

Obtaining PVC/CNT nanocomposites with the use of dispersing agents

Katarzyna SKÓRCZEWSKA, Danuta CHMIELEWSKA, Kazimierz PISZCZEK, Jolanta TOMASZEWSKA, Tomasz STERZYŃSKI - Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences, Bydgoszcz

Please cited as: CHEMIK 2011, **65**, 4, 337-342

Introduction

Since the discovery of carbon nanotubes in 1991 [2] much attention is being given to the preparation of materials that contain these nanoparticles. An important issue is the transposition of the unusual properties of individual carbon nanotubes onto macro scale polymeric materials. Properties of a nanocomposite with carbon nanotubes are associated with the dispersion degree and arrangement of nanotubes [3, 4], and also with the high shape factor of these nanofillers, which promotes formation of strong interactions and a tendency to agglomerate. This is also a major issue in the case of obtaining PVC/CNT nanocomposites by the method of solvent evaporation [5].

Overcoming the van der Waals potential between CNT particles (500 eV/ μm) [6] and formation of a homogenous and stable dispersion requires the application of mechanical energy or the use of surfactants and dispersants to reduce the interparticle potential [7-10].

One method frequently used to disperse CNT in solvents is by applying ultrasounds of appropriate frequency. Ultrasounds generate local shearing stresses in the sonicated mixture and break or disentangle CNT bundles [12]. As carbon nanotubes exhibit hydrophobic behaviour, it was expected that their tendency to aggregate into entangled bundles will be diminished in organic solvents. However, CNTs exhibit optimum (sufficient) solubility in some solvents only. The applicable solvents are those, which have no adverse effect on CNT properties, and in the case of polymer solutions, do not change their properties.

Joint action of ultrasounds and dispersing agents facilitates the dispersion of carbon nanotubes [12, 13]. Dispersing aids are mainly substances of long hydrocarbon chain, halogen derivatives with C atoms in the chain (6 to 40 atoms) with an alkene or alkyl group and with at least one side chain of carboxylic, phosphoric, sulphonic acid or an ester thereof. The hydrophobic-hydrophilic interaction between the nanotubes and molecules of the dispersant induces steric stabilization of nanoparticles in solvents when subjected to the action of various disintegrating factors (sonication in most cases).

Dispersing agents stabilize the suspension of disaggregated carbon nanotubes, preventing the destruction thereof [14, 15]. This is one of the methods of noncovalent functionalisation of nanoparticles [16].

The tendency of CNTs to agglomerate poses a serious obstacle in industrial applications, where materials of reproducible properties are required. Therefore, solutions that are sought (and applied) must enable obtaining stable CNT suspensions, without compromising the properties of the nanocomposite produced [17, 18]. The use of dispersing agents and surfactants enables formation of stable and homogenous dispersions of carbon nanotubes by increasing the repulsive steric or electrostatic interactions between individual nanoparticles, preventing them from aggregating [19].

Little attention has so far been given in the literature to modification of PVC with carbon nanotubes. The first to propose such modification was a research team of the University of Technology and Life Sciences (UTP) in Bydgoszcz [20]. Of considerable importance in the production of PVC/CNT nanocomposites is the development of

an optimum method of disintegration of agglomerates and controlled distribution of individual carbon nanotubes in the PVC matrix.

Objective

The aim of the study was to analyse the effect of dispersants on the quality and stability of MWCNT dispersion in a solution of PVC in THF and on the homogeneity of nanocomposite films produced.

Starting materials

The polymer matrix of the nanocomposites comprised suspension poly(vinyl chloride) PVC S61 (Anwil S. A. Włocławek). Multi-walled carbon nanotubes MWCNT from Aldrich Chemistry were used, outer diameter 7-15 nm, length 0.5-200 μm . PVC additives: MOK17 (ester of thioglycolic acid and di-n-butyltin) and organotin thermal stabilizer Mark 17M (Acros, Belgium). The solvent used was tetrahydrofuran, 98.5% $\text{C}_4\text{H}_8\text{O}$ (THF), whereas the dispersants included oleic acid $\text{C}_{18}\text{H}_{34}\text{O}_2$ (OA) and methyl oleate $\text{C}_{19}\text{H}_{36}\text{O}_2$ (MO).

