CHANGES IN THE MECHANICAL PROPERTIES OF POLYPROPYLENE BY ADDITION TWO TYPES OF NANOFILLERS: CARBON NANOTUBES AND ORGANOCLAY

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Abstract: The present work is focused on the mechanicalcharacterization of the prepared via extrusion mixing hybrid nanocomposites composed from two different nanofillers in polymer matrix. These nanocomposites include organoclay (OC) and multiwall carbon nanotubes (MWCNTs) in various combinations as fillers in an isotactic polypropylene (iPP) matrix. Three-phase polypropylene nanocomposites give comprehensive information about the macro-, micro- and nano-mechanical properties and provide information for better understanding the extent of reinforcement via nanoparticles.The carried out experiments give good overview of the changes in modulus of elasticity and elongation at maximum strength as well as scratch coefficient of friction, nano hardness and Young's modulus with variation of the fillers concentrations.

Keywords: polypropylene, nanofillers, mechanical properties, three-phase nanocomposites

I. INTRODUCTION

Polypropylene (PP) is the second most commonly used synthetic plastic in the world (after polyethylene), the revenue of which is expected to exceed $ 145 billion by 2019. PP's sales are expected to grow at 5.8% per annum by 2021. [1] Among the existing wide range of materials used as nanoparticles, carbon nanotubes (CNTs) are considered to be among the best fillers due to their extraordinary structural, physicaland mechanical properties. [2-4] The inclusion of CNTs in PP can potentially provide structural materials with a dramatic increase in both hardness and strength. On the other hand, nanocomposites containing organoclay in polypropylene (PP/OC) have been extensively studied.[5-7]Organoclays can give high levels of polymers reinforcement in low concentrations, making it attractive for replacing conventional fillers in many applications. Depending on the resulting structure of nanocomposites containing OC (intercalated, exfoliated or phase-separated), barrier properties of the polymer may be dramatically increased. Nowadays, for these two binary systems based on PP (PP/CNTs and PP/OC), there is a considerable amount of information in the literature, and their properties are widely explored. However, there is limited information in the literature for higher level nanocomposites (three-phase nanocomposites) with combination of nano-sized fillers such as CNTs and OC in PP.

Salawudeen et al. studied and compared the mechanical properties of a conventional binary nanocomposite and ternary nanocomposite that combines CNTs and modified clay as reinforcement agents in a PP matrix. [8] The results show that the addition of MWCNT to PP/modified clay increaseswith 42% in the modulus, 26.20% in the tensile strength and 13,30 Kj.m-2 impact strength when compared with binary combination of PP/Clay nanocomposites. This behavior justifies the potential properties of carbon nanotubes. However, the XRD analysis of structure shows the combination of intercalated and micro mixing due to some agglomeration formed during the process.

V. Levchenko and colleagues observed the effect of the addition of a third phase (OC) on the structure, electrical, thermal, and mechanical properties of two-phase polymer composites of PP/MWCNT. [9] The introduction of OC and MWCNTs in the PP matrix strongly affects the crystallization of matrix as well as changes in the electrical and mechanical properties of PP. Addition of organoclay (MWCNT/OC ratio was 1/1) reduced the percolation threshold of PP/MWCNT nanocomposites from Φc = 0.95 vol.% to Φc = 0.68 vol.% of carbon nanotubes, while the level of conductivity became 2–4 orders of magnitude higher. Differential scanning calorimetry (DSC) and Dynamic mechanical analysis (DMA) analyzes shows that the influence of organoclay on the thermal and mechanical properties of the material is more significant in the three-phase nanocomposites compared to two-phases PP/OC.

Three-phase nanocomposites could be considered as a hybrid type of nanocomposites due to their nature because they content several components. [10] Hybrid systems contain at least three phases, making the relationship between structure and properties much more complex than well-known two-phase systems. Therefore, obtaining three-phase nanocomposites is a difficult task due to the additional technological production steps.

