Properties/Structure Relationships in Innovative PCL-SiO$_2$ Nanocomposites

Maurizio Avella,[1] *Federica Bondioli,*[2] *Valeria Cannello,*[2] *Simona Cosco,*[1]
*Maria Emanuela Errico,**[1] *Anna Maria Ferrari,*[3] *Bonaventura Focher,*[2]
Mario Malinconico[1]

[1] Institute of Chemistry and Technology of Polymers (ICTP)-CNR, Via Campi Flegrei, 34 c/o Comprensorio Olivetti, 80072 Pozzuoli (NA), Italy
E-mail: bors@irtemp.na.cnr.it
[2] University of Modena and Reggio Emilia, Department of Materials and Environment Engineering, Via Vignolese 905/a, 41100 Modena, Italy
[3] University of Modena and Reggio Emilia, Department of Science and Methods Engineering, Viale Allegri,15 I-42100 Reggio Emilia, Italy

Summary: Poly(caprolactone) (PCL) based nanocomposites filled with silica (SiO$_2$) nanoparticles were prepared and the relationships between their structure and properties were investigated.
Silica nanoparticles were synthesized by Stöber method. Surface of silica nanoparticles were successively functionalized in order to promote matrix/filler compatibilization and to improve interfacial adhesion. Morphological analysis performed on the fractured surface of samples revealed that the compatibilization process permitted to obtain an homogeneous and discrete distribution of the nanoparticles into polymeric matrix. Mechanical test showed that in the presence of a strong interphase, the elastic modulus increases of about 25% than the neat polymeric matrix value. Preliminary modelling analysis was also performed in order to assess the correlation existing between a computational model and experimental data.

Keywords: compatibilization; mechanical properties; modeling; nanocomposites; polymer

Introduction

In the last decades new materials based on particle filled polymers for which at least one dimension of the dispersed particle is in nanometer range are rapidly developed.

Nowadays the preparation methodologies of nanocomposites allow to achieve two interconnected phase raging from 5 to 100 nm. This morphology confers to the materials often peculiar characteristics such as superconductivity, magnetism, nonlinear optics, thermal stability etc. that can be achieved owing to the enormous surface to volume ratio characteristic of nanoparticle. [1-3] As a matter of fact, dispersing uniformly nanosized filler particles produces very large interfacial area per volume between the nanoreinforce and matrix polymer. This enormous interfacial region represents the peculiar characteristic of the polymer

DOI: 10.1002/masy.200451421

based nanostructured materials and constitutes the difference from traditional composites. [4-7] However the different nature of the nanofiller (inorganic) respect to the matrix (organic) is responsible of a strong nanofillers tendency to form aggregate, so a homogeneous dispersion of nanoparticles in a polymeric matrix is a very difficult giving rise to nanoparticle clusters formation and decreasing of some properties. To break down these nanoparticle agglomerates many researches are focused on the approach to obtain polymer based nanocomposites with a controlled composition and microstructure together with a good polymer-nanoparticle interface that remain the key role in the determining the final performances of materials. For this purpose it is also important to develop a general understanding of the morphology-property relationships for the mechanical, barrier and thermal response of these systems.

Moreover as for other materials typologies, modelling and simulations of nanocomposites is a prerequisite for an effective design. In particular, nanocomposites are a challenging field for modelling, due to the characteristic length scale (up to a few hundreds nanometers). Atomistic approaches, such as molecular dynamics techniques, can be accurate, but are limited to very small time and length scales and therefore cannot deal with larger scales in nanocomposites. On the other hand, traditional models often applied to composites, such as models based on continuum mechanics equations, have to be adapted to the nanoscale; moreover their applicability should be tested.

In this work results about PCL based nanocomposites filled with silica particles are reported. PCL is a biodegradable polyester characterized by low Tg and modulus and high elongation at break that finds large use as component in starch based formulations of biodegradable film packaging, [8] and also in the biomedical sector for suture filaments and as a component in polylactide (PLA) based blends, where its resistance to hydrolysis, compared to PLA, permits a longer permanence of the article within body[9] The drawbacks of PCL are its low melting temperature and, mainly, its low modulus and poor abrasion. Our main aim was to investigate on the influence of silica nanoparticles on the PCL properties considering that the presence of this nanofiller should improve the PCL performances specially if no interfacial tensions are generated in the composite formation. As matter of fact, the approach of this research was to prepare PCL based nanocomposites by using a reactive preparation technology. In particular silica nanoparticles were previously functionalised by grafting a low molecular weight PCL by means a coupling agent and these modified nanoparticles were successively processed with the PCL matrix. Thermal, morphological and mechanical analysis on the produced materials were performed. Finally preliminary results obtained by using a modelling analysis on the prepared nanocomposites are reported and discussed.

