

Effect of Modified Clay on the Morphology and Electric Properties of PC/ABS-MWCNT Composites

Stefano Besco,¹ Michele Modesti,¹ Alessandra Lorenzetti,¹ Stefano Donadi,¹ Tony McNally²

¹Department of Process Chemical Engineering, University of Padova, 35131, Padova, Italy

²School of Mechanical and Aerospace Engineering, Queen's University of Belfast, BT95AH, Belfast, United Kingdom

Received 10 December 2010; accepted 22 April 2011

DOI 10.1002/app.34727

Published online 22 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Composites of MWCNTs and an organically modified partially synthetic layered silicate (OMLS) with PC/ABS were prepared by melt blending and the relationship between morphology and electric properties as a function of composite composition examined. The concept of double percolation was investigated and confirmed, as a consequence of CNT preferential segregation within one polymer phase (PC). A role of OMLS in hin-

dering the formation of an effective electrically conductive network was observed above a certain clay loading, resulting in a shifting of electrical percolation threshold towards higher values. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3617–3625, 2012

Key words: nanotubes; layered silicate; double percolation; melt blending; electric properties

INTRODUCTION

Polymers generally have a high electrical resistivity, which accounts for the insulating character of these materials. While for many applications this is a desirable feature, electrically conducting polymers represents an interesting solution for specific applications (e.g., automotive and electronics). Traditionally the less expensive and most conventional method to enhance electrical conductivity of polymers by orders of magnitude is to melt mix them with conductive carbon-based fillers like carbon black (CB).

To obtain materials with high conductivity, high amounts of CB are needed often leading to a worsening of other physical properties of the polymer. Recently, carbon nanotubes (CNTs) have been introduced as effective electrically conducting fillers: they can be described as long and slender fullerenes with hexagonal carbon (graphite) structure and can either be single walled (SWCNTs) or multiwalled (MWCNTs). Till now, CNTs have been added to several polymer systems¹ including thermosets,² thermoplastics,^{3–7} and elastomers.^{9,10} CNT-filled polymer composites exhibit good electrical conductivity at much lower filler loadings if compared to those acquired by CB or metal powder-filled polymer composites, and as such polymer/CNT composites are ideal candidates for antistatic, electrostatic

dissipative, or electromagnetic radiation shielding materials.

More recently increasing attention has also been focused on the incorporation of conductive fillers into immiscible polymer blends to improve their conductivity at much lower filler content due to the double percolation phenomenon. It refers to the percolation of a conductive filler within one phase in a polymer blend (first percolation), which itself percolates in the mixture (second percolation). The first studies in this direction were presented by Sumita et al.¹¹ with the analysis of immiscible blends filled with carbon black. Sumita et al.¹² also reported about polyethylene/polypropylene/CB composites where the filler located preferentially in the polyethylene phase, yielding a high electrical conductivity for a very low carbon black loading.

Gilman et al. examined the electrical conductivity of short carbon fiber filled polyolefin-based blends¹³ and showed that the percolation threshold could be considerably reduced when the carbon fiber had a high aspect ratio. Other studies considered PC/polypropylene/MWCNTs/clay blends¹⁴, polyamide 6/acrylonitrile-butadiene-styrene/MWCNTs systems¹⁵ and polyamide6/polypropylene/MWCNTs composites¹⁶. In each instance an enhanced electrical conductivity of the composite was achieved due to filler double percolation and to the cocontinuous phase morphology of the polymer blend.

Pötschke et al. reported about PC/polyethylene (PE) blends with MWCNTs prepared by melt mixing^{17–19}, observing that significantly increased conductivity values of the blends could be achieved in the composition range in that PC forms a continuous

Correspondence to: M. Modesti (michele.modesti@unipd.it).

phase within PE due the double percolation phenomena¹⁷.

With regard to PC/acrylonitrile-butadiene-styrene/MWCNTs (PC/ABS/MWCNTs) blends, specific studies by Sun et al.²⁰ recently focused on the evaluation of the effect of ABS rubber content on the localization of MWCNTs and subsequent composite morphology and electrical properties.

Moreover Goldel et al.²¹ investigated the selective localization and migration of MWCNTs in PC/styrene acrylonitrile blends (SAN) observing as, regardless the way of introducing nanotubes, they exclusively located within PC phase, resulting in a much lower electrical resistivity than the one of pure PC and SAN. The phenomena has been explained by the differences in interfacial energies of the filler and polymers, which originates from the differing polarities and surface energies.

In our article we examine the correlation between the morphology of PC/ABS/MWCNTs blends and their electrical properties when a hybrid filler system of MWCNTs and an organically modified synthetic mica (OMLS) is introduced. Considering the cited results from specific literature, the effects of the OMLS on nanotube localization and consequently on the percolation threshold value were investigated using a multiscale approach based on the comparison of electrical and morphological properties, that were examined by means of electron microscopy, XRD analyses, and static electrical tests and dielectric analyses.

EXPERIMENTAL

Raw materials and processing

A polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) blend (Bayblend T45, Bayer Materials GmbH.) characterized by a ratio PC : ABS of 45 : 55 and a MVR of 12 cm³/10 min (260°C, 5 kg) was ground to a fine powder using a Wedco single stage grinding mill and chilling the system with liquid nitrogen. MWCNTs were produced by Sun Nanotech by carbon vapor deposition (CVD) with a > 90% purity (after purification), an average diameter of 10–30 nm and average length of 1–10 μm.

A synthetic clay (Somasis MTE, CO-OP Chemical, Japan) based on a fluoromica ion exchanged with (3-*n*-octyl,1-methyl) ammonium chloride was used together with MWCNTs to prepare PC/ABS-MWCNT-OMLS composites containing different quantities of MWCNTs (0.5, 1, 1.5, 2, 4, and 6 wt %) and two different OMLS loadings (0, 1, or 3 wt %).

The polymer, in powder form, was dry blended with the OMLS and MWCNT powders and then dried at 90°C overnight. The composites were prepared by melt mixing using a twin screw extruder

Collin GmbH. model ZK25 and using a melt temperature of 260°C and a screw speed of 100 rpm, when steady flow was reached. A Collin P200P platen press was used to prepare thin disks (60 mm diameter, 0.4–0.6 mm thickness) from extruded pellets, for DC electrical measurements.

