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Dynamic-Mechanical Behavior and Morphology of Polystyrene/Perovskite Composites: Effects of Filler Size

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Abstract

Composites based on a commercial grade polystyrene resin containing 5 wt% of non commercial perovskite particles were prepared by melt blending and analyzed in terms of dynamic-mechanical behavior and morphology. In particular, micro- and nanosized perovskites $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, synthesized by using an innovative microwave-assisted hydrothermal route, were considered.

Flexural dynamic-mechanical evaluations in terms of storage modulus showed better performance for nanofilled systems with respect to ones containing micro particles: evidence explained also in terms of different reinforcing mechanisms normally occurring with variation of filler size and temperature.

Finally, preliminary morphological observations emphasized the achievement of a satisfactory level of filler dispersion for micro composite formulations.

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1. Introduction

In the last decades filled polymers have gained special interest according to their superior mechanical properties. After many successes documented by composite systems reinforced with micrometric additives, recently the attention is particularly focused on nano-filled polymers for which not only the volume fraction of incorporated filler but also the ratio of the internal surface of the filler with respect to

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the volume influences the effective final properties [1-4]. Moreover, it is well established that in nanocomposites more numerous and stronger filler clusters are formed than in microcomposites influencing mechanical properties and viscoelastic behavior of polymer matrices.

In this work micro- and nano-scale particles of strontium-doped lanthanum manganites ($\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$), well known also as perovskites, were synthesized by using a novel microwave-assisted hydrothermal method and included directly in the melt of a commercial grade polystyrene to obtain compounds containing up to 5 % by weight of filler. Extruded materials were compression molded into sheets from which it was possible to derive samples with adequate sizes for mechanical testing. The dynamic moduli and the damping signals ($\text{Tan } \delta$) of the composites filled with nanosized perovskites were compared to those of the corresponding microcomposites, in order to get insight into the effect of particle size on dynamic-mechanical properties of investigated materials. Finally, morphological evaluations have been performed by now only on microcomposites with the aim to correlate final properties of the hybrid systems with the actual degree of filler dispersion.

2. Experimental

2.1. Materials

A commercial grade polystyrene coded as N2982 purchased by Polimeri Europa and characterized by parameters collected in the following Table 1 was considered as the polymer matrix.

Micro and nanoparticles of perovskites, strontium-doped lanthanum manganites $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, used as fillers were synthesised by using a microwave-assisted hydrothermal route from a mixture of lanthanum nitrate, strontium nitrate, manganese(II) nitrate, potassium permanganate and potassium hydroxide as a mineralizer following a route detailed elsewhere [5].

Table 1. Physical characteristics of polystyrene matrix

M_w	M_w/M_n	ρ	T_g
125430	1.98	0.95 g cm^{-3}	$98 \text{ }^\circ\text{C}$

2.2. Compound preparation

Compounds with 1, 3 and 5% by weight of the inorganic nanofiller were prepared by using a DSM Xplore micro co-rotating twin-screw extruder. Melt compounding were performed at 200°C , with a screw speed of 70 rpm. In case of microcomposites, given the limited available amount of this filler, preliminary attention has been focused on the compound filled with 5 wt% of micro-perovskites.

For all investigated materials, specimens for mechanical testing were obtained by compression moulding at 200°C of extruded materials using a LabTech Engineering Company Ltd hydraulic press (Model LP 20B).

To relate evaluations with the actual content of incorporated filler, compounds were systematically tested by thermogravimetric analysis. These evaluations have always shown a satisfactory coincidence of the percentage of residual weight at high temperature with the nominal content of included filler.

Polystyrene matrix processed by the same route has been always considered as the reference material.

2.3. Characterization techniques

Dynamic-mechanical (DMA) properties were analysed using a Triton 2000 Analyser. Dynamic-mechanical spectra were recorded for all materials in three-point bending mode, at a frequency of 1 Hz and using a heating rate of 4 °C/min in the range 0-160 °C.

Morphological observations have been carried out by a Scanning Electron Microscope Quanta 200 ESEM FEG from FEI equipped with a Schottky field emission gun (FEG) for optimal spatial resolution. All specimens were coated with a thin layer of a gold-palladium alloy prior to imaging. In particular, in this manuscript, micrographs of cryo-fractured surfaces of microparticle filled materials are reported while work is in progress to estimate the filler dispersion of nanocomposites also by electron microscopy but operating in transmission mode, more appropriate approach for nanostructured systems.

3. Results and discussion

Dynamic-mechanical behaviour has been investigated for all materials and results are here reported in terms of storage modulus and damping factor ($\tan \delta$) as a function of the temperature. In details, storage modulus of nano filled systems are compared in Figure 1 in the temperature range from 0 to 160 °C.