The focus of this survey is on the study the changes in the mechanical properties of three-phase nanocomposites containing small amounts of two types of nanofillers: varying amount of MWCNT in the range of 0.5-5 wt.% and a constant amount of 3 wt. % OC.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

Isotactic polypropylene, PP6231 (Lukoil Neftochim Bourgas AD) is the matrix polymer. Organically modified clay, Cloisite 30B (Southern Clay Products, Inc) and Plasticil PP2001 - commercial masterbach of 20 wt.% MWCNT in PP are used as fillers. For the preparation of nanocomposites 20 wt.% clay is dispersed by extrusion mixing in PP adding 12 wt.% MA-g-PP (Fusabond 613, Maleic anhydride content 0.5 wt.%, Du Pont), as a compatibiliser. Then, the appropriate amount of both masterbatches - 20 wt.% MWCNT/PP and 20 wt.% OC/PP are diluted with the polypropylene by melt mixing with a double screw extruder Collin Teach-line Compounder. The composites were produced at the screw speed of 45 rpm in the temperature range 180-200 □C. In order to improve the nanofillers dispersion, the compositions were extruded in three runs. Variety of compositions was prepared containing 3 wt.% OC and 0.5-5 wt.% MWCNT in PP.

The mechanical properties of obtained three-phase nanocomposites were evaluated on three levels as follows: 1) tensile tests were performed to determine the macro-mechanical characteristics; 2) the tribological (micro-mechanical) properties are evaluated by a scratch test; and 3) the nano-mechanical properties (nano-hardness and Young's modulus) are defined by nanoindentation tests.

Tensile tests and scratch tests were carried out on UMT-2 Universal Tester (modular system) developed by Bruker. Tensile tests were performed by using 1-100 kg (1000 N) sensor. The set tensile speed is 1 mm/min at room temperature. The тensile tests was determined by testing 10 samples of each compositionfor more accurate research results. The scratch tests conditions were: a diamond scratch blade with 0.8 mm tip radius is exerting 2N constant normal force (Fz) while scratching the sample surface with constant velocity of 0.083 mm for 10 mm linear displacement (X).

The nanoindentation tests were carried out on UNMT Material Tester developed by Bruker. The test conditions were as follows: a diamond Berkovich type indenter is exerting gradually increasing normal load from 0 to100mN.

RESULTS AND DISCUSSION

As can be seen from fig.1(a) the addition of only 0.5 wt.% MWCNTs sharply increases the Young's modulus of 780 MPa for the pure PP, up to 850 MPa for PP/0.5CNT. This significant increase of Young's modulus at low filling can be explained by the influence of MWCNTs on the PP crystallization process. Further addition of nanofillers lead to a linear increase of Young's modulus. Thus, in a content of 5 wt.% MWCNTs, the value of Young's modulus is PP5CNT = 985 MPa, with 26%higher than PP. This tendency is also maintained for the three-phase materials, so for highest amount of fillers (total 8 wt.%) the value of Young's modulus is PPMA5CNT3OC = 1070 MPa, with 38% higher than pure PP. Tensile strength increased (~ 18%)with a sharp jump from 33 MPa for PP to 39 MPa for PP5CNT, observed at low content of 0.5 wt.% MWCNTs, seen from fig.1(b).While,by the addition of 3 wt.% OCthe tensile strength remains almost unchanged regarding tothree-phasenanocomposites.Elongation at ultimate strength decreases proportionally with increasing the amount of nanofillers in polypropylene for both nanocomposites materials two- and three-phases.(fig.1c). The tribological behavior for two-phase and three-phase systems differs with respect to scratch coefficient of friction are shown on Fig.2.

