European Polymer Journal 79 (2016) 187–197

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Visualization of carbon nanotubes dispersion in composite by using confocal laser scanning microscopy

Markéta Ilčíková [a], Martin Danko [a,*], Mikheil Doroshenko [b], Andreas Best [b], Miroslav Mrlík [c], Katarína Csomorová [a], Miroslav Šlouf [d], Dušan Chorvát Jr. [e], Kaloian Koynov [b], Jaroslav Mosnáček [a]

[a] Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[b] Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany
[c] Centre of Polymer Systems, University Institute, Tomáš Bat'a University in Zlín, Třída T. Bati 5678, 760 01 Zlín, Czech Republic
[d] Institute of Macromolecular Chemistry AS CR, Heyrovského nám. 2, 16206 Praha 6, Czech Republic
[e] International Laser Centre, Ilkovičova 3, 84104 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form 9 February 2016
Accepted 17 February 2016
Available online 27 February 2016

Keywords:
Confocal laser scanning microscopy
Composites
Carbon nanotubes dispersion

ABSTRACT

Nanocomposites of polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer (SIS) and various types of neat and polystyrene-modified carbon nanotubes (CNT-PS) were prepared and distribution of the CNT-PS throughout the polymer matrix was evaluated using confocal laser scanning microscopy (CLSM). The Nanoamor MWCNT-PS with highest thickness of 25–60 nm were readily visualized using both reflection mode without necessity of fluorescent labelling and fluorescent mode after addition of free dye to the nanocomposite. Visualization of Nanocyl MWCNT-PS with thickness of 8–18 nm and SWCNT-PS was achieved after covalent labelling of the CNT-PS with benzothioxanthene fluorescent dye. The CLSM can serve as a non-invasive method for evaluation of quality of dispersion of nanofillers on quite large area and at various depth of polymer film.

1. Introduction

During the last decade carbon nanotubes (CNT) have been utilized in polymer nanocomposites to introduce new properties, especially electrical conductivity and/or improve mechanical properties of polymers [1–3]. Their wide use in industrial applications however still remains far behind the expectations. The limiting factor remains good dispersion and distribution of the entangled tubes [4].

Even though the quality of nanoparticle dispersion and distribution is considered as crucial for gaining the desired composite properties, there has not been adapted any general procedure for dispersion and distribution assessment in nanoscale so far. There were many attempts to suggest ways for quantification of the dispersion in nanocomposites [5–10], but none of them have been accepted by broad research community due to lack of simplicity and generality. The subjective comments on transmission electron microscopy (TEM) images remains the most frequently used method for evaluation of dispersion and distribution of filler in polymer matrix.

* Corresponding author.
E-mail addresses: marketa.ilcikova@savba.sk (M. Ilčíková), martin.danko@savba.sk (M. Danko), doroshenko@mpip.de (M. Doroshenko), best@mpip-mainz.mpg.de (A. Best), mrlik@utb.cz (M. Mrlík), katarina.csomorova@savba.sk (K. Csomorová), slouf@imc.cas.cz (M. Šlouf), dusan@ilc.sk (D. Chorvát Jr.), koynov@mpip.de (K. Koynov), jaroslav.mosnacek@savba.sk (J. Mosnáček).

http://dx.doi.org/10.1016/j.eurpolymj.2016.02.015
0014-3057/

During the last few decades, different techniques of optical fluorescence microscopy have become of a great importance in monitoring of various processes in non-living and living media. In this respect, confocal laser scanning microscopy (CLSM) is a particularly prominent example, because in contrast to conventional wide-field fluorescence microscopy, it allows for a strong depth discrimination. This is achieved by scanning a strongly focused laser beams across the specimen and proper use of a confocal pinhole in the image plane. In such configuration, only light coming from the focal point is detected and the obtained images are practically optical sections. Thus, thicker specimens can be studied without disturbance from out-of-focus light, which results in sharper images. Because the resolution achieved by the CLSM (~150 nm with the currently used conventional devices [11]), is somewhat better than that achieved in a wide-field light microscopy, but not as great as that of the transmission electron microscopy (~0.1 nm), CLSM has bridged the gap between these two commonly used techniques. The use of CLSM is further promoted by the fact that it provides information from much larger area of the investigated samples compared to microscopy techniques suitable for nanometer scale investigation (e.g. AFM, SEM, TEM, etc.) and also offers the possibility for 3D imaging by combining sequentially obtained optical sections. The depth of the 3D imaging is nowadays restricted to about hundred micrometers due to working distance of the commonly used high numerical aperture microscope objectives and the scattering in the studied samples.