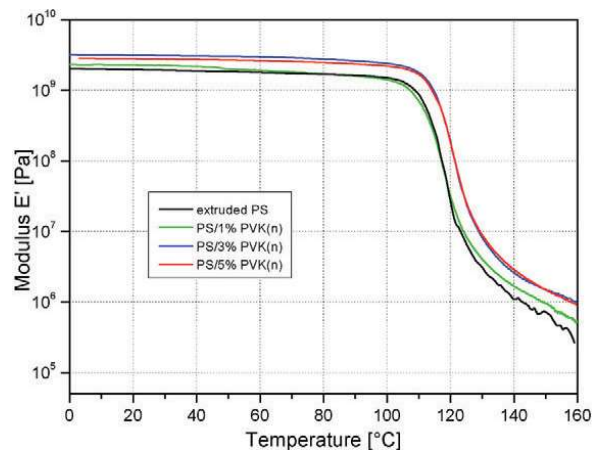


Fig. 1. Effect of temperature on the storage modulus, E' , of polystyrene nanocomposites

It is clear that although this viscoelastic parameter is not significantly influenced by the minimum filler loading (1% by weight), for superior contents storage modulus values for composites are higher than that of the pure matrix throughout the whole temperature range herein considered. Particularly, it has been evaluated that at 20 °C (glassy region) and 140 °C (rubbery region) the storage modulus is incremented by 48.5% and 54.5%, respectively. In addition, Figure 1 representing the results averaged over at least 5 samples, evidently shows that these benefits, already achieved in presence of 3% of nanofiller, are not further improved by increasing the nanofiller content.

The interpretation of these results has been made in light of rheological evidences collected in dynamic mode but not reported in this paper being alien to the objectives of the same. In details, it appears that, for systems loaded at 1%, shear storage modulus curves is actually overlapped at the neat polystyrene one as a sign that the distance between the particles included in the host matrix do not allow the organization of the same in network reinforcement. By increasing the filler content at 3 wt% of nano-perovskites, incipient percolation phenomena are highlighted by a reduction in the slope of the storage modulus curves at low frequencies. This trend, apparently not further emphasized in nanocomposites including 5 wt% of

perovskites, justifies the increase in stiffness of the nanostructured amorphous phase in the glassy region but, more importantly, it improves the consistency of the amorphous phase for temperatures above the glass transition one.

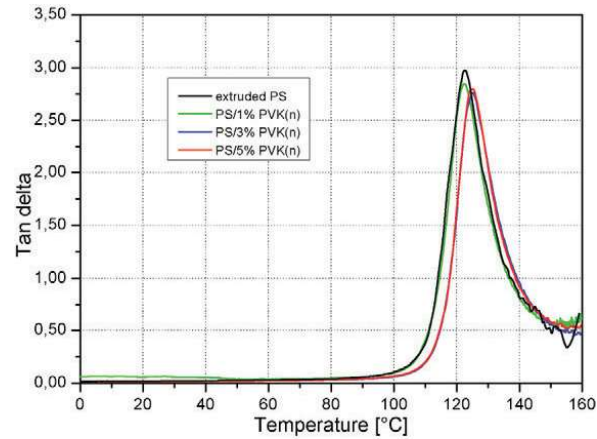


Fig. 2. Temperature dependence of damping factor, Tan δ , of polystyrene nanocomposites

From Figure 2, the addition of nanoparticles appears to reduce the height of the damping signal and, furthermore, to shift the maximum of this signal at higher temperatures. Considering the temperature of the Tan δ peak as the glass transition temperature (T_g) of the examined systems, it is possible to assume that for nanocomposites containing 3 and 5% by weight of perovskites a slight increase of this thermal parameter occurs. Since the glass transition process is related to the molecular motion, the T_g is considered to be affected by molecular packing, chain rigidity and linearity [6]. In light of these considerations, the increase in glass-transition temperature has been ascribed to restrictions of chain mobility, typically occurring in presence of nanometric fillers, near the organic-inorganic interface.

About filler size effects, Figure 3 compares storage modulus curve of neat polystyrene with those obtained for nano- and micro-composites containing 5 wt% of perovskite particles. Clearly, despite the apparent improvement shown by the storage modulus of nano-structured systems, the same content of microfiller is not likely to induce an increase of this parameter for temperatures below the T_g but it manifests itself as a sharp increase in the rubbery modulus at values even higher than that achieved for nanofilled systems.

To explain these experimental evidences, it is worth to note that, for composites with poor adhesion at the filler-matrix interface, any adjustment of the glass transition temperature of the matrix can be explained in terms of the balance between two phenomena with opposite effect:

- increases of the matrix free volume due to the greater difficulty of packing of the macromolecules constituting the matrix amorphous phase (reduction of T_g);
- restricted mobility of macromolecules, especially of longer ones having the highest relaxation times, near the included rigid particles (increase of T_g).

As above, the shift of the signals in Figure 4 can be explained by assuming the predominance of the former effects for micrometric particles. In case of nano-fillers, instead, in line with what is widely documented in the literature, expected restrictions of molecular mobility may explain the slight shift of the peak signal of Tan δ towards temperatures higher than in the case of the pure matrix.