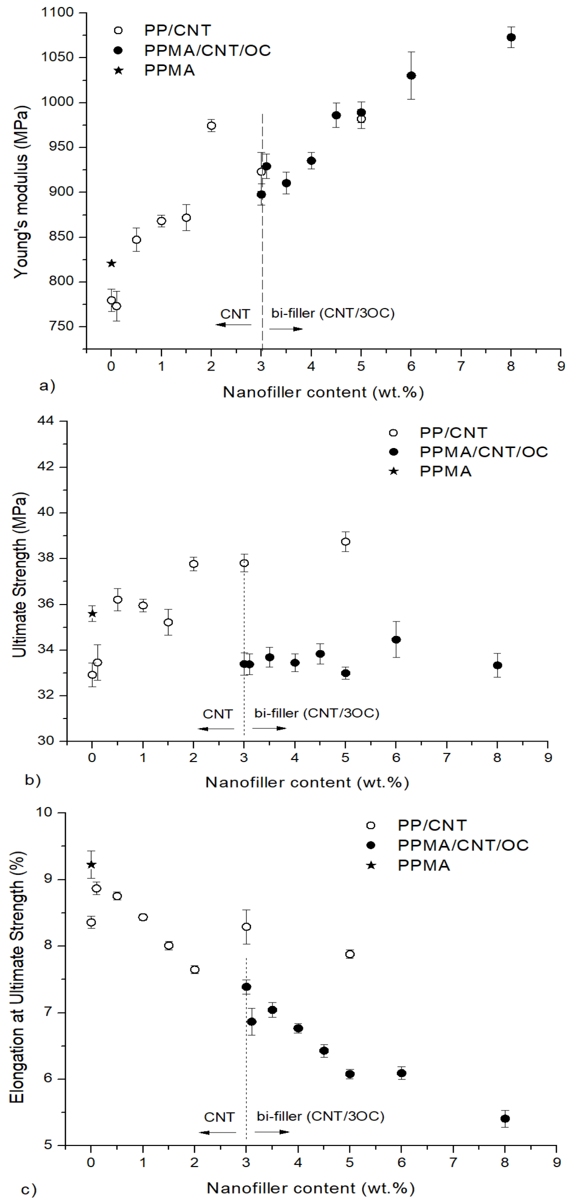


Fig.1.Young's modulus (a), Ultimate strength (b) and Elongation at ultimate strength (c) from tensile tests vs. total amount of filler content (8 wt. % CNT and OC) for two-phase and three-phase nanocomposites

Differences in scratch resistance have been observed on the behavior of two- and three-phase systems, which is the effect of adding MWCNTs at different concentrations to the polymer. The scratch coefficient of friction indicate that the two-phase systems show a significant reduction (-20%) in the coefficient of frictionat 5 wt.% MWCNTs. This significant effect of improving the tribological characteristics of PP is due to the excellent frictional properties of MWCNTs. On the other hand, three-phase systems have a lower (-24%) scratch coefficient of friction comparedto the two-phase systems primarily due to the influence of the maleic anhydride modifier on the PP structure.

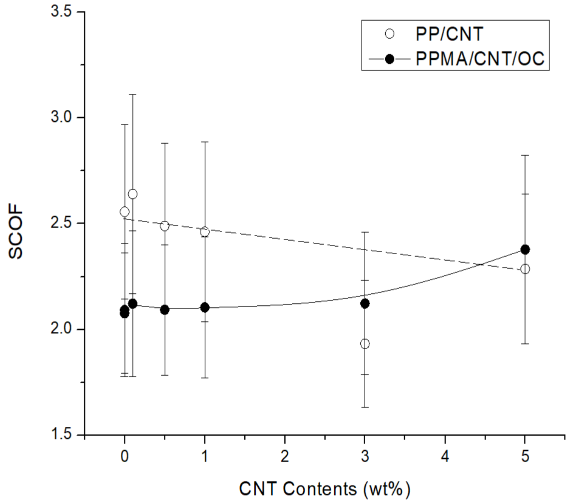
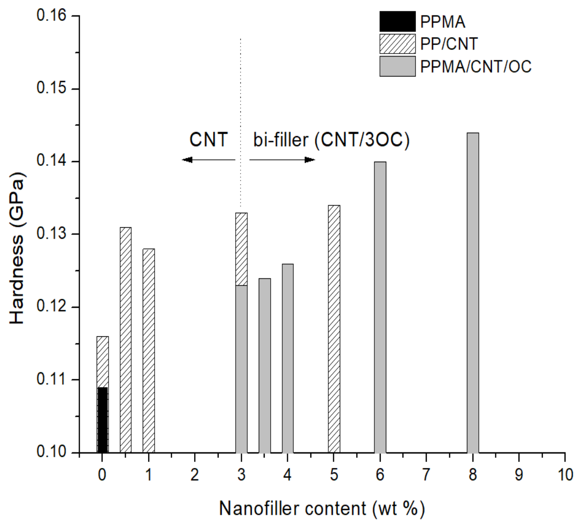