Characterization

Structure and morphology

Composite morphology and the degree of filler dispersion and distribution were investigated using transmission electron microscopy. Thin slices of thickness of about 100 nm were obtained with a LKB ULTRATOME V, stained using an OsO₄ solution and then examined with an electron transmission microscope model FEI CM 120 using a voltage of 80 kV.

WAXD patterns were recorded in a 2θ angular range from 1.5° to 40° with a Philips X'Pert PRO diffractometer (reflection geometry) equipped with a graphite monochromator on the diffracted beam (Cu-K_α radiation) using a scan step size of 0.02° 2θ.

Electric and dielectric properties

The volume resistivity (DC) of all materials was measured on compression molded samples (60 mm × 0.4 to 0.6 mm). For poorer electrically conducting samples (i.e., volume resistivity higher than 10⁸ Ω cm), a Keithley 8009 Resistivity Test Fixture combined with a Keithley electrometer Model 6517 was used, with the application of a voltage of 500 V. For more conductive samples (i.e., volume resistivity less than 10⁸ Ω cm) strips with dimensions of 50 × 10 mm² were tested by means of a Keithley electrometer (Model DMM 2000) using silver paste to minimize contact resistance. A minimum of five specimens were analyzed for each sample.

To measure the frequency dependent (AC) conductivity a dielectric analyzer (DEA) TA Instruments 2970 was employed at a frequency analysis ranged from 10⁻¹ Hz to 10⁴ Hz at 60°C under nitrogen 0.5 L/min. The measurements were carried out on hot pressed squared films of about 20 mm in width and 0.4–0.6 mm thickness and contact with electrodes was obtained with the application of a force of 400N. A minimum of five specimens were analyzed for each sample.

RESULTS AND DISCUSSION

Electric and dielectric properties

The volume resistivity of the different composites is shown in Figure 1 as a function of MWCNT loading. For the PC/ABS-MWCNT composites (i.e., without OMLS) an electrical percolation threshold of

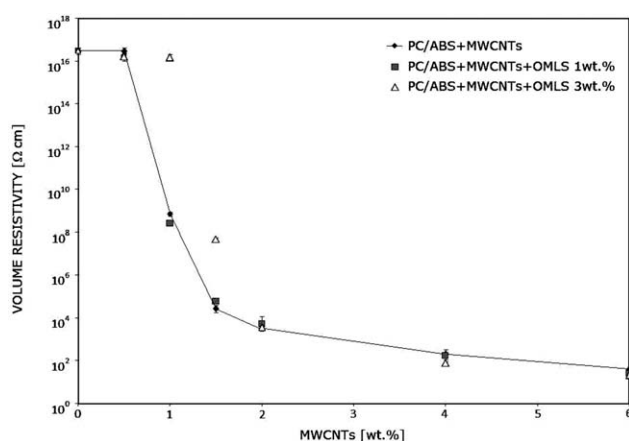


Figure 1 Volume resistivity of PC/ABS based composites varying MWCNTs and OMLS contents.

between 0.5 wt % and 1 wt % was achieved and for the composite with 2 wt % MWCNTs, the resistivity decreased significantly by about 12 orders of magnitude from 10^{16} to 10^4 Ohm/cm. For loadings above 1 wt % MWCNTs, the composites are electrically conducting. Dealing with PC/ABS/MWCNTs blends the influence of ABS copolymer on MWCNT dispersion and localization within a specific component (PC) was recently confirmed by Sun et al.²⁰ The authors observed that when PC represents the continuous phase (with cocontinuous morphology) and MWCNTs are selectively localized only in the PC phase, the addition of ABS increased the effective concentration of MWCNTs within PC (the volume of MWCNTs to the sum of the volume of MWCNTs and the polymer) and thus the electrical resistivity decreases. When instead ABS content is very high (70-100 wt %), PC becomes the dispersed phase and ABS the continuous phase: hence, with MWCNTs confined in the isolated PC particles, conductive path cannot be formed and as a result the electrical resistivity becomes very high.

Also Goldel et al.²¹ reported that volume resistivity of PC/SAN/MWCNTs blends, if compared with those of neat PC/MWNTs and SAN/MWNTs, are strongly reduced at the same filler loadings confirming the morphological observation of double percolation phenomena. Dealing with our investigations we observed that when OMLS (1 wt %) was added to PC/ABS-MWCNT composites, the volume resistivity behavior was not affected by clay content, while the addition of higher OMLS loadings (3 wt %) resulted in a shift of the percolation threshold towards higher values, between 1 wt % and 2 wt %. Statistical percolation theory predicts the dependence of composite conductivity from filler concentration using a scaling law in the form^{22,23}:

$$\sigma = \sigma_0(\Phi - \Phi_c)^t \quad (1)$$

where σ represents volume resistivity, Φ is the generic MWCNT weight fraction, Φ_c is the weight fraction threshold value, and t is defined as the critical exponent.

To estimate the percolation threshold, the experimental data were fitted using the power law reported above for the composite conductivity near percolation threshold²²⁻²⁵ and basically $\log \sigma$ versus $\log(\Phi - \Phi_c)$ data have been plotted incrementally varying Φ_c until the best linear fit has been obtained by linear regression (maximization of R^2 value).

The scaling law indicates a low percolation threshold of 0.98 wt % MWCNTs for composites without OMLS and with 1 wt % of clay, while the addition of 3 wt % OMLS yields to a remarkable increase of Φ_c ($\Phi_c = 1.55$).

Furthermore, for the blend system in this study, the variation in σ as a function of MWCNT and OMLS content gave the best fits using the scaling law with a critical exponent $t = 2.89$ for composites without OMLS. The addition of the lowest amount of OMLS (1 wt %) does not alter this value (as previously observed from the σ versus Φ curves), while for the composite with the highest OMLS amount (3 wt %) a slight decrease of t was obtained, with $t = 2.26$ and $\sigma_0 = 1.6 \cdot 10^{-3}$.

