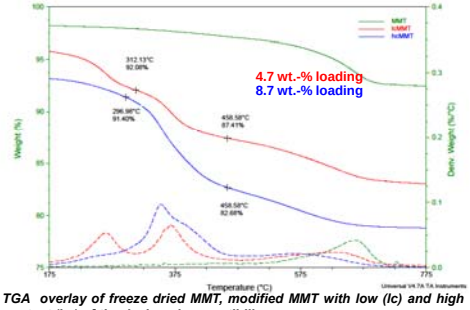


Synthesis of quaternized PEB-b-PDMAEMA$_{35}$N$^+$

The size of the hydrophilic block was varied, which increasingly caused better dispersibility of the block copolymer in water. This was essential for the exchange of the Na^+ ions of the used NCl (3.8 wt.-% aq. dispersion of montmorillonite, MMT from Laviosa Chimica Mineralia, Italy) by the synthesized charged block copolymer, which was performed in water. The modified MMT was then washed with water/ethanol until no Na^+ was detected (0.1 M $AgNO_3$) and freeze dried.



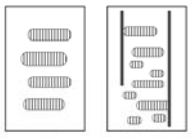
Possible intercalation with the charged block copolymer



TGA overlay of freeze dried MMT, modified MMT with low (lc) and high content (hc) of the designed compatibilizer

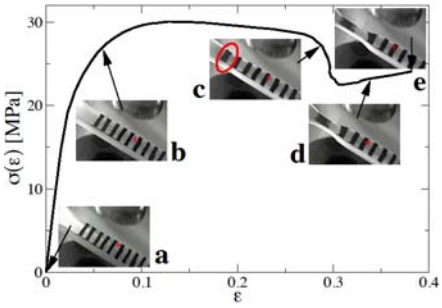
Abstract

Novel amphiphilic block copolymer has been designed, characterized and tested as a compatibilizer in PP-MMT nanocomposites in 2 different contents. SAXS has been used to monitor slow mechanical tests. The MMT acts like a nucleating agent to the PP that starts competitive nucleation of crystallites in the PP during manufacturing. Consequently, the PP crystallites in the composites are small and imperfect - the self-reinforcement of the PP is replaced by alien-reinforcement.

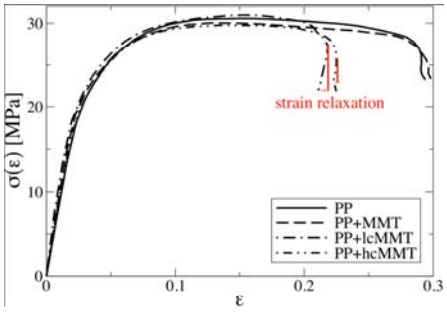


Simplified structural model for the semicrystalline structure of pure PP (left) and of the PP phase in the MMT nanocomposits (right). The thin vertical domains are drawn only to indicate that the composite contains MMT layers

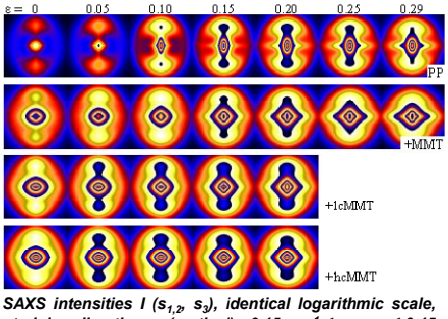
Stress relaxation



Stress relaxation and spot translation caused by necking in a true-stress curve σ (ε) as function of the local strain ε
a: *Start of test. The X-ray beam spot is indicated by a cross.* **b**: *Homogeneous stretching. Spot does not move.* **c**: *Necking has started (see ellipse). Material shows stress relaxation.* **d**: *Spot moving towards neck.* **e**: *End of testing.*

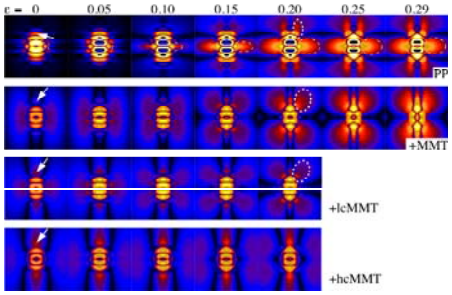


Tensile testing of PP/MMT nanocomposites. True stress σ (ε) as a function of local strain ε at the position of irradiation. Compatibilized materials exhibit even relaxation of local strain ε

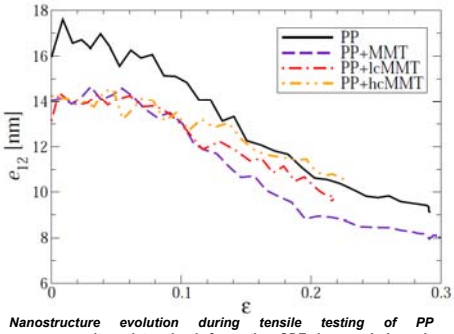


SAXS intensities I ($s_{1,2}$, s_3), identical logarithmic scale, straining direction s_3 (vertical), -0.15 nm^{-1} ≤ $s_{1,2}$, s_3 ≤ 0.15 nm^{-1}. Full patterns ranging to 0.25 nm^{-1}.

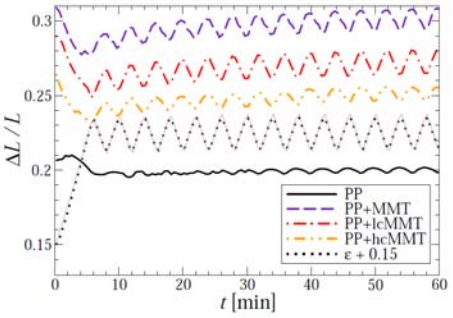
Nanostructure evolution



CDFs $|z(\gamma_{12}\gamma_3)\gamma|$ computed from SAXS, identical logarithmic scale, straining direction γ_3 (vertical), -60 nm ≤ $\gamma_{12}\gamma_3$ ≤ 60 nm



Nanostructure evolution during tensile testing of PP nanocomposites determined from the CDF long-period peak. Average lateral extension $e_{1,2}$ of the crystalline PP domains as a function of the local macroscopic strain ε in the irradiated volume



Nanostructure evolution during load cycling of PP nanocomposites determined from the CDF long-period peak. Relative standard deviation ΔL/Lof the long period distribution as a function of the elapsed time. Additionally the local macroscopic strain ε(t) is shown

Conclusions

- Novel block copolymer has been designed and tested as compatibilizer for PP/MMT nanocomposite.
- Missing improvement of the tensile properties appears to result predominantly from the inhibition of a load-bearing semicrystalline morphology inside the PP by the MMT.
- From the respective half-lives we have for the first time assessed the reinforcement of the composite and the weakening of the PP.

Acknowledgments

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