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DIELECTRIC ANALYSIS OF INTEGRITY IN POLYPROPYLENE - NANOCARBON COMPOSITES

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ABSTRACT

Composite materials of polypropylene and graphene nanoplatelets were synthesized by *in situ* polymerization. GNP particles consist of 3 - 5 graphene layers and have aspect ratio 40. In composites with pristine GNP particles their aspect ratio is 110, whereas ultrasonic processing reduces it to 40 - 50. This change of aspect ratio of filler particles and their aggregates results in different properties of composites with pristine and sonicated GNP. Percolation threshold for composites with pristine GNP is 0.25% vol. In composites with sonicated GNP it is 2-3% vol. This is due to reduction in the size of filler particles aggregates and more uniform distribution of particles in polymer matrix after ultrasonic treatment.

Keywords: dielectric analysis, polypropylene, nanocarbon, graphene, nanocomposites.

INTRODUCTION

Electrical properties of polymer nanocomposites strongly depend on the method of preparation. Percolation threshold increases in the sequence: mixing in solution - polymerization *in situ* - mixing in the melt (Verdejo, 2011). The method of *in situ* polymerization makes it easy to adjust many characteristics of nanocomposites, such as concentration of filler, the average distance between particles, etc. Accordingly, this research was aimed at the synthesis of nanocomposites using well-characterized graphene nanoplatelets particles and investigation of their electrical properties in a wide frequency range, with dielectric analysis allowing to evaluate structural parameters of nanocomposites, which have potentially wide practical applications (Kim, 2010).

Composite materials of isotactic polypropylene (iPP) and graphene nanoplatelets (GNP) were synthesized by *in situ* polymerization in liquid propylene with the use of metallocene catalyst system. Graphene nanoplatelets (GNP) were prepared by the method of chemical oxidation of graphite and its subsequent reduction. Combined Raman and X-ray data show, that the length of crystallites in **a** direction is equal to 45 nm and the ratio of crystallites size in directions **a** and **c** (particles aspect ratio) equals 40. Dielectric properties of nanocomposites in microwave range (3.2-20 GHz) were evaluated by the cavity resonance method with rectangular-shaped resonators (H_{01n} operating mode). Real and imaginary permittivity and conductivity in frequency range 10^{-2} – $10^{7}cs^{-1}$ were measured using impedance analyzer Novocontrol Alpha-A equipped with dielectric cell ZGS Alpha Active Sample Cell and gold-plated disk electrodes 20 and 30 mm in diameter.

RESULTS

NANOCOMPOSITES WITH GNP MECHANICAL PROPERTIES

The stress–strain properties of the nanocomposites were studied under quasistatic tension. From σ–ε curves the values of elasticity modulus *E*, yield point σ_f, and ultimate strength and strain at break were determined. It was found that low filler content increases tensile modulus. At 1–1.5 vol % GNP, modulus is 25–35% higher, compared to the matrix polymer. The dependences of relative elongation at break and yield points on GNP content, both pristine and sonicated, are presented in Fig. 1.

The introduction of filler results in a drastic drop in strain properties of the composites, which is more pronounced for composites with the pristine GNP (Fig. 1a). For composites with pristine GNP σ_f decreases by 15% at 1.25 vol % of the filler, whereas for sonicated GNP σ_f is practically independent of composition (Fig. 1b), which conforms to the changes in deformation behaviour of PP, filled with smaller and higher specific surface particles (Dubnikova, 2003).