The critical exponent t is expected to depend on system dimensionality, with calculated values of $t = 1.33$ in 2 and t above 2 in 3 dimensions, respectively.²⁰ Several authors have fit their experimental data for polymer/CNT composites obtaining values of predominantly in the range between 1.6 and 2.0.¹⁶ However, published experimental results have also reported critical exponents varying from 1.2 to 3.1.^{16,26} This approach is somewhat limited in extracting geometrical information about the CNT network from experimentally determined values of t . First, scaling is limited to a concentration range very close to the percolation threshold. Moreover, the results of statistical percolation theory are derived for ideal systems which contain a homogeneous dispersion of identical particles while polymer/CNT composites are far away from being ideal systems. A further complication arises from the kinetic factors influencing percolation thresholds, which makes the application of statistical percolation theory questionable in this instance¹⁶.

It has also been proposed that the curvature or flexibility of MWCNTs within the matrix can influence the critical exponent.²⁷ It was demonstrated theoretically for a random CNT network that if the CNTs are very twisted, the critical exponent increases because MWCNTs tend to reach a more "sphere-like" structure. Furthermore, twisted MWCNTs are apparently shorter with smaller aspect ratios. Considering that MWCNTs have a lower degree of dispersion in the styrenic phase,²⁰ it is possible that they tend to twist to keep within the

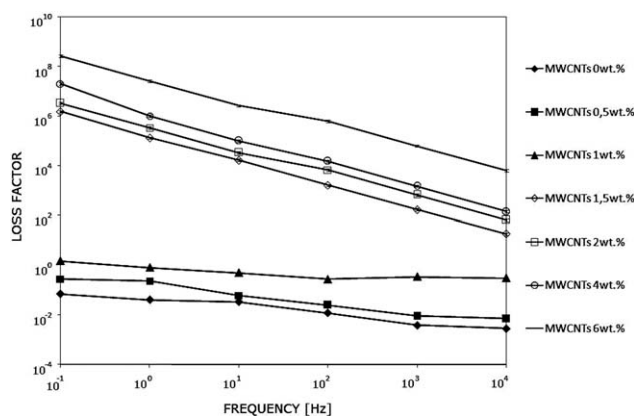


Figure 2 Loss factor as a function of the test frequency varying MWCNTs content in PC/ABSMWCNTs composites (60°C). Error bars are represented but smaller than symbols.

PC phase, as previously hypothesized by Fragneaud et al. considering similar systems in which selective localization occurs.²⁶

To get more information about composites properties dielectric behavior has been analyzed in a range between 0.1 Hz and 10^4 Hz. Figure 2 shows the variation in loss factor, ϵ'' for PC/ABS-MWCNT composites (without OMLS) with filler content as a function of frequency for isothermal conditions (60°C). The curves obtained can be readily distinguished into two groups. Similar tests were also carried out at different temperatures and showed the same qualitative behavior to those obtained at 60°C. For brevity, only the data obtained at 60°C is reported here.

The composites with 0.5 wt % and 1.0 wt % MWCNTs have a nearly constant ϵ'' value whereas, the composites with MWCNT loading higher than 1.0 wt % show a significantly different behavior. Here, ϵ'' decreased with increasing frequency. Non-percolating materials have a typical dielectric response in which the conductivity, that is proportionally dependent on ϵ'' from Debye equations, is a function of frequency. Moreover, for these materials, the AC conductivity increased with increasing MWCNT weight fraction. This result is particularly evident in Figure 3, where the conductivity of PC/ABS-MWCNTs without OMLS are observed with varying MWCNT content in a range of frequencies of six decades (from 0.1 to 10,000 Hz). Some authors reported that the phenomenon is probably due to the capacitive effect of the filler in the matrix²⁶: each tube acts as an isopotential metallic filler, and forms locally a nano-capacitance with its neighbors. As a consequence, the higher the MWCNT weight fraction the lower the distance between conducting particles.²⁶ This is in good agreement with our observations from the DC conductivity tests (Fig. 1), which is a measure of the long range movement of the

charge carriers when an electric fields frequency tends to zero.

The electrical conductivity has been calculated from ϵ'' values²⁸ using the following expression where f represents frequency (Hz) and ϵ_0 is $8.854 \cdot 10^{-12}$ F/m:

$$\sigma = \epsilon''(2\pi f)\epsilon_0 \quad (2)$$

In Figure 3 above a critical weight fraction the appearance of a conductivity plateau can be observed, with values that are independent of frequency and with a dramatic change in the conductivity of about seven/eight orders of magnitude. The continuous plateau is representative of the ohmic conduction due to the continuous network of nanotubes embedded within the matrix. However, for low concentrations of nanotubes, many isolated particles are still acting as nanocapacitors and the capacitive transport effect, that is frequency dependent, starts to become more important than the ohmic one.^{29,30}

When OMLS was added to PC/ABS-MWCNTs composites the percolation threshold tended to slightly shift towards higher MWCNT content for both 1 wt % OMLS and 3 wt % OMLS (Fig. 4) addition, with respect to the composites with MWCNTs only and independent of the AC frequency employed. Moreover, at higher frequencies (100 Hz) higher values of loss factor are possible due to the influence of the capacitive contribution of MWCNTs.

Hence, to give an explanation of the observed phenomena regarding the effect of OMLS on percolation threshold a microscale morphological approach is required to investigate the effect of the clay on nanotubes dispersion and localization.

Structure and morphology

TEM has been used to investigate blend structure and the extent of MWCNTs/OMLS dispersion and

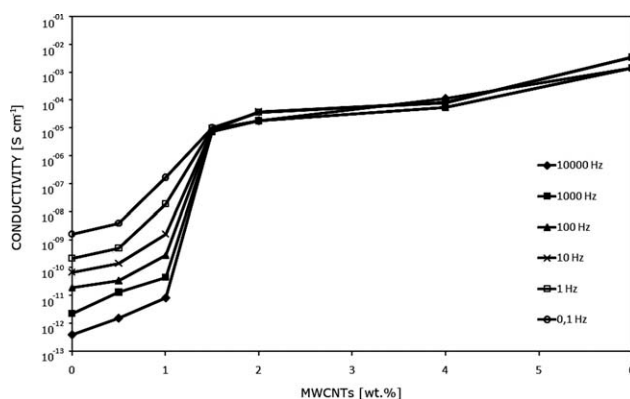


Figure 3 Electrical conductivity as a function of MWCNTs content and frequency in isothermal conditions (60°C). Error bars are not represented because smaller than symbols.

