12th National Congress on Theoretical and Applied Mechanics
23-26 September 2013, Saints Constantine and Helena, Varna, Bulgaria

INVESTIGATION ELECTRICAL AND RHEOLOGICAL PROPERTIES OF PP/MWCNT/OC NANOCOMPOSITES

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ABSTRACT. There is limited information about the three-phase hybrid nanocomposites combining two types of nanofiller in polymer matrix, while the incorporating nanofiller in different polymer matrix are developed and investigated for years. In such three-phase nanocomposite the joint effect of the two nanofillers on the optimum property improvement of the polypropylene nanocomposites will be evaluated depending on microstructure, dispersion state and the ratio between the two nano-phases.

KEY WORDS: nanocomposites, electrical properties, rheology, nanofillers

1. Introduction
In this work, the influence of multi-walled carbon nanotubes (MWCNT) and organoclay (OC) on electrical and rheological properties of isotactic polypropylene (iPP) nanocomposites is studied [1, 3]. The reinforcing effect of organoclay and carbon nanoparticles has been estimated with two approaches based on rheology and molecular dynamics [2, 4] evaluated by dielectric relaxation spectroscopy (DRS), and thermally stimulated depolarization current (TSDC) [5, 6]. Rheology is used as a very sensitive method for characterization of the degree of dispersion of MWCNTs and organoclay at various mixing. DRS were used to measure the dielectric properties of the nanocomposites as a function of frequency. It was based on the interaction of an external field with the electric dipole moment of the sample, or expressed by permittivity. TSDC method was used to measure the thermally activated release of stored dielectric polarisation. It corresponds to measuring dielectric losses against temperature at constant low frequencies 10² - 10⁴ Hz.
2. Materials and method
The present nanocomposites include organoclay and MWCNTs in various combinations as fillers in isotactic polypropylene as a matrix. Commercial masterbatch of 20 wt% MWCNT/PP, handedly prepared masterbatch 20 wt% Cloisite 30B/PP and MA-g-PP were used for the nanocomposites preparation. The nanocomposites were made in Institute of Chemistry and Technology of Polymers, CNR, Pozzuoli, Italy by melt mixing method which consist: double screw extruder Collin Teach-line Compounder and Collin Teach-line Strand Pelletizer apparatus in temperature zones: 180 °C; 200 °C; 200 °C, 190 °C, 180 °C; 40 - 50 rpm; and 3 run.

To performing the measurements disk-shaped samples with diameter of 20 mm and thickness of 1mm was prepared by compression moulding in a press at 80 °C for 6 min.

3. Equipment
The rheological characteristics of those nanocomposites were measured using AR-G2 Rheometer with Electrically Heated Plate geometry. Dynamic viscosity, storage and loss moduli were measured in the angular frequency of 0.03÷100 Rad/s at low strain amplitude of 0.01. The linear viscoelastic range of the strain amplitude was determined by strain sweep test at angular frequency of 1 Hz.

Dielectric relaxation spectroscopy was measured using a Novocontrol Alpha Analyzer at temperature 30 °C. In this technique the sample is placed between the plates of a capacitor, an alternate voltage is applied, and the response of the system is studied.

Thermally Stimulated Depolarization Currents is complementary technique to DRS. It consists of recording the thermally activated release of frozen-in polarization and corresponds to the measurement of dielectric losses as a function of temperature at constant low frequencies in the range of 10⁻² - 10⁻⁴ Hz using Novocontrol Quatro Cryosystem.

3. Experimental results
3.1. Rheology
Figure 1 visualizes storage and loss moduli (G’, G”) versus angular frequency. With increasing nanotube loading we observed significantly increasing of storage and loss moduli (a) for PP/MWCNT. The behavior on PP/MWCNT/OC nanocomposites (b) is similar to the binary PP/MWCNT system - by increasing the nanofiller content is observed proportionally increasing of storage and loss moduli values. Moreover, in the volume fraction of 3 % G’ and G” shows trend to an equilibrium plateau in the terminal region, (G’> G”) and this could be related to the formation of a network structure (solid-like behaviour).

The dynamic viscosity shown on figure 2 strongly increases by increasing the nanotube content above 1 wt% for the PP/MWCNT compositions and above 0.5 wt% for the PP/MWCNT/Clay. The shear thinning behavior of the PP/MWCNT
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melts observed with increasing the filler content is attributed to the strong nanotube interactions in the melt dispersions.