Results and Discussion

Silica nanoparticles were prepared by Stöber method.[10] This method is basically a two step hydrolysis-condensation reaction of tetraethoxysilane (TEOS). The silica particles, so prepared, present a regular spherical shape and their size distribution ranges between 100–200 nm.

It is known that enhanced properties in a nanocomposite are strictly correlated to a good nanoparticles dispersion into polymeric matrix. Less considered so far is the role of the interfacial adhesion. Since the nature of silica (inorganic) is incompatible with the organic nature of the PCL, it was believed necessary, in order to prepare well performing PCL-silica nanocomposites, to modify the silica surface introducing organophilic molecules onto it, in order to improve the nanoparticles dispersion into the polymeric matrix. In particular PCL (OH_2) chains, characterized by a molecular weight of about 10000 Da was anchored on the silica surface. This chemical modification was performed through different reactions.

In a first step, γ-aminopropyltriethoxysilane (APTEOS) was used to introduce functional groups on silica surface, Fig. 1. The reaction was carried out in solution at 70°C for 24 hrs.

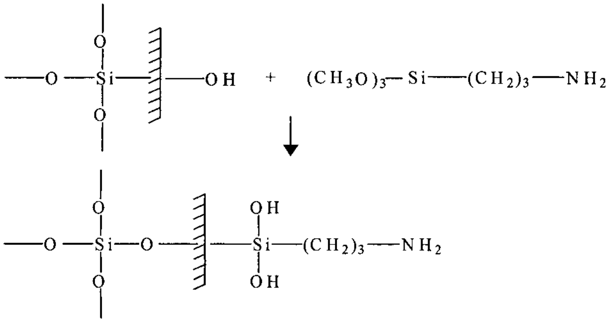

Fig. 1. Scheme of silica functionalization with APTEOS

Since the silanized silica alone can not create a chemical bond between silica particles and polyester (PCL), it was treated with hexamethylendiisocyanate (HMDI). The reaction was carried out at 70°C in chloroform for 24 hrs in a APTEOS/HMDI molar ratio1:1. HMDI was selected because an isocyanate-end capped modified silica is able to anchor OH-terminated PCL chains onto SiO_2. The reaction occurred according to the following mechanism, Fig. 2:

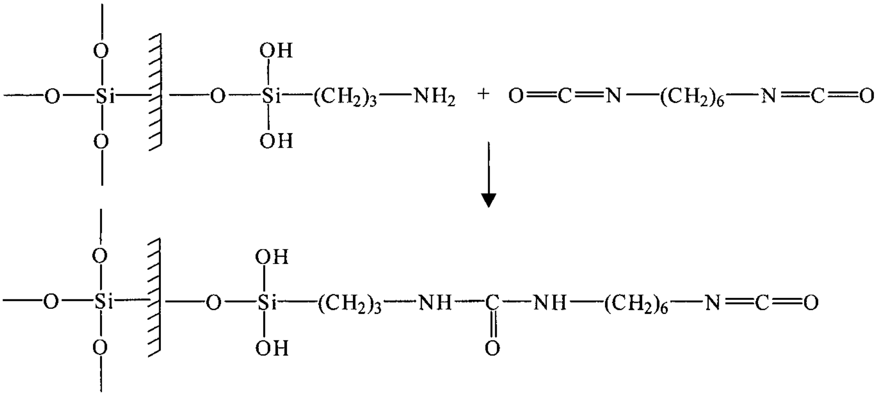

Fig. 2. Scheme of reaction of APTEOS- silica with HMDI

Finally this compound was mixed with the PCL $(OH)_2$ in chloroform for 24 hrs at reflux. The isocyanate-end capped group reacts with hydroxyl end capped PCL group with the formation of an urethane bond, Fig 3.

The reaction is nearly quantitative, as evidenced by the absence of residue to chloroform extraction.