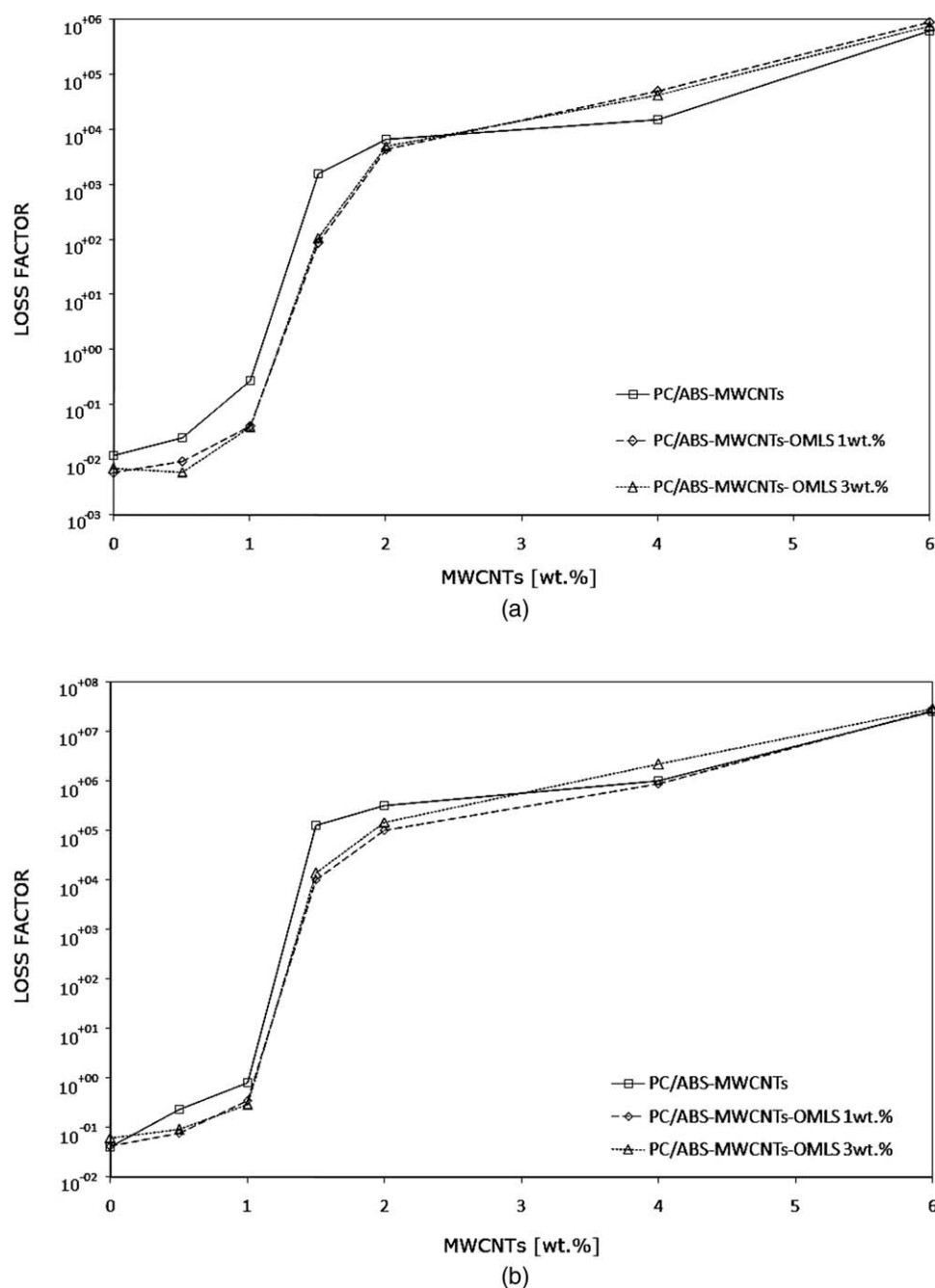


Figure 4 Loss factor as a function of MWCNTs and OMLS amounts measured at 100 Hz (a) and 1 Hz (b) in isothermal conditions (60°C).

distribution in the composite matrix. By way of example, for the PC/ABS-MWCNTs composites the 2 wt % composite was analyzed to examine the micro-structure of the conductive network just above the electrical percolation threshold (as observed by DC electrical resistivity and AC dielectric tests). Because of the low voltage used (80 kV) for the images shown in Figure 5, the brighter continuous phase represents PC while the darker gray areas with a size of 0.5–2 μm are ABS. Moreover, as reported previously,³¹ ABS has a complicated struc-

ture where styrene-acrylonitrile (SAN) phase contains islands of black polybutadiene (PB) rubber (stained by OsO₄) in which white particles of SAN are embedded. Comparing these micrographs the MWNTs appear to be homogeneously dispersed within the PC phase and are mainly present as single particles.

To assess in particular OMLS dispersion, for the PC/ABS-MWCNTs-OMLS composites, representative images of the composite containing 2 wt % MWCNTs and 3 wt % OMLS are shown in Figure 6.

