FORMULATION OF NANOCOMPOSITES FOR FOOTWEAR WITH ENHANCED COMFORT AND SAFETY PROPERTIES

MARIA ANGELES PÉREZ-LIMIÑANA, ELENA ORGILÉS-CALPENA, MARIA JOSE ESCOTO-PALACIOS, FRANCISCA ARÁN-AÍS, CESAR ORGILÉS-BARCELÓ

INESCOP. Center for Technology and Innovation. Polig. Ind. Campo Alto, s/n. 03600 Elda, Alicante (Spain). aran@inescop.es

Over the last years, huge research has been made on the developing of advanced, innovative, high-performance, nanotechnology-based polymeric materials. As a result, the development of nanofilled plastics, the so-called polymer nanocomposites, has allowed the introduction of new combinations of properties, which consequently enables new applications for plastics. For this purpose, INESCOP is working in the European project NANOFOOT (FP7-SME-2013-2-606570) which focuses on the implementation of nanotechnology in footwear materials and components in order to impart antimicrobial properties, electrical and thermal conductivity, water resistance, breathability, etc., with the main objective of obtaining high added value and marketable materials and footwear. The development of thermally conductive nanocomposites is expected to contribute to an improvement of comfort, since such materials would improve the dissipation of overheating which is produced within the footwear during use. With regards to antistatic nanocomposites, their implementation in the footwear industry would improve both comfort and security as they will reduce the electrostatic charges accumulation. Last but not least, the development of nanocomposites with antibacterial and antifungal properties will improve both comfort and foot health. This paper focuses on the development of foamed EVA-base nanocomposites for insoles, with expected electrical and thermal conductivity properties. Several aspects related to the nanocomposite processability have been evaluated.

Keywords: insole, nanofiller, antistatic.

INTRODUCTION

Over the last years, huge research has been made on the developing of advanced, innovative, high-performance, nanotechnology-based polymeric materials. As a result, the development of nanofilled plastics, the so-called polymer nanocomposites, has allowed the introduction of new combinations of properties, which consequently enables new applications for plastics (Ray, 2013).

The interest in applying nanoscaled fillers into polymeric matrices is the expected achievement of unique properties attributable to the nanoscopic dimensions and intrinsic extreme aspect ratios of nanofillers. Thus, the possibility of incorporating nanofillers to polymers opens a new range of innovative solutions for the footwear industry and related fields. Specifically, there is a trend towards the implementation of nanotechnology in footwear components in order to impart antimicrobial properties, electrical and thermal conductivity, water resistance, breathability, etc., with the main objective of obtaining high added value and marketable materials and footwear.

Thermally conductive polymer nanocomposites have been developed as a light-weight, corrosion-resistant substitute for metallic parts in several applications, such as electronic appliances, electric motor and generators, heat exchangers etc. In the case of footwear, the development of thermally conductive nanocomposites is expected to contribute to an improvement of comfort, since such materials would improve the dissipation of overheating which is produced within the footwear during use.

Different nanoparticles have been described in the literature to improve thermal conductivity of polymers. Silica, boron and aluminium nitrides and aluminium and magnesium oxide nanofillers are considered as convenient fillers in the formulation of composites for electronic appliances, due to their capability to impart thermal dissipative properties and their electrically insulating character (Kochetov, 2012). Boron nitride has been reported to improve thermal conductivity of poly(dimethyl siloxane) (Yu and Cennini, 2014) and polypropylene (Muratov *et al.*, 2014) for LED applications. Boron nitride nanotubes (BNNT) have been reported to impart up to 21.1-fold improvements of thermal conductivity to polystyrene, poly(ethylene vinyl alcohol), poly(vinyl butyral) and poly(methyl methacrylate) based nanocomposites (Zhi *et al.*, 2009). Silica nanofibres can lead to 2-fold improvement of thermal conductivity of epoxy resins (Ren *et al.*, 2014).

With regards to carbon-based nanofillers, graphene nanosheets have proved to improve thermal conductivity of nanocomposites based on polyimide (PI) and on poly(ethylene-vinyl acetate) (Song *et al.*, 2012). Carbon nanofibre and carbon nanotubes (either single wall-SWCNT or multi wall-MWCNT) have also been reported to improve thermal conductivity of polymer composites.

What is more, some authors have reported a synergic effect when formulating nanocomposites with a mixture of nanofillers. Polyphenylene sulphide (PPS) filled with a mixture of boron nitride and MWCNTs can reach a thermal conductivity of 1.74 W/mK (Pak *et al.*, 2012), and epoxy resins filled with a mixture of single-layer graphene and boron nitride can reach thermal conductivity values of ~21.6W/mK (Liem and Choy, 2013).