Fig.2. Scratch coefficient of friction (SCOF) as a function of MWCNTs content for two-phase and three-phase nanocomposites

Hardness and Young's modulus obtained from nanoindentation testversustotal amount of filler content of the two-phase and three-phase nanocomposites at maximum load of 100 mN, are shown on fig,3. Arrows point the flocculation ($\Phi c \sim 0.5$ wt. %)and the percolationthresholds ($\Phi p = 1.5$ wt.% MWCNTs for two-phase and $\Phi p = 2$ wt.% MWCNTs for three-phase systems)defined rheologically on previous publications. [11,12]



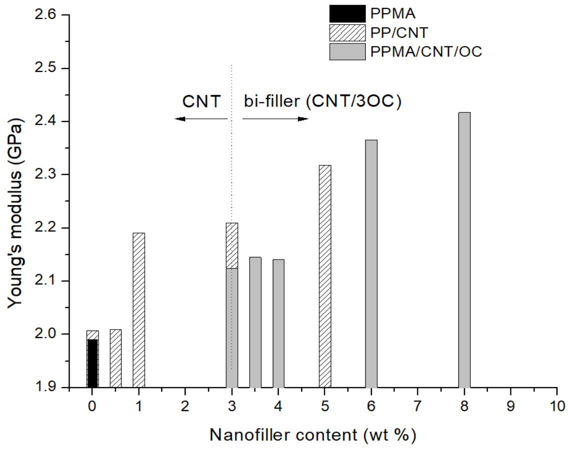


Fig.3. Hardness (a) and Young's modulus (b) from nanoindentation test vs. total amount of filler content of the two-phase (PP/MWCNT) and three-phase (PP/MWCNT/OC) composites at maximum load of 100 mN.

The indentation investigations show comparison of the changes of hardness and Young's modulus, observed with adding different concentrations of MWCNTs, with and without OC. The present graphs demonstrate general improvement of the hardness and elastic properties for both two-phase and three-phase systems. The main difference comes from the fact that the two-phase system exhibits transition to plateau formation between 0.5 and 1 wt.% loadings, while the properties of the three-phase system begin to rapidly improve after these values of MWCNTs concentrations. The joint effect on three-phase systems (PPMA/CNT/OC) for enhancing the hardness and elastic modulus of nanoconduction is explained by the interpenetrated structured network of MWCNTs fractals and finely dispersed clay layers.

CONCLUSIONS

This research work is aimed at studying the changes on the mechanical properties of PP nanocomposites containing two nanofillers.

The tensile test results show a significant increase (9-10%) of the Young's modulus and tensile strength at low concentration of CNTs (0.5 wt.%) due to the influence of CNT on the crystallization processes of PP and size reduction of the spherulites. The subsequent increase in filler content resulted in a significant increase in Young's modulus. However, the tensile strength of the three-phase materials remains almost unchanged, which can be explained by the poor interfacial interactions after the addition of the second filler.

Improved hardness and scratch resistance in a small amount of 0.5 wt.% CNT results in a hardness jump of about 20% in CNT/PP but retains the elastic characteristics of PP. This is due to the effect of nanotubes on the structure and morphology of the polymer and the reduction of PP spherolites.

The presence of OC in three-phase systems slightly decreases the effect of MWCNTs about threshold flocculation, but greatly increases the reinforcing effect of the filler above the flocculation and around the threshold of percolation. Thus, ternary systems with two types of fillers become stronger and more rigid than binary systems and both of fillers participate in the formation of the percolating structure.

These results can serve as a solid base for conducting additional experiments, improvement of material design parameters and further research in order to create material suitable for food packaging applications, which meets all European standards and regulations.

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