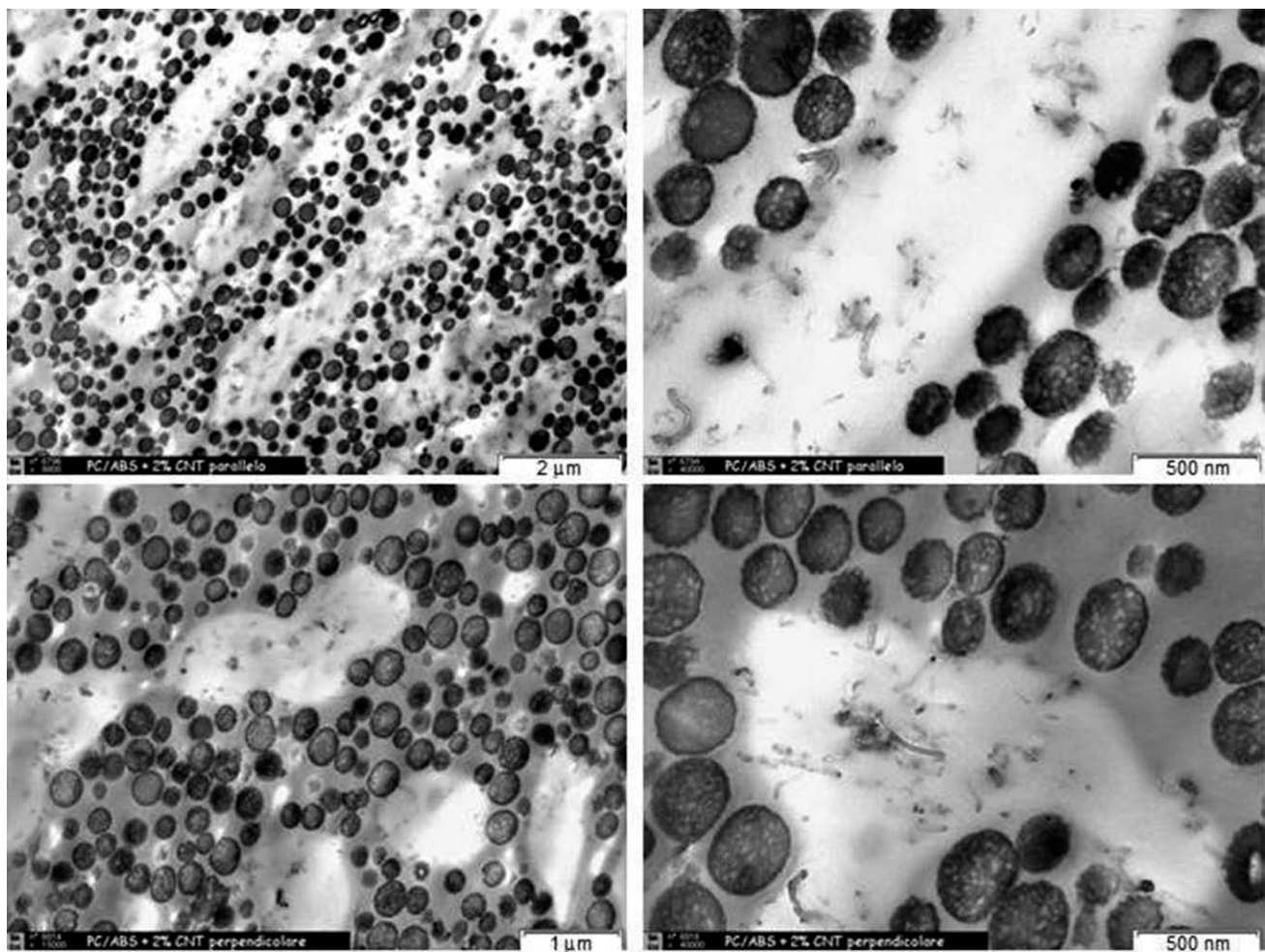


Figure 5 TEM micrographs of PC/ABS-MWCNTs 2 wt % composite.

The OMLS were dispersed as small stacks and submicron size agglomerates, suggesting a predominately intercalated morphology. Exfoliated layers of OMLS were found mainly within the SAN phase at

the interface between SAN and PB particles, a behavior observed previously by several authors studying ABS/montmorillonite nanocomposites.³² The mean dimensions of OMLS intercalated

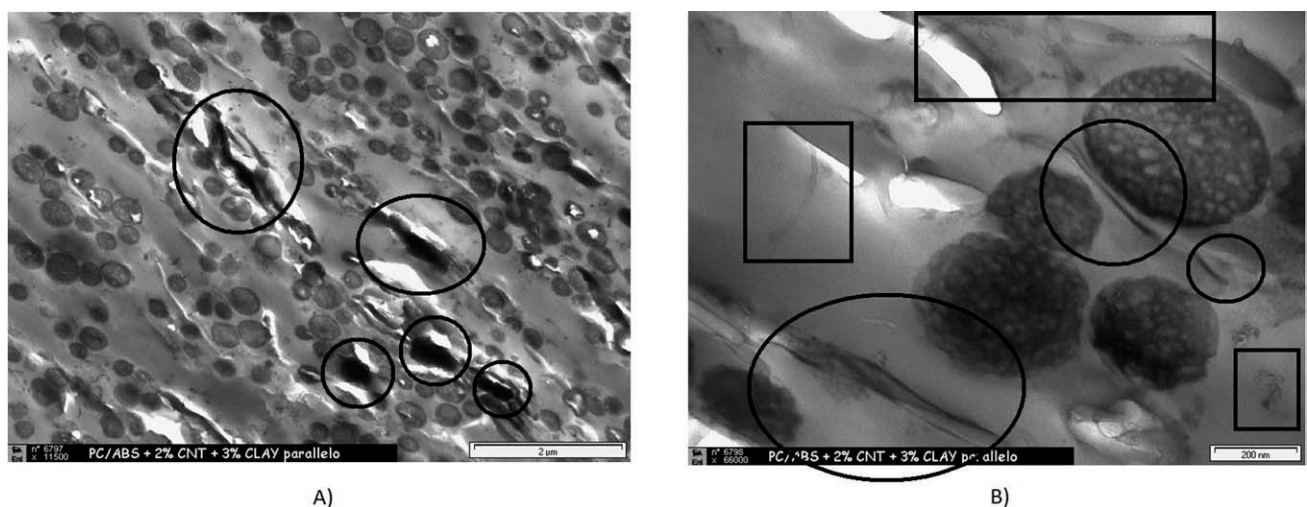


Figure 6 TEM micrographs of PC/ABS-MWCNTs 2 wt % composite with OMLS 3 wt %: particulars of OMLS dispersion. OMLS particles are marked with circles while CNTs are evidenced by rectangles.