The implementation of antistatic nanocomposites in the casual and mainly safety footwear industry would improve both comfort and security as they will reduce the electrostatic charges accumulation.

Carbon-based nanofillers, including nanotubes, carbon black and nanofibres, have been reported by several authors to improve electrical conductivity to different polymeric matrices, such as polyurethane (Orgilés-Calpena, 2013), EVA (Sohi, 2011), polyethylene (Jin *et al.*, 2013), polyethersulphone (Jin *et al.*, 2013), among others. Metal-based nanofillers and organometallics (Wypych, 2014) are also able to impart antistatic properties to polymers. Other antistatic additives that can be explored in combination with nanofillers, include inorganic and organic chemicals, as well as inherently conducting polymers (Casado *et al.*, 2014).

Nevertheless, processing of polymer nanocomposites is still a challenge, particularly using conventional melt-blending technologies, mainly due to their low loading concentrations and difficulties in achieving adequate nanofiller dispersion. In general, nanoparticles tend to aggregate during processing with polymers, limiting their possible nanoscale reinforcement effect and resulting in defect sites that limit the overall mechanical and transport performance of the resulting composite. It is crucial to adequately control the addition of nanoparticles into the polymer matrix and later processing in order to minimize re-aggregation or re-agglomeration of the nanoparticles in the resulting nanocomposite.

Currently, INESCOP is working in the European project NANOFOOT (FP7-SME-2013-2-606570) which focuses on the implementation of nanotechnology in footwear materials and components in order to impart antimicrobial properties, electrical and thermal conductivity, water resistance, breathability, etc.

In this work, foamed EVA formulations were produced. Thermal and electrical conductive nanoparticles of different nature were considered, including carbon based nanoparticles, metallic-based nanoparticles, and other organic antistatic additives.

MATERIALS AND PROCEDURES

Materials

Ethylene-vinyl acetate copolymer (EVA) was used as polymeric matrix. Standard EVA formulation and components were provided by the company EVATHINK, S.L. (Aspe, Alicante, Spain), according to technical and processing requirements for EVA as insole material, provided by Todo Para Sus Pies, S.L. (Elda, Alicante, Spain).

Antistatic and electrical/thermal conductive fillers used in this work are listed in Table 1. Fillers were dosed as recommended by suppliers.

Table 1. Selected fillers used in this work

Reference	Description
NF1	Alkaline salt +quaternary N-compound
NF2	Masterbatch of MWCNT in EVA
NF3	Ionomer resin
NF4	Organo-Ti(IV) mixture + silica

Nanocomposites Processing

EVA nanocomposite blend formulations were made in a laboratory-scale internal batch mixer (Banbury-type). The blend-batch was dropped onto a two-roll mill mixer where crosslinking and foaming agents were incorporated and the nanocomposite was sheeted out. Nanocomposite sheets were compression-moulded using a hydraulic press. During the moulding process, EVA curing and foaming took place.

Nanofillers and the rest of additives were handled and processed following the safety recommendations given by the National Institute for Safety and Health at Work and the required personal protective equipment was wore by the personnel.

Composites Characterisation

The curing characteristics of EVA composites were analyzed in a moving die rheometer (MDR). The stiffness change of the nanocomposite, which is compressed between two heated dies is oscillated and measured by the rotor. As a result, a cure curve representing the evolution of the elastic modulus (S’, also known as storage modules or in phase modulus, measured in lbs·in) as a function of time is produced by the MDR. In this work, the evolution of S’ as a function of the time was measured at 170ºC, with an oscillation frequency of 1.6 Hz.

The homogeneity of the dispersion of Ti based additive in blends was assessed by Inductively coupled plasma mass spectrometry (ICP-MS). Three samples were taken at different positions in the uncured nanocomposite sheets and Ti concentration was determined.

RESULTS AND DISCUSSION

Blank EVA and 7 formulations including antistatic nanoadditives have been prepared (see Table 2).

Table 2. EVA base nanocomposites formulations

Batch Reference	Antistatic additive	Dosage
Blank	-	
PNC1-1	NF1	recommended
PNC1-2		>
PNC2-1	NF2	recommended
PNC3-1	NF3	<
PNC3-2		recommended
PNC4-1	NF4	recommended
PNC4-2		>

PNC1-1 and PNC1-2 nanocomposites showed an oily aspect and migration of some component seemed to occur in the uncured sheet. Even though this aspect disappeared after curing in the curemeter, a further processing of the sheets in a calander prior to press-moulding produced the exfoliation of PNC1-2, showing the typical aspect of incompatible polymer blends.