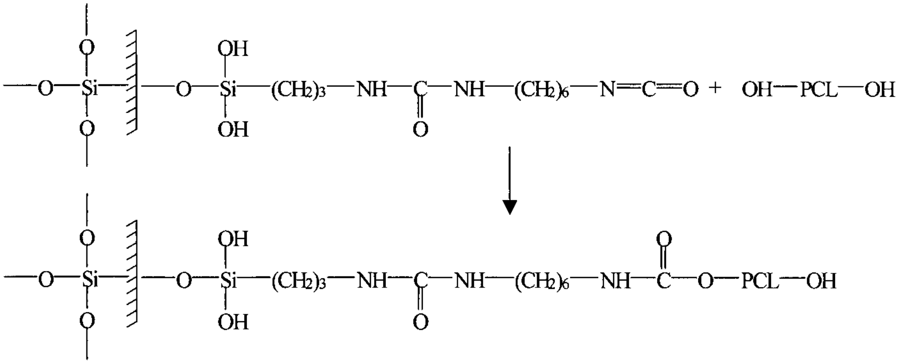

Fig. 3. Preparation of compatibilizing agent

The preparation of PCL (Mw= 50000) based nanocomposites was performed by an extrusion process carried out at 120°C. Nanocomposites containing 1 and 2.5% of modified silica were prepared. For comparison, nanocomposites containing 2.5% of neat silica was also prepared. Scanning electron microscopy was performed on fractured nanocomposites surfaces. In Fig. 4, 5, the micrographs of PCL filled with highest content (2.5%) of modified and neat silica are reported respectively as example. As shown in the figures, the modified nanoparticles are homogeneously dispersed into the matrix and a high number of very small discrete particles, quite welded to the polymer, is observable, also at highest content. On the other hand, in the PCL/ neat silica (Fig. 5), nanoparticles are also welded to the matrix but evident agglomeration phenomena occur. As a matter of fact, it can be assessed that the silica functionalization permit to improve the emulsification between the organic and inorganic components and to obstacle the strong nanofillers tendency to form aggregates.

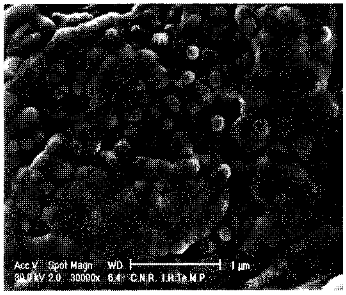

Fig. 4. SEM micrograph of compatibilized PCL/SiO$_2$ (2.5%)

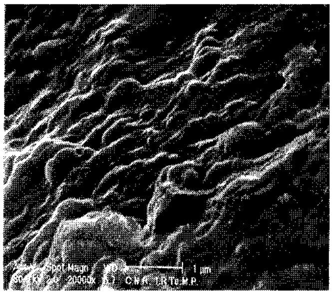

Fig. 5. SEM micrograph of PCL/SiO$_2$ (2.5%)

Mechanical dynamic analysis (DMTA) of nanocomposites is reported in Figs. 6. Neat PCL shows a drop in the storage modulus (E') centered at –41.3 °C followed by a quite distinct rubbery before melting temperature (at about 60°C), (Fig. 6a). In the presence of 1% of modified silica nanoparticles an increase in the damping temperature of about 9°C, (from – 41 to - 32°C) is observed as consequence of a strong enhancement in the rigidity of the amorphous phase, the nanofillers working as physical cross- links (Fig. 6b). It has to be stressed that at least 10 % of silica microbeads would be necessary in a classical composite to produce the same increase in glass transition temperature. The much large surface to volume available in a nanocomposite is hence responsible of the increased rigidity of the matrix.

Increasing the amount of nanofillers to 2,5% does not lead to any further change increase in the damping temperature, thus indicating that already 1% of nano filler is sufficient to fill completely the available surface (Fig. 6c). The addition of 2,5% of non modified nanoparticles also increases the Tg of a similar extent (Fig. 6d). Probably, 2,5% is an amount of nanofiller which is overestimated, thus even in the presence of large amounts of agglomerated particles [as shown by scanning electron microscopy analysis (SEM)], the behavior of the nanocomposites level off. Actually, as evidenced by morphological analysis, non-modified silica nanoparticles appear well bonded to the polymeric matrix and this is probably responsible for a reduced mobility of the PCL macromolecules. In the Figures, it has to be noticed a second peak (shoulder) in tan δ which appears in all the compositions, at a T lower than that of the starting PCL. This shoulder is absent in the PCL, and can be tentatively attributed to a remaining amount of PCL not interacting with the nanofillers. We likely attribute the larger dumping to the PCL chains which are in contact with the surface of nanoparticles. Due to the large surface area, the number of interacting macromolecules must be much higher that that of not interacting one. This is another strong difference between nano and micro composites.