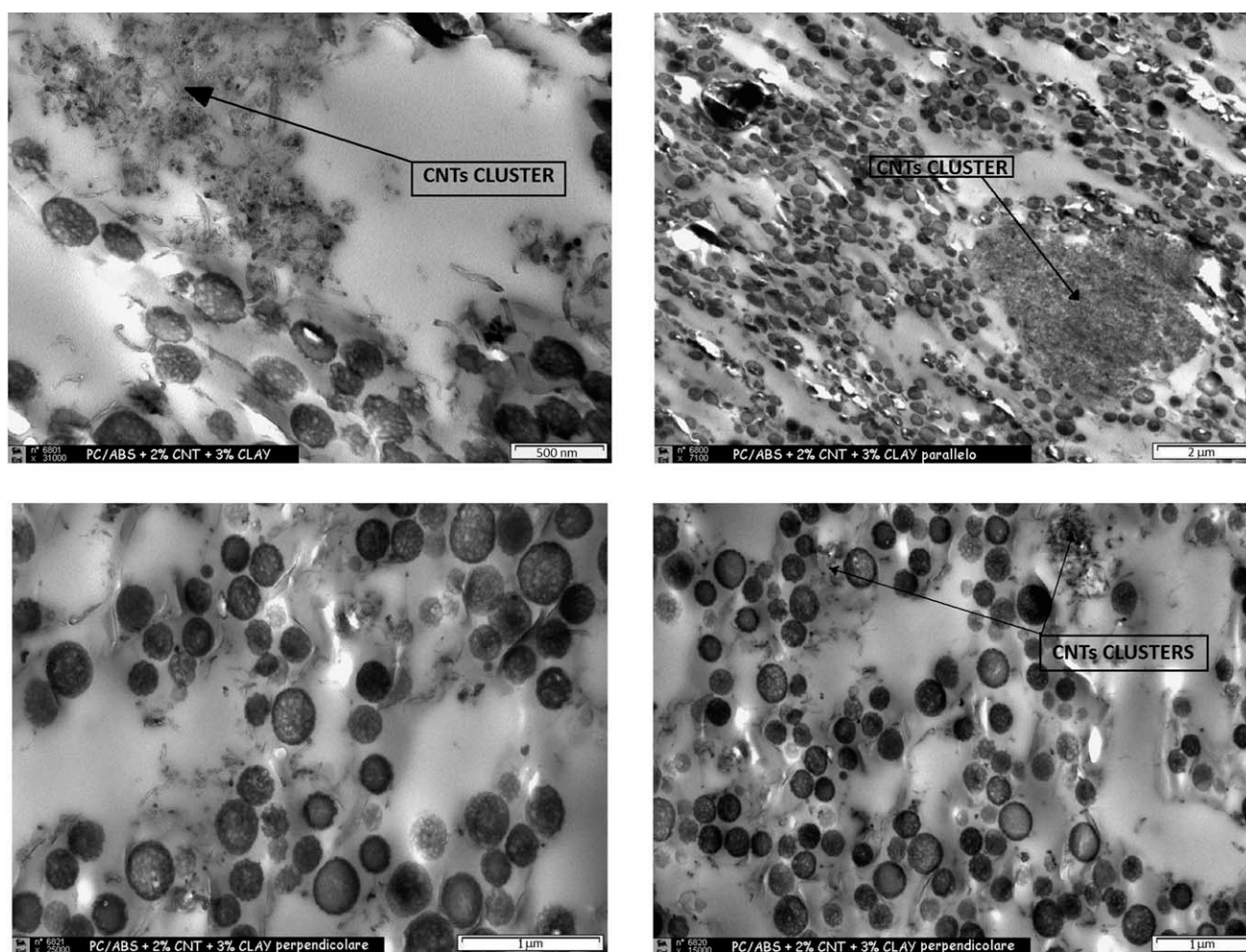


Figure 7 TEM micrographs of PC/ABS-MWCNTs 2 wt % composite with OMLS 3 wt %: particulars of CNTs dispersion.

agglomerates are of about 500 μm and they show a low degree of interaction with the matrix, obvious from the absence of an interface between them and the matrix (holes) in several cases. This aspect will be then further investigated using WAXD to compare the composites containing different amounts of OMLS.

Other authors attributed this phenomenon to an excessive difference of the surface tensions of the two components which is too large to allow intercalation of the clay and break-up of clay tactoids.^{33–34} Furthermore, the distribution of clay particles within the SAN phase indicates the preferential affinity of the filler with this phase.

The most important information about the influence of OMLS on the distribution of MWCNTs in the polymer matrix arise from the comparison between the images in Figure 5 with those in Figure 7. When OMLS 3 wt % is present in the blend, large poorly dispersed MWCNT agglomerates can be observed outside brighter PC domains (see Fig. 7) suggesting that an hindering effect of the clay on nanotube dispersion.

Poor MWCNT dispersion within the continuous PC phase together with the presence of agglomerated nanotubes bundles will result in a less effective nanotube network in particular when CNTs content is lower than the one observed (hence below 2 wt %) such that the composites have a relatively high electrical resistivity and higher percolation threshold. This observation is in agreement with electrical and dielectric analyses, that showed an increase in electrical percolation threshold when OMLS was added to the composite material.

As observed by Goldel et al.²¹ the preferential localization of a filler in one of the phases has commonly been explained by the differences in interfacial energies of the filler and the respective polymers, which originates from the differing polarities and surface energies. If, as reported by several papers^{25,35–39} about the role of organoclay in polymer blends, OMLS can act as a compatibilizer modifying interfacial energies, this can be an hypothesis to explain the changes in CNTs localization and distribution when clay is present above a certain amount in the considered systems (OMLS 3 wt %).