Experimental setup and procedure

MWCNT dispersions in 6% PVC solution in THF were prepared with various content of two types of dispersing agents. MWCNT content in all dispersions was 1% wt. in relation to PVC, while the variable content of dispersants was related to the nanotubes content. Dispersion composition is presented in Table I. The mixtures were subjected for 100 minutes at ambient temperature to ultrasound disintegration using a Bandelin SONOPULS homogenizer with a bar probe. 10 cm^3 of each dispersion were put into glass measuring cylinders to visually monitor the process of reagglomeration and sedimentation of nanotubes.

The remaining portions of dispersions obtained were poured onto glass plates. Thin films of nanocomposites of PVC and carbon nanotubes were formed upon evaporation of the solvent at ambient temperature.

Table I

Composition of dispersions and PVC/MWCNT nanocomposites obtained therefrom

Sample	PVC, parts by wt.	MWCNT, parts by wt.	Methyl oleate (MO), parts by wt.	Oleic acid (OA), parts by wt.
A	100	1	-	-
B	100	1	0.02	-
C	100	1	-	0.02
D	100	1	0.01	-
E	100	1	-	0.01

Results

The process of reagglomeration and sedimentation of the sonicated CNT dispersion in PVC solution was observed visually. Figure 1 shows the dispersions after 14 hours and after 60 days.

Complete reagglomeration and sedimentation of the dispersion which was produced without addition of dispersants (A) was observed

already after 24 hours. Nanotubes in the dispersion with 0.02 parts by weight of methyl oleate (B) started to reaggregate and sediment after ca. 12 days. In the case of the dispersion with 0.02 parts by weight of oleic acid (C), the process was observed after 25 days.

CNT dispersions of lower dispersant content (D, E) retained the stability of nanoparticle dispersion throughout the entire observation period (60 days). It was found that oleic acid, in relation to methyl oleate, demonstrated better dispersing properties, as it maintained MWCNT in dispersion for a longer time (E). In the dispersant-free sample (A) a distinct separation of phases was observed: MWCNT sunk to the bottom and formed the bottom phase, leaving a clear PVC solution above. The use of a smaller quantity of dispersants had a better effect on the stability of CNT dispersion in THF solution of PVC.

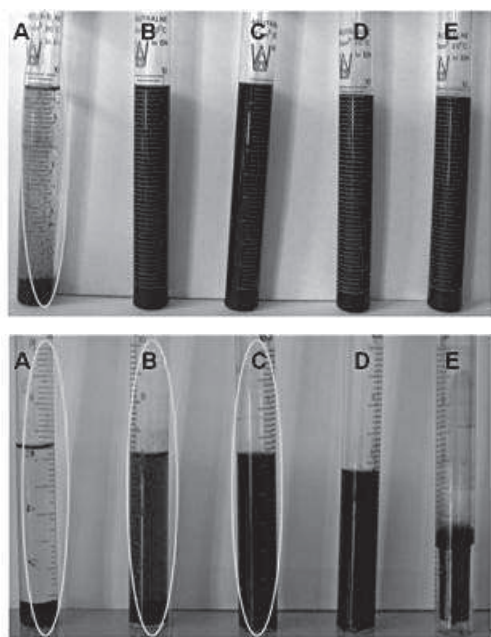


Fig. 1. Carbon nanotubes dispersion (MWCNT content 1% wt.) in PVC solution in THF with various quantities of dispersants after 24 hours and after 60 days. Dispersion composition as shown in Table I

The quality of carbon nanotubes dispersion in the nanocomposite films produced was also assessed. Significant differences in the homogeneity of nanofiller distribution were observed in the photographs of nanocomposites. MWCNT in films that contained a dispersant were dispersed better and formed less clusters than in the film produced without the use of a dispersant (A). It was also observed that nanocomposite films produced with less dispersant added (D, E) had a more homogenous structure than films produced with higher content of dispersants.