Figure 1 Storage and Loss moduli (G’, G”) versus Angular frequency (ω) on the (a) PP 6231 and two-phase PP/MWCNT nanocomposites; (b) PP+12%MAgPP, two-phase PP+3%Clay and three-phase PP/MWCNT/OC nanocomposites in various combinations.

Figure 2 Dynamic viscosity (η’) versus Angular frequency (ω): (a) on the pure PP 6231 and PP/MWCNT nanocomposites and (b) PP+12% MA-g-PP, PP+3% Clay and PP/MWCNT/OC nanocomposites in various combinations

Rheology can provide information for both the percolated network structure and the interaction between filler and polymer matrix.

Figure 3 shows $G'_0$ versus MWCNT content on the PP/MWCNT and PP/MWCNT/OC nanocomposites. It can be seen the slope of $G'_0 (\phi)$ function
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(scaling exponent μ) changes strongly above 1 wt% MWCNTs in both two and three-phase nanocomposites. We relate these critical nanotube contents with the rheological percolation threshold, \( \varphi_p \). \( G'_0 \sim \varphi \mu \)

![Figure 3](image.png)

**Figure 3** \( G'_0 \) values (at \( \omega = 10^3 \text{ s}^{-1} \)) versus MWCNT content on the PP/MWCNT and PP/MWCNT/OC nanocomposites

### 3.2. DRS

Figure 4 illustrate imaginary part (\( \varepsilon'' \)) of the dielectric permittivity versus the frequency (f).

![Figure 4](image.png)

**Figure 4** Imaginary part (\( \varepsilon'' \)) of the dielectric permittivity versus the frequency (f): (a) on PP 6231 and PP/MWCNT nanocomposites and (b) PP+12% MA-g-PP, PP+3% Clay and PP/MWCNT/OC nanocomposites in various combinations

As can be seen from the graphs there is two conductive samples: PP+3%MWCNT and PP+3%MWCNT+3%Clay, meaning that addition on MWCNT
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between 1% and 3% made PP conductive (electrical percolation threshold). Further more PP+3%MWCNT+3%Clay ternary nanocomposite (Fig. 4, b) shows higher value of the dielectric permittivity compared with PP+3%MWCNT which probably is joint effect between MWCNTs and clay.

3.3. TSDC

TSDC results are shown on Figure 5. Pure PP and PP+MWCNTs samples give weak relaxation peaks in the temperature range of -40 to +40 °C – TSDC graphs (a, b). The impressive result is the peak (at around 0 °C) observed in the samples with 3% clay (a, c). This peak may be associated with free charges polarization mechanism, but this has also to be confirmed by other measurements.

4. Conclusions

The dynamic storage and loss moduli increased significantly with increasing nanofiller loading, particularly in the low frequency region for PP/MWCNT similar to the behavior on ternary PP/MWCNT/OC nanocomposites. The volume fraction of 3 % G’ and G” shows trend to an equilibrium plateau in the terminal region, and this could be related to the formation of a network structure. The dynamic viscosity strongly increases by increasing the nanotube content above 1 wt% for the PP/MWCNT compositions and above 0.5 wt% for the PP/MWCNT/Clay. The shear thinning behavior of the PP/MWCNT melts observed with increasing the filler content is attributed to the strong nanotube interactions in the melt dispersions.

Generally for dielectric and electrical properties it was observed a clear tendency of increasing conductivity with increasing the content of conductive nanofiller carbon nanotube in the non-conductive polymer matrices of polypropylene. The dc conductivity appears above the percolation threshold (φ ≥
Due to the peculiarity in the network structure and interfaces, the conductivity values observed for the new ternary nanocomposites are higher, if compared to that of the two phase nanocomposites.

Acknowledgement
This research work was financially supported by the COST Action FA 0904 and COST Action MP 1202.

I wish to thank Dr. S. Cimmino, Prof. C. Silvestre, Dr. D. Duraccio, Dr. M. Pezzuto from Institute of Chemistry and Technology of Polymers, CNR, Pozzuoli, Italy, as well as to Dr. A. Kyritsis and C. Chatzimanolis-Moustakas from NTUA, Athens, Greece. Also thanks my supervisors Prof R. Kotsilkova and Dr. E Ivanov.

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