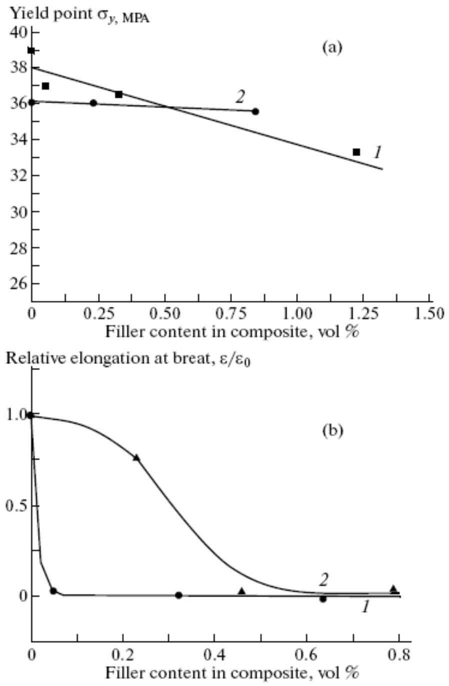

Fig. 1. Dependence of relative elongation at break $\varepsilon/\varepsilon_0$ (a) and yield point σ_y (b) of composites on filler content: (1) pristine GNP and (2) sonicated GNP (20 min).

DIELECTRIC PROPERTIES

For all composites *dc* conductivity σ_{dc} and dielectric properties were studied in the range 10^2–10^6 c/s and in the microwave range (3×10^9–3×10^{10} Hz). For composites with pristine GNP conductivity of 1.9×10^{-7} (Ohm cm)$^{-1}$ was found in composite with 2.4 vol % of filler. The composites with sonicated GNP have conductivity of 1.5×10^{-10} and 1×10^{-6} (Ohm cm)$^{-1}$ at GNP content of 2.9 and 5.6 vol %, respectively. This gives the value of percolation threshold of 2–3 vol %, which is significantly lower compared to *in situ* polymerized IPP with graphite (Nedorezova, 2004). Measurements of *ac* conductivity indicate transition from dielectric behaviour to conducting regime and, consequently the value of the threshold (Fig. 2,3).

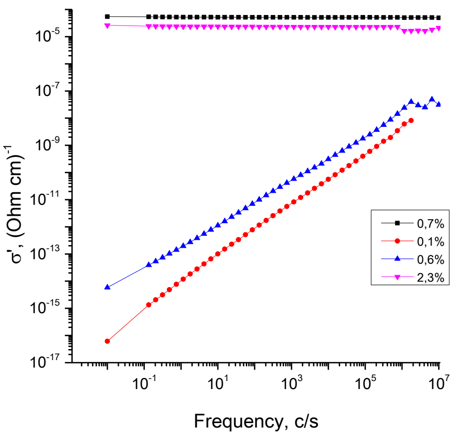

Fig. 2. Frequency dependence of real conductivity σ' for composites with pristine GNP particles at different filler concentrations.

From the data of Figure 2 we can conclude that the value of percolation threshold is approximately 0.3 % vol.

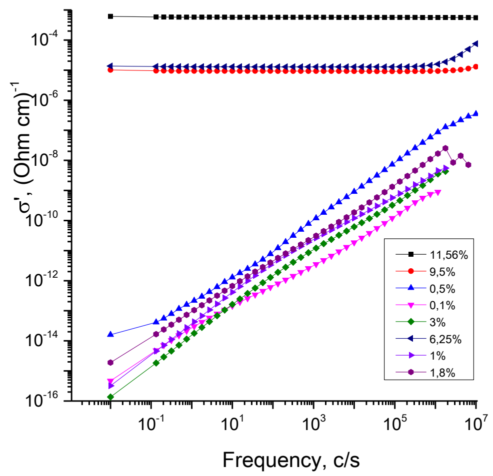

Fig. 3. Frequency dependence of real conductivity σ' for composites with sonicated GNP particles at different filler concentrations.

From these data we can conclude that the value of percolation threshold is ~ 0.05 wt. fraction, or ~ 2.5 vol. %, which is much higher than in the case of pristine graphene particles.