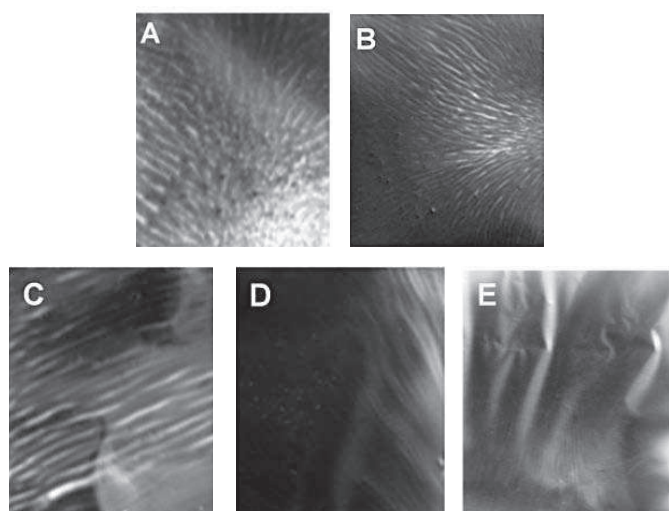


Fig. 2. PVC/MWCNT nanocomposite films with 1% wt. MWCNT content produced with the use of dispersants

Microscopic observations in transmitted light were conducted in order to study in more detail the effect of dispersants on the distribution of carbon nanotubes in nanocomposite films.

These observations have revealed that the produced PVC nanocomposites contained clusters of carbon nanotubes of various shape and size (Fig. 3).

The largest MWCNT agglomerates in PVC were found in the sample obtained with no dispersing agent added (A). These agglomerates were much larger than those in nanocomposites which had dispersant added, irrespective of its type.

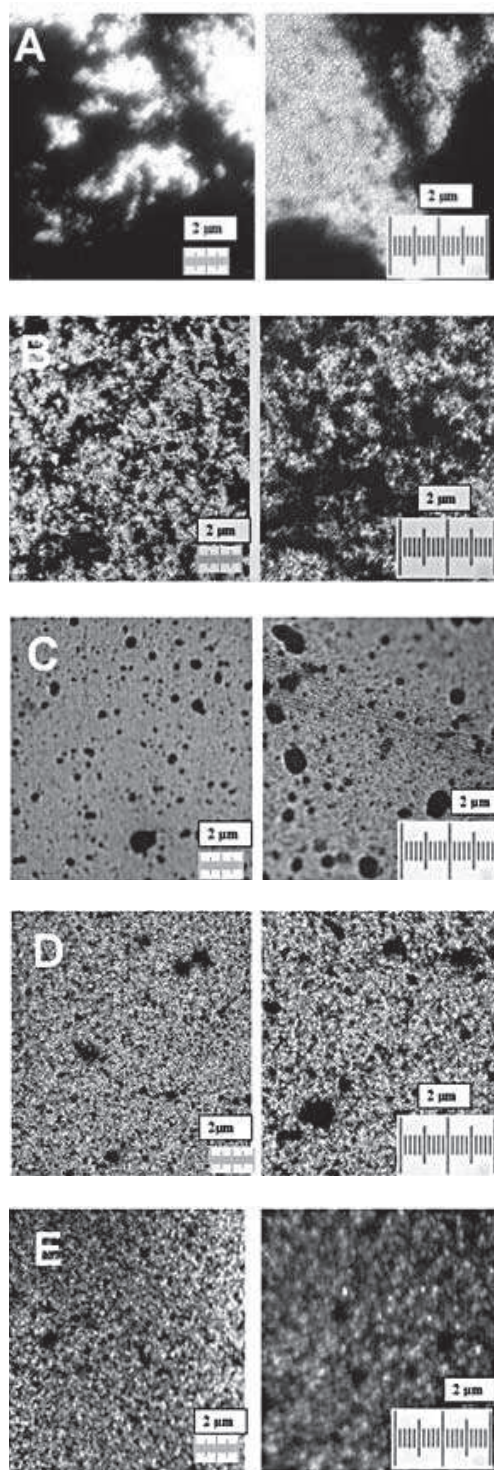


Fig. 3. Microscopic images of PVC/MWCNT nanocomposite films produced without and with the use of dispersants