With regards to nanocomposite PNC2-1, the dispersion of black nanofillers within the EVA matrix leads to the formation of uniformly black samples. The carbon base nanofillers dispersion and distribution throughout the EVA matrices can thus be considered as macroscopically homogeneous. Nevertheless, EVA nanocomposites should be evaluated by transmission electron microscopy (TEM) in order to asses the suitable dispersion of the nanofillers into the polymer matrix at nanoscale.

Some difficulties have arisen when compounding PNC3 formulations. They were too sticky and difficult to be handled during processing. A revision of the formulations was made. Nevertheless, composites based in NF3 still showed difficulties in handling.

The increment of nanoadditive concentration in PNC4 series had a plastifying effect and in the case of PNC4-2 a reduction of the shear during blending in the Banbury-type mixer is produced. This effect was considered to potentially lead to a poor dispersion of the nanofiller and other components into the polymer matrix. This assumption was confirmed by ICP-MS analysis. Three samples were taken at different positions in the uncured nanocomposite sheet. Concentration of Ti was evaluated and standard deviation of measured values was considered as an indicator of dispersion effectiveness.

It has been observed that a homogeneous dispersion of the nanofiller has been achieved in PNC4-1 (standard deviation $\sigma = 0.45$). Nevertheless, PNC4-2 shows a heterogeneous distribution of the additive (standard deviation $\sigma = 253$). Such result confirms the assumption that a poor mixing of components could have taken place during PNC4-2 formulation due to a plastifying effect of this nanoadditive. Therefore, the whole EVA nanocomposite formulation and mixing process must be revised in a next step.

Therefore, and from a point of view of processability, PNC1-1, PNC2-1 and PNC4-1 are potential candidates for the development conductive EVA-based nanocomposites.

Finally, Figure 1 shows, for each reference, the curing curve from the moving die rheometer. Curing curves of the different EVA nanocomposites are compared with the one obtained for blank EVA. The effect of the nanoadditive concentration has also been assessed.

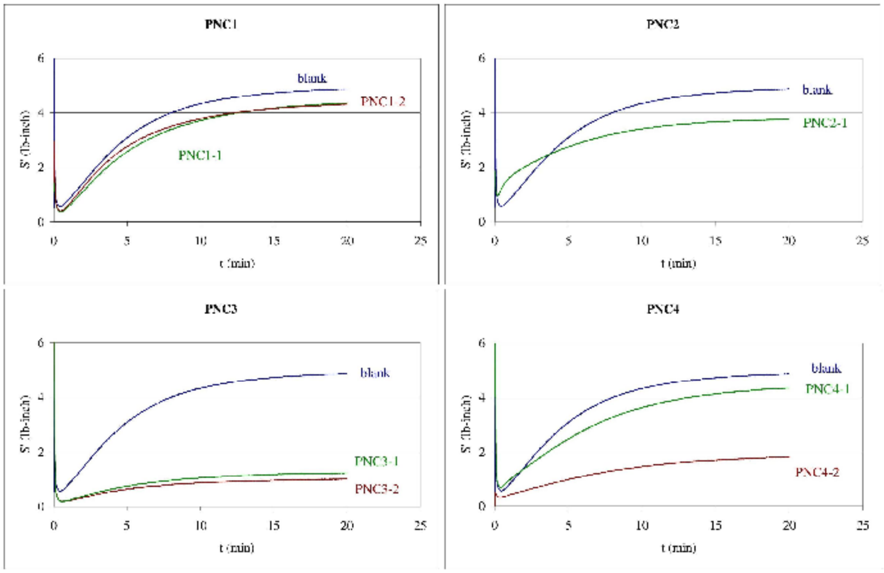

Figure 1. Nanocomposites of EVA. Effect of nanofillers in the curing curve

Curing curves show that, in general, the value of maximum elastic modulus (S'max) decreases after the addition of nanofillers. This decrease is more evident when increasing the percentage of nanoadditive. Therefore, the incorporation of nanofillers can affect both curing and foaming processes during moulding, thus affecting the final physical-mechanical properties of the nanocomposites. An important loss of properties is expected in those nanocomposites showing a more dramatic drop in S'max value, namely PNC3 series and PNC4-2.