IPP/GNP composites are characterized by high values of permittivity (ε') and dielectric losses (ε'') in the microwave range. Permittivity and dielectric losses increase with increasing filler content, especially for composites with pristine GNP (Fig. 4). In the whole range of frequencies (3.2–11 GHz), permittivity of the composites with sonicated GNP is substantially lower than in the case of pristine GNP. The dependences of ε' on GNP concentration were analyzed using a mathematical model, proposed by the authors earlier (Kovalchuk, 2008). The calculations show that the effective particles aspect ratio (or their aggregates) of pristine GNP in composite is equal to 112; for sonicated GNP aspect ratio reduces to 48 (20 min) and further to 39 (60 min). This suggests that GNP particles in composite form small-sized anisotropic aggregates. Ultrasonic processing provides, apparently, a more uniform distribution of GNP particles, which in nanocomposite remain largely individualized. Therefore, nanoparticles of GNP in the composite are in the form of extended anisotropic forms (these can include particle aggregates, since the model allows to define the aspect ratio rather than absolute sizes) (Shevchenko, 2012).

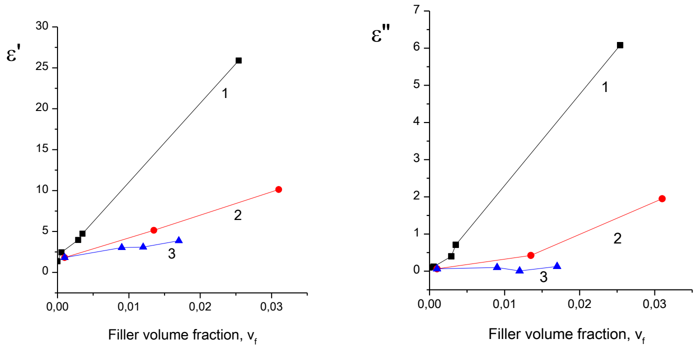

Fig. 4. Dependence of permittivity and losses on filler concentration (4.8 GHz). 1) Pristine GNP particles; 2) GNP sonicated 60 min; 3) GNP sonicated 20 min.

The change in filler particles aspect ratio is probably responsible for differences in the properties of composites with sonicated GNP. GNP as a filler with high conductivity imparts polymer composites the ability to absorb high frequency electromagnetic radiation. An important factor is that percolation threshold is relatively high and local conductivity is combined with the absence of essential bulk conductivity. This significantly increases dielectric losses, while permittivity still remains considerably lower than in the presence of bulk conductivity. For IPP and IPP/GNP composites, coefficients of reflection for microwave electromagnetic waves from 26 to 35 GHz for the samples placed on a metal substrate are shown in Table.

Table. Coefficients of reflection (R) from the samples of IPP and IPP/GNP composites at different frequencies

GNP, vol.%	R, dB (26 GHz)	R, dB (30 GHz)	R, dB (35 GHz)
IPP	-	-	98%
IPP/GNP (pristine)			
0.05	-0.3 (93%)	-0.2 (95.5%)	-0.5 (89%)
0.35	-0.6 (87%)	-0.93 (81%)	-0.8 (83%)
1.1	-1.3 (74%)	-2.0 (63%)	-3.0 (50%)
IPP/GNP (sonicated 20 min)			
1	-0.7 (85%)	-0.9 (81%)	-1.5 (71%)
4.6	-7.1 (19%)	-7.5 (18%)	-5.2 (30%)

Since film thickness was as low as 300 μm, these data show that the composites possess good electrodynamic properties and are promising materials for development of electromagnetic radiation shields of absorbing type. Sonication of GNP changes the effective aspect ratio of the filler particles, while this ratio defines the frequency and width of the maximum of dielectric losses. Therefore, sonication of filler allows to control the parameters of absorption band of electromagnetic radiation shield (width and median frequency). Hence, the synthesis of PP-based composite materials with nanocarbon fillers via *in situ* polymerization can provide quite uniform distribution of filler and result in materials with advanced properties.