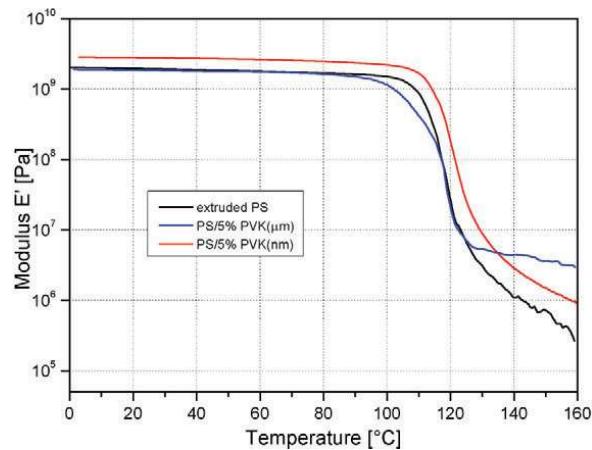


Fig. 3. Effect of the filler size on the storage modulus, E' , of polystyrene composites

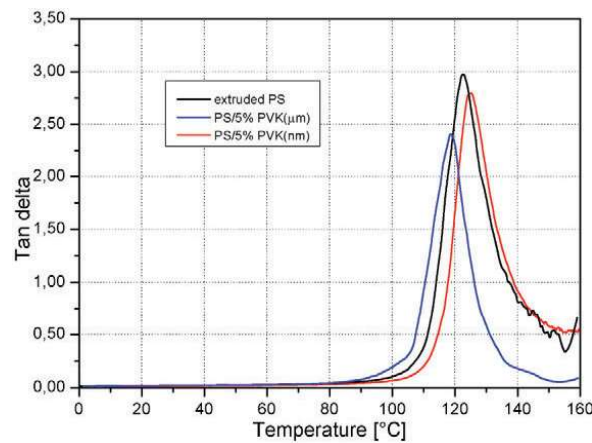


Fig. 4. Effect of the filler size on the damping factor, $\text{Tan } \delta$, of polystyrene composites

Finally, about morphological issues, in Figure 5 micrographs at two magnifications (500x and 2000x) of systems containing 5% by weight of micrometric perovskite are reported. It is possible to note the existence of a uniform distribution of cubic-shaped crystallites and holes probably caused by the expulsion of filler particles during the operation of fracture. Furthermore, the smooth surfaces of the holes confirm the absence of interactions between the dispersed phase and the matrix.

4. Conclusions

Particles of perovskites, strontium-doped lanthanum manganites $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, synthesised by a novel microwave assisted route and with micrometer and nanometer sizes were incorporated in a commercial polystyrene resin by melt blending. Compounds containing 1, 3 and 5% by weight of filler has been compared with the neat polystyrene matrix in terms of dynamic mechanical behaviour while a preliminary morphological investigation has been carried out exclusively on microcomposite systems.

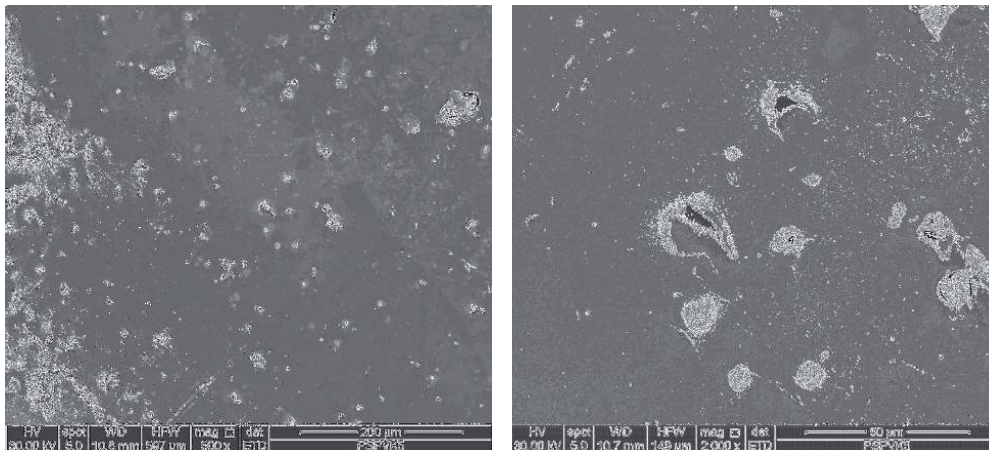


Fig. 5. SEM micrographs of cryofractured surfaces of polystyrene microcomposite samples

The research, confirming the achievement of major benefits in presence of nano particles than in the case of systems loaded with the same amounts of micro-particles, highlights size effects of the dispersed phase on the thermal performance (T_g) of studied materials.

Finally, a satisfactory level of filler dispersion seems to be verified for the highest considered loading at least in the case of microcomposite systems.

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