CONCLUSIONS

In general, the addition of nanofillers affects processability of EVA-based formulations, being this effect more evident when increasing the percentage of additive.

Furthermore, the curing curve is affected in some extent by the addition of nanofillers. Therefore, an effect on the physical-mechanical properties of the EVA foam is expected.

According to this work, PNC1-1, PNC2-1 and PNC4-1 seems to be the most promising nanocomposites considered, since they show adequate processability, and an apparently good dispersion of the nanofiller. Furthermore, they show a low decrease in the maximum elastic modulus in the curing curve, and minor effects in the mechanical properties of the composite are expected.

Nevertheless, care must be taken in the dosage of NF1 and NF4, since composites formulated with higher percentages can show incompatibility with EVA matrix (PNC1-2) or an ineffective dispersion of the filler plus expected low properties of foamed material (PNC4-2).

Acknowledgments

This work has received funding from the European Union's Seventh Programme for research, technological development and demonstration, under grant agreement No 606570.

REFERENCES

Casado, U.M., Aranguren, M.I., Marcovich, N.E. (2014), "Preparation and characterization of conductive nanostructured particles based on polyaniline and cellulose nanofibers", *Ultrasnics Sonochemistry*, 21, 1641-1648.

Jin, J., Lin, Y., Song, M., Gui, C., Leesirisan, S. (2013), "Enhancing the electrical conductivity of polymer composites", *European Polymer Journal*, 49, 1066–1072.

Kochetov, R. (2012), "Thermal and Electrical Properties of Nanocomposites, Including Material Processing. Thesis. Saint-Petersburg State Electrotechnical University 'LETI', Russia.

Liem, H., Choy, H.S. (2013), "Superior thermal conductivity of polymer nanocomposites by using graphene and boron nitride as fillers", *Solid State Communications*, 163, 41–45.

Muratov, D.S., Kuznetsov, D.V., Il'inykh, I.A., Mazov, I.N., Stepashkin, A.A., Tcherdyntsev, V.V. (2014), "Thermal conductivity of polypropylene filled with inorganic particles", *Journal of Alloys and Compounds* , 586, S451–S454.

Orgilés-Calpena, E., Arán-Ais, F., Torró-Palau, A.M., Orgilés-Barceló, C. (2013), "Chemical Functionalization and Dispersion of Carbon Nanofibers in Waterborne Polyurethane Adhesives", *The Journal of Adhesion*, 89(3), 174-191.

Pak, S.Y., Kim, H.M., Kim, S.Y., Youn, J.R. (2012), "Synergistic improvement of thermal conductivity of thermoplastic composites with mixed boron nitride and multi-walled carbon nanotube fillers" *CARBON*, 50, 4830-4838

Ray, S.S. (Ed.) (2013), *Environmentally friendly polymer nanocomposites. Types, processing and properties. Part I: Types, processing and characterization*, Woodhead Publishing Limited.

Ren, L., Pashay, K., Fard, H.R., Kotha, S.P., Borca-Tasciuc, T., Ozisik, R. (2014), "Engineering the coefficient of thermal expansion and thermal conductivity of polymers filled with high aspect ratio silica nanofibers", *Composites: Part B*, 58, 228–234.

Sohi, N.J.S., Bhadra, S., Khastgir, D. (2011), "The effect of different carbon fillers on the electrical conductivity of ethylene vinyl acetate copolymer-based composites and the applicability of different conductivity models", *CARBON*, 49, 1349-1361.

Song, W.L., Veca, L.M., Kong, C.Y., Ghose, S., Connell. J.W., Wang, P., Cao, L., Lin, Y., Meziani, M.J., Qian, H., LeCroy, G.E., Sun, Y.P. (2012), "Polymeric nanocomposites with graphene sheets e Materials and device for superior thermal transport properties", *Polymer*, 53, 3910-3916.

Wypych, G. (2014), *Databook of Antistatics*, ChemTec Publishing. Elsevier Inc. Toronto.

Yu, J.H., Cennini, G. (2014), "Improving thermal conductivity of polymer composites in embedded LEDs systems", *Microelectron. J*, in press, http://dx.doi.org/10.1016/j.mejo.2014.01.017.

Zhi, C., Bando, Y., Terao, T., Tang, C., Kuwahara, H., Golberg, D. (2009), "Towards thermoconductive, electrically insulating polymeric composites with boron nitride nanotubes as fillers", *Adv Funct Mater*, 19, 1857–1862.