The best MWCNT dispersion in PVC polymer matrix was observed in the nanocomposite produced with 0.01 parts by weight of oleic acid as the dispersant (E), wherein the size of carbon nanotube agglomerates was ca. 0.1-1 μm . The nanocomposite of

PVC and carbon nanotubes produced with larger quantity of oleic acid (C), contained a higher number of fine MWCNT clusters and agglomerates and the material was much less homogenous.

The use of 0.01 parts by wt. of methyl oleate provided a good dispersion of the nanofiller in the PVC matrix (D). The sample contained a large number of fine carbon nanotube agglomerates varying in size between 0.1 and 1 μm . In the sample with a larger quantity of dispersant added (B), MWCNTs were less dispersed and formed a larger number of agglomerates.

Conclusions

The dispersants used (oleic acid and methyl oleate) improved the dispersability of carbon nanotubes in PVC matrix. In addition, nanotube dispersions produced with dispersants added demonstrated higher persistence (stability) and slower rate of reagglomeration and sedimentation in comparison to dispersions with no dispersants.

Despite the application of ultrasound disintegration and addition of dispersants, the produced nanocomposites of PVC and carbon nanotubes contained agglomerates of nanoparticles. It was found, however, that nanocomposites produced with less aids added, contained less agglomerates. Microscopic images have demonstrated that the best distribution of carbon nanotubes in PVC matrix was attained when lower concentration of methyl oleate was used.

Further investigations of PVC/CNT nanocomposites produced with the use of dispersing agents are required to determine the effect of dispersant content on mechanical and thermal properties of these nanocomposites.