Due to the above mentioned characteristics CLSM has become a favourite technique in the biomedical research and is often used for visualization of the interior of individual living cells and tissues in thin samples or even in body of living organisms [12]. On the other hand, the applications of CLSM in polymer science are still not that numerous, and to date the method was mostly used to study the phase separated morphology of polymer blends [13–15]. Carbon based materials such as CNT and graphene can quench the fluorescence of dyes stacked on their surface and thus were employed in the construction of fluorescence sensors [16]. However, only few examples of CNT visualization in solutions or in glass substrates based on fluorescent dyes and fluorescence light microscopy appeared in literature. These visualizations were carried out by direct interaction of fluorescent polymer [17], free [18–21] or covalently bound dyes [22–25] or quantum dots [26] with unmodified [16–20] or modified [21–24] CNT surface. Visualization of pristine CNT was also performed by using near-infrared fluorescence region [27]. On the other hand, there are only three works describing utilization of CLSM microscopy for visualization of CNT in volume of polymeric nanocomposites. Kashiwagi et al. used the CLSM in reflection mode to obtain quantitative spatial dispersion levels and calculate 'relative dispersion index' representing the uniformity of the dispersion of SWNTs in poly(methyl methacrylate) matrix. However, since they used neat SWCNT only bundles and aggregates of various size were observed [10]. Cipriano et al. [28] obtained direct evidence of enhanced conductivity throughout CLSM reflection mode visualization of relatively large carbon nanofibers in PS matrix where conductive ways of the nearby and connected carbon nanofibers was visible. In an alternative approach, Bellayer et al. [29] visualized physically modified MWCNTs in polystyrene (PS) – based composite by dyeing the polymer matrix with freely dispersed dye, such as Nile blue A perchlorate and using CLSM in inverse contrast fluorescence mode. The obtained images were then used in addition to TEM to visualize the distribution of the MWCNT at larger scale. This system allowed quite good quantitative evaluation of the presence of MWCNT bundles and aggregates, however due to low diameter of MWCNT (below 50 nm) individual MWCNTs were hardly visible [29].

In this work we investigated different approaches for CLSM visualization of neat and covalently modified CNT with various lengths and diameters in polymer nanocomposites. Our main aim was to check the applicability and the limitations of CLSM technique to evaluate dispersion of nanofiller in polymer matrix, which is important parameter for final material properties. CNTs are available in various thickness and length and could be considered as a model of various 1D nano/micro fillers for polymer composites. To the best of our knowledge, such complex evaluation of various types of covalently modified CNT, with improved dispersibility, in polymer matrix volume was not reported so far. We investigated three types of CNT with different lengths and diameters dispersed in polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer (SIS) matrix. To improve dispersibility the CNT were modified by covalent attachment of polystyrene chains on CNT surface using surface initiated atom transfer radical polymerization. CLSM visualization was performed either in reflection mode or in fluorescence mode using highly fluorescent benzothioxanthene dye freely added to the polymer matrix or covalently linked to the CNT fillers.

2. Experimental

2.1. Materials

The two types of multi walled carbon nanotubes (MWCNT) and one type of single walled carbon nanotubes (SWCNT) were used. The Nanoamor MWCNT (Nanostructured & Amorphous Materials, Inc.; Houston, TX 77084, USA) were characterized by provider to have purity of more than 95%, the outer diameter in the range of 60–100 nm, the length in the range of 5–15 μm and the surface area of 64 m^2/g. However, according to our TEM analysis, the diameter of the Nanoamor MWCNT was determined in the range of 25–60 nm. The Nanocyl MWCNT (Nanocyl 7000; Nanocyl, Belgium) were characterized by provider to have purity of 90%, outer diameter of 9.5 nm, the length of 1.5 μm and surface area of 250–300 m^2/g. Our analysis showed Nanocyl MWCNT with diameter in the range of 8–18 nm, which is in good accordance with the supplier average value. The SWCNT (Nanolab Inc., Waltham, MA 02451, USA) were characterized by provider to have purity of more than 95%, diameter 1.5 nm, length of 1–5 μm, and the surface area of 1020.48 m^2/g. A commercially