To deeply assess the interlamellar spacing of the OMLS can be determined by means of X-Ray diffraction. In most cases polymer chains intercalate between the OMLS layers resulting in an increase in the interlamellar spacing, i.e., the distance between the clay platelets increases. This is observed as a shift of the diffraction peaks towards lower 2θ angles, the d -spacing can be determined from Bragg's equation and the particle dimensions estimated using Sherrer's theory. The unfilled polymer matrix (PC/ABS), is amorphous and interacts with X-Ray radiation giving only incoherent diffuse scattering resulting in a broad peak area between 5° and 30° 2θ with an absolute maximum at about 18° 2θ (see Fig. 8). From Figure 8 it can also be seen that the OMLS exhibits a narrow first order diffraction peak at 3.7° 2θ corresponding to 001 plane scattering⁴⁰ and a d -spacing of about 24 Å. A second order diffraction peak can also be observed at about 7.4° 2θ when the clay is dispersed within polymer matrix. This is probably due to the presence of highly ordered smectic structures if compared with the pristine OMLS.^{40–43} Addition of OMLS to PC/ABS did not result in a change in the angular position of the 001 diffraction (d_{001}) peak when 1 wt % OMLS was added while only a slight 0.06° increase of the

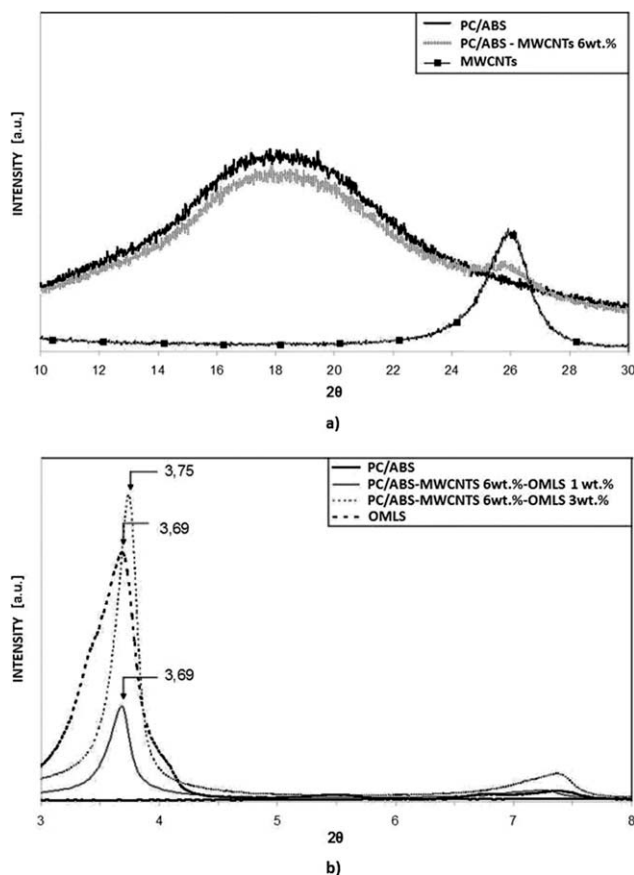


Figure 8 WAXD patterns for PC/ABS, MWCNTs, OMLS, and their blends.

TABLE I
Results of WAXD Experimental Data Fitting with Clay Interlamellar Spacing and Number of Platelets Estimations

| OMLS (wt %) | B_0 (FWHM) ($^\circ$) | $2\theta_{d001}$ ($^\circ$) | d_{001} (Å) | L_{001} (Å) | N (-) |
|----------------|---------------------------|-------------------------------|---------------|---------------|---------|
| 100 (pristine) | – | 3.69 | 23.9 | – | – |
| 1 | 0.216 | 3.69 | 23.9 | 746 | 31 |
| 3 | 0.213 | 3.75 | 23.6 | 756 | 32 |

2θ value was registered for composites containing MWCNTs and 3 wt % clay (leading to a slight decrease from 24.0 to 23.6 Å in interlamellar distance). The thickness of intercalated OMLS particles has been estimated by means of the Sherrer equation for PC/ABS-OMLS-MWCNTs (97/1/2 wt %) and PC-ABS/OMLS/MWCNTs (95/3/2 wt %).⁴³ PEAK-FIT v.4.12 (Seasolve Inc.) was used to fit experimental data using Pearson IV functions, hence particle thickness L_{hkl} in the direction perpendicular to hkl plans was evaluated using:

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos \theta}$$

where, K is dependent on crystal shape (0.91 for typical smectitic like structures²⁸), λ is the wavelength of radiation (1.54184 Å), β_0 is the width evaluated at the peak half height for 001 peaks (rad) and θ is the diffraction angle (rad). Dividing L_{hkl} by the respective values for d -spacing (calculated from Bragg's law and assuming that each lamellae has a thickness of 1 nm), it is possible to evaluate the approximate number of platelets (N) forming intercalated clusters. The values for L and N obtained for PC/ABS-OMLS-MWCNTs (97/1/2 wt %) and PC/ABS-OMLS-MWCNTs (95/3/2 wt %) are also listed in Table I. The mean dimensions of intercalated stacks in both cases are about 750 Å (or 30 platelets, if a thickness of 1 nm is assumed for each platelet and an approximate intergallery spacing of 1.5 nm). This result is in good agreement with our observations from TEM of these composites, see Figure 7.

CONCLUSIONS

The influence of OMLS content on the morphology and electrical properties of PC/ABS-MWCNTs composites was investigated. The results confirmed that when ABS is blended with PC, MWCNTs are selectively localized in the PC phase due to their higher affinity for this polymer with respect to SAN and PB. Thus the effective concentration of MWCNTs within the PC rich phase results in a remarkable reduction in electrical resistivity and a low percolation threshold. Addition of OMLS to PC/ABS-

MWCNT composites tends to hinder MWCNT dispersion and, at the same time, a depletion of MWCNTs within PC phase can be observed. The electrical conductivity and dielectric properties of PC/ABS-MWCNTs composites are strongly affected by MWCNT localization/dispersion and when MWCNT concentration within PC phase decreases the conductive network becomes less effective leading to an increase in composite electric percolation threshold. This is true in particular below a certain CNTs content (2 wt %), because above this limit electrical conductivity can be reached due to high CNTs overall concentration.

The authors thank Dr. P. Lomellini, Dr. D. Ferri, and Polimeri Europa Research Centre in Mantova (ITALY).