Literature

- Patent application WO 2008/054472 A2, Heintz A., Cafmeyer J., Elhard J., Vijayendran B.: *Methods of dispersing carbon nanotubes*.
- Iijima S.: *Helical microtubules of graphitic carbon*. Nature 1991, **354**, 56.
- Luo D., Wang W.X., Takao Y.: *Effects of the distribution and geometry of carbon nanotubes on the macroscopic stiffness and microscopic stresses of nanocomposites*. Composites Science and Technology 2007, **67**, 2947.
- Foster J., Singamaneni S., Kattumenu R., Bliznyuk V.: *Dispersion and phase separation of carbon nanotubes in ultrathin polymer films*. Journal of Colloidal and Interface Science 2005, **28**, 167.
- Patent application P 387740 Piszczek K.: *Sposób wytwarzania nanokompozytów z poli(chloru winylu) i kopolimerów chloru winylu z nanorurkami węglowymi (Method of preparing nanocomposites of poly(vinyl chloride) and vinyl chloride copolymers with carbon nanotubes)*.
- Girifalco L. A., Hodak M., Lee R. S.: *Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential*. Phys. Rev. 2000, **B 62**, 13104.
- Vaisman L., Wagner H.D., Marom G.: *The role of surfactants in dispersion of carbon nanotubes*. Advances in Colloid and Interface Science 2006, **128-130**, 37.
- Etika K. C., Cox M. A., Grunlan J. C.: *Tailored dispersion of carbon nanotubes in water with pH-responsive polymers*. Polymer 2010, **51**, 1761.
- Lin D., Liu N., Yang K., Xing B., Wu F.: *Different stabilities of multiwalled carbon nanotubes in fresh surface water samples*. Environmental Pollution 2010, **158**, 1270.
- Hilding J., Grulke E., Zhang G., Lockwood F.: *Dispersion of carbon nanotubes in liquids*. Journal of Dispersion Science and Technology 2003, **24**, 1.
- Sato H., Sano M.: *Characteristics of ultrasonic dispersion of carbon nanotubes aided by antifoam*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2008, **322**, (1-3), 103.
- Yao Wang, Jun Wu, Fei Wei: *A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio*. Carbon 2003, **41**, 2939.
- Caneba G.T., Dutta C., Agrawal V., Rao M.: *Novel ultrasonic dispersion of carbon nanotubes*. Journal of Minerals and Materials Characterization and Engineering 2010, **9**, 165.
- Chen J., Liu H.Y., Weimer W.A., Halls M.D., Waldeck H.D., Walker G.C.: *Noncovalent engineering of carbon nanotube surfaces by rigid, functional conjugated polymers*. Journal of the American Chemical Society 2002, **124**, 9034.
- O'Connell M.J., Boul P., Ericson L.M., Huffman C., Wang Y.H., Haroz E.: *Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping*. Chemical Physics Letters 2001, **342**, 265.
- Yurekli K., Mitchell C., Krishnamoorti R.: *Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes*. Journal of the American Chemical Society 2002, **126**, 9902.
- Morcom M., Atkinson K., Simon G.P.: *The effect of carbon nanotube properties on the degree of dispersion and reinforcement of high density polyethylene*. Polymer 2010, **51**, 3540.
- Ayewah D., Davis D., Krishnamoorti R., Lagoudas D., Sue H.-J., Willson M.: *A surfactant dispersed SWCNT-polystyrene composite characterized for electrical and mechanical properties*. Composites Part A 2010, **41**, 842.
- Ajayan P.M., Tour J.M.: *Nanotube composites*. Nature 2007, **447**, 1066.
- Broza G., Piszczek K., Schulte K., Sterzynski T.: *Nanocomposite of poly(vinyl chloride) with carbon nanotubes*. Composite Science and Technology 2007, **67**, 890.

Katarzyna SKÓRCZEWSKA, M.Sc., is a graduate of the Faculty of Chemical Technology and Engineering of the University of Technology and Life Sciences in Bydgoszcz (UTP) (2007). At present, a doctoral student at the Poznań University of Technology, research assistant at the Division of Polymer Technology at UTP, specializes in polymer technology, particularly in the production and properties of nanocomposite materials.

Danuta CHMIELEWSKA, M.Sc., is a graduate of the Faculty of Chemical Technology and Engineering of UTP in Bydgoszcz (2010). At present, a doctoral student at the Poznań University of Technology, specializes in cross-linked polymer technology.

Kazimierz PISZCZEK Ph.D., He got his degree in chemistry at the Faculty of Mathematics, Physics and Chemistry of the Nicolaus Copernicus University in Toruń. Head of the Division of Polymer Technology of the Faculty of Chemical Technology and Engineering at UTP in Bydgoszcz. He published more than 100 papers on the modification of thermoplastic polymers, particularly PVC.

Jolanta TOMASZEWSKA, Ph.D., is a graduate of the Faculty of Chemical Technology and Engineering of the University of Technology and Life Sciences in Bydgoszcz (2010). Research associate at the Division of Polymer Technology of UTP in Bydgoszcz. She specializes in polymer technology, particularly in modification of thermoplastics with natural fillers and hybrid nanocomposite materials.

Tomasz STERZYŃSKI (Sc.D., Eng), Professor, is a graduate of the Faculty of Mechanical Technological Faculty of the Poznań University of Technology, where he is now the head of the Division of Plastics. Gives lectures and manages research work at the Faculty of Chemical Technology and Engineering of UTP in Bydgoszcz. He published more than 200 papers on basic and applied research on modified polymers, participates in a number of major research projects. Particularly he cares about the development of young research personnel, supervisor of 8 doctoral theses and a reviewer in many doctoral and postdoctoral proceedings. His area of interest includes the structure and rheology of polymers and nanocomposites.