NANOCOMPOSITES WITH MULTIWALLED CARBON NANOTUBES

DIELECTRIC PROPERTIES

Analyzing electrical properties of the materials in microwave range provides deep insight into the microstructural features of the synthesized PP/MWCNT composites. Microwave studies indicate conspicuous difference in the electrical properties of the isotactic iPP/MWCNT nanocomposites as compared to the syndiotactic sPP/MWCNT. Thus, the iPP/MWCNT nanocomposites exhibit considerably higher permittivity values in comparison with the sPP/MWCNT materials. Slower growth of the sPP/MWCNT permittivity with increasing filler content is attributed to the nanotube agglomeration. The slope characterizing linear dependence between permittivity of composite and MWCNT concentration depends on the filler particles depolarization coefficient, which is determined by the aspect ratio of filler particles (length/diameter ratio for nanotubes). As a result, the approximate nanotube aspect ratio for the iPP/MWCNT nanocomposites is ~25, and for the sPP/MWCNT it is ~10. These values obtained from microwave electrical measurements only roughly correspond to the actual CNT aspect ratios in synthesized materials and can be used only for the relative comparison of nanotube aspect ratios in two systems. Accordingly, we can conclude about the formation of less anisotropic MWCNT clusters in the sPP/MWCNT composites with diameter ~2.5 times higher as compared to those in iPP/MWCNT nanocomposites. Thus, microwave electrical analysis provides easy solution for studying nanotube agglomeration in various composite systems and their comparison. Dielectric loss factor of the materials also correlates with the interfacial area in the composites. Consequently, the iPP/MWCNT nanocomposites exhibit higher dielectric losses in the comparison with the sPP/MWCNT materials

Functionalized nanotubes are better compatible with polymer and hence will rearrange differently in the matrix. Microwave measurements demonstrate differences in the electrical properties between the composites containing purified and functionalized MWCNTs revealing structural transformations in the materials caused by the nanotube functionalization. The angle of slope of the near linear dependences between the nanocomposite permittivity and filler concentration is increased for the composites filled with C_{11}-MWCNTs. The slope of the respective line depends on the depolarization coefficient of filler particles, which is determined by the aspect ratio (*l/d*) of nanotubes. According to calculations, the relative average aspect ratio for nanotubes increases from ∼25 for iPP/MWCNT to ∼32 for the iPP/C_{11}-MWCNT system and from ∼10 for sPP/MWCNT to ∼19 for sPP/C_{11}-MWCNT. The given values do not correspond to the actual nanotube aspect ratios in the investigated composites and only allow us to make approximate comparison of MWCNT anisotropy coefficients in different composite systems. These results demonstrate considerable improvement in the MWCNT dispersion efficiency achieved by the chemical functionalization for the sPP-based composites, functionalized nanotubes more fully exhibit their "native" aspect ratio in composite material. Incorporation of MWCNTs in iPP or sPP imparts electromagnetic absorbance properties to the polymers. The increased aspect ratio in combination with the method of synthesis preventing electrical contacts between individual nanotubes makes these materials suitable for effective absorption of electromagnetic radiation. Considerable dielectric losses (electromagnetic energy dissipation) within the iPP/MWCNT nanocomposites have been detected in microwave range. The sPP/MWCNT composites displayed notably reduced electromagnetic energy dissipation as a result of much lower interfacial area that has been discussed above. The better nanotube dispersion in the sPP/C_{11}-MWCNT materials caused by the chemical functionalization improves electromagnetic absorbance properties of the composites. The iPP/C_{11}-MWCNT nanocomposites, however, exhibit some reduction in dielectric losses in comparison with the iPP/MWCNT materials despite the improved nanotube dispersion. This fact can be attributed to the distortion of the nanotube π conjugated electronic structure caused by the chemical functionalization that leads to sacrificing microwave absorbance properties of the composites.

CONCLUSIONS

GNP as filler with high electrical conductivity imparts to polymer composites the ability to absorb high-frequency electromagnetic radiation. An important factor is that the percolation threshold is relatively high: high local electrical conductivity is combined with the lack of significant bulk conduction. This greatly increases dielectric losses, with dielectric constant being much smaller than in the presence of bulk conduction, which reduces reflection of electromagnetic waves at the interface free space - nanocomposite. Analysis of electrical properties of the nanocomposites in a microwave range provides deep insight into the microstructural features and integrity of the synthesized materials. Microwave electrical analysis provides convenient solution for studying nanoparticles aggregation in various polymer composite systems.

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