References

- McClory, C.; Chin, S. J.; McNally, T. *Aust J Chem* 2009, 62, 762.
- McClory, C.; McNally, T.; Brennan, G. P.; Erskine, J. *J Appl Polym Sci* 2007, 105, 1003.
- Pötschke, P.; Dudkin, S. M.; Alig, I. *Polymer* 2003, 44, 5023.
- Mamunya, Y.; Boudenne, A.; Lebovka, N.; Ibos, L.; Candau, Y.; Lisunova, M. *Comp Sci Technol* 2008, 68, 1981.
- Lee, S.; Cho, E.; Jeon, S.; Youn, J. *Carbon* 2007, 45, 2810.
- Kashiwagi, T.; Fagan, J.; Douglas, J. F.; Yamamoto, K.; Heckert, A. N.; Leigh, S. D.; Obrzut, J.; Du, F.; Lin-Gibson, S.; Mu, M.; Wine, K. I.; Haggenueller, R. *Polymer* 2007, 48, 4855.
- McNally, T.; Pötschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* 2005, 46, 8222.
- Wang, Q.; Dai, J.; Li, W.; Wie, Z.; Jiang, J. *Comp Sci Technol* 2008, 68, 1644.
- Bokobza, L. *Polymer* 2007, 48, 4907.
- Li, Y.; Shimizu, H. *Macromolecules* 2009, 42, 2587.
- Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Tanemura, M. *Coll Polym Sci* 1992, 270, 134.
- Zhang, C.; Han, H. F.; Yi, X. S.; Asai, S.; Sumita, M. *Compos Interf* 1999, 6, 227.
- Gilman, J. W.; Jackson, C. L.; Morgan, A. B. *Chem Mater* 2000, 12, 1866.
- Pötschke, P.; Kretschmar, B.; Janke, A. *Comp Sci Tech* 2007, 67, 855.
- Bose, S.; Bhattacharyya, A. R.; Kulkarni, A. R.; Pötschke, P. *Comp Sci Tech* 2009, 69, 365.
- Bauhofer, W.; Kovacs, J. Z. *Comp Sci Tech* 2009, 69, 1486.
- Pötschke, P.; Bhattacharyya, A. R.; Abdel-Goad, M.; Janke, A.; Goering, M. In: *Adv in Polycarbonates*, Brunelle, D. J.; Korn, M. R. ACS Symposium Series 898, Oxford University Press 2005, Chapter 13.
- Pötschke, P.; Bhattacharyya, A. R.; Janke, A. *Carbon* 2004, 42, 965.
- Pötschke, P.; Bhattacharyya, A. R.; Janke, A. *Polymer* 2003, 44, 8061.
- Sun, Y.; Guo, Z. X.; Yu, J. *Macromol Mater Eng* 2010, 295, 263.
- Göldel, A.; Kasaliwal, G.; Pötschke, P. *Macromol Rapid Commun* 2009, 30, 423.
- Chang, T. E.; Kisliuk, A.; Rhodes, S. M.; Brittain, W. J.; Sokolov, A. P. *Polymer* 2006, 47, 7740.
- Kovacs, J. Z.; Velagala, B. S.; Schulte, K.; Bauhofer, W. *Compos Sci Technol* 2007, 67, 922.
- Kirkpatrick, S. *Rev Mod Phys* 1973, 45, 574.
- Stauffer, D.; Aharony, A.; *Introduction to Percolation Theory*; Taylor and Francis: London, 1992.
- Fragneaud, B.; Masenelli Varlot, K.; González Montiel, A.; Terrones, M.; Cavaille, J. Y. *Chem Phys Lett* 2007, 444, 1.
- Dalmas, F. PhD thesis, INSA de Lyon 2005.
- Besco, S. Ottimizzazione formulativa e di processo nella sintesi di tecnopolimeri nanocompositi, PhD Thesis, University of Padova, Italy, December 2008.
- Barrau, S.; Demont, P.; Peignet, A.; Laurent, C.; Lacabanne, C. *Macromolecules* 2003, 36, 5187.
- Dyre, J. C.; Schroder, T. B. *Rev Mod Phys* 2000, 72, 873.
- Qian, D.; Dickey, E. C.; Andrews, R.; Rantell, T. *Appl Phys Lett* 2000, 76, 2868.
- Stretz, H. A.; Paul, D. R.; Cassidy, P. E. *Polymer* 2005, 46, 3818.
- Du, F. M.; Fischer, J. E.; Winey, K. I. *Phys Rev B* 2005, 72, 1.
- Du, F. M.; Scogna, R. C.; Zhou, W.; Brand, S.; Fischer, J. E.; Winey, K. I. *Macromolecules* 2004, 37, 9048.
- Voulgaris, D.; Petridis, D. *Polymer* 2002, 43, 2213.
- Gelfer, M. Y.; Song, H. H.; Liu, L.; Hsiao, B. S.; Chu, B.; Rafailovich, M.; Si, M.; Zaitsev, V. *J Polym Sci B Polym Phys* 2003, 41, 44.
- Lipatov, Y. S. *Prog Polym Sci* 2002, 27, 1721.
- Khatua, B. B.; Lee, D. J.; Kim, H. Y.; Kim, J. K. *Macromolecules* 2004, 37, 2454.
- Ray, S. S.; Bousmina, M.; Ray, S. S.; Pouliot, S.; Bousmina, M.; Utracki, L. A. *Polymer* 2004, 45, 8403.
- Maiti, P.; Nam, P. H.; Okamoto, M.; Hasegawa, N.; Usuki, A. *Macromolecules* 2002, 35, 2042.
- Causin, V.; Marega, C.; Marigo, A.; Ferrara, G. *Polymer* 2005, 46, 9533.
- Modesti, M.; Besco, S.; Lorenzetti, A.; Zammarano, M.; Causin, V.; Marega, C.; Gilman, J. W.; Fox, D. M.; Trulove, P. C.; De Long, H. C.; Maupin, P. H. *Polym Adv Technol* 2008, 19, 1576.
- Modesti, M.; Besco, S.; Lorenzetti, A.; Causin, V.; Marega, C.; Gilman, J. W.; Fox, D. M.; Trulove, P. C.; DeLong, H. C.; Zammarano, M. *Polym Degrad Stabil* 2007, 92, 2206.