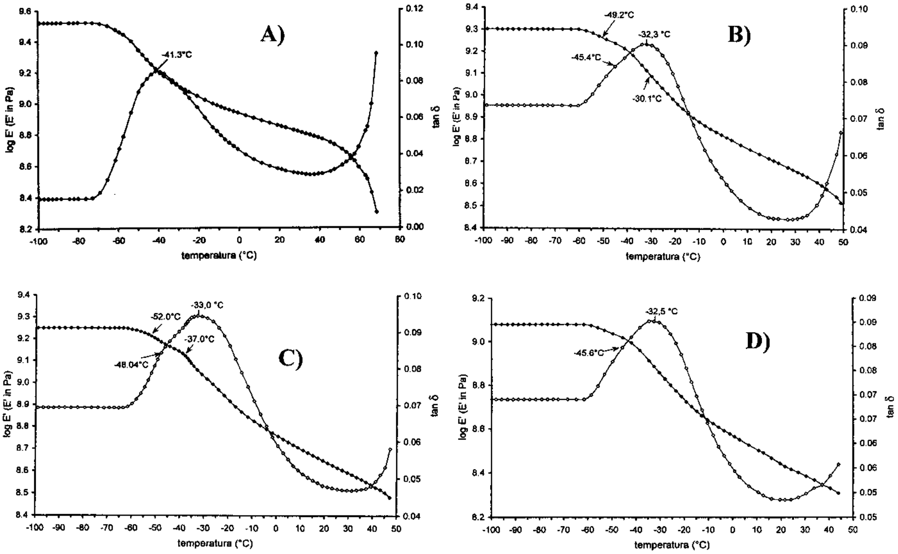

Fig. 6. DMTA curves of A) neat PCL, B) compatibilized PCL/SiO_2 (1 wt%), C) compatibilized PCL/SiO_2 (2.5 wt%) and D) non-compatibilized PCL/SiO_2 (2.5 wt%)

Modelling of mechanical performances

In some recent papers, the finite element method (FEM) has been successfully used to model different nanocomposites.[11,12] In particular, numerical approaches were developed, based on the so-called representative volume element (RVE). In this paper, we adopt an approach that directly maps the microstructure properties onto a finite element mesh and uses a FEM solver to determine the mechanical response of the specimen.

On the basis of the microstructure observed by SEM analysis, a computer code has been adopted in order to generate digitized images of the microstructure, corresponding to a 2.5% fraction of nanoparticles, randomly dispersed in the polymer matrix. The dimension of the reinforcements can be specified as an input parameter (in this case about 100nm). A typical so-generated microstructure is reported in Fig. 7.

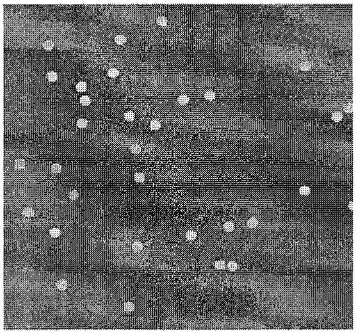

Fig. 7. A microstructure of the nanocomposite, corresponding to 2,5% particles.

Starting from this image it is very easy to distinguish between the two phases (PCL matrix and silica particles). A finite element mesh that displays the exact microstructure of Fig. 7 is generating using OOF [13], a finite element code which allows to take as input a digitized image of the material. Thus a computational grid is created. This grid is reported in Fig 8. In this way, it is possible to attribute to each portion of the microstructure the corresponding materials properties (those of the polymer matrix and the ceramic particles in dark and light gray, respectively).

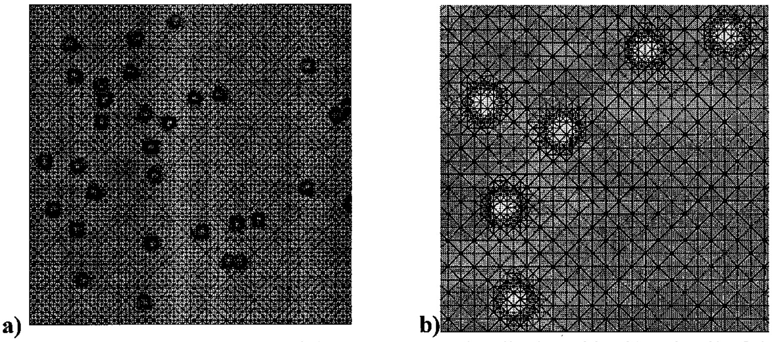

Fig. 8. a) Finite element grid of the nanocomposite displayed in; b) a detail of the mesh

The properties of the two constituents are summarized in Table 1. The elastic modulus of the PCL was experimentally determined. Other values are taken from the literature. [14]

Table 1. Thermomechanical properties of the nanocomposite constituents.

	PCL	Silica particles
E [MPa]	265	80000
Poisson ratio	0.35	0.17
Thermal expansion coefficient α	$6.30\ 10^{-4}\ °C^{-1}$	$0.55\ 10^{-6}\ °C^{-1}$
Density [g/ cm^3]	1.146	2.2

It is assumed that the matrix and the nanofiller are linear elastic, perfectly isotropic materials. This hypothesis is reasonable for small strains (within the elastic range). It cannot be taken into account the influence of the chemical modification of silica surface by the grafted PCL chains. The only assumption we can make is that there is a good adhesion between silica and PCL homopolymer. The so constructed computational grid is used in order to determine the elastic response of the composite material. In particular, the sample is subjected to a pull test and stress-strains curves are recorded, in order to obtain the elastic modulus from the slope of the linear part of the curve.

Two different microstructures are considered, corresponding to fraction of particles equal to 1% and 2.5% respectively. The results are summarized in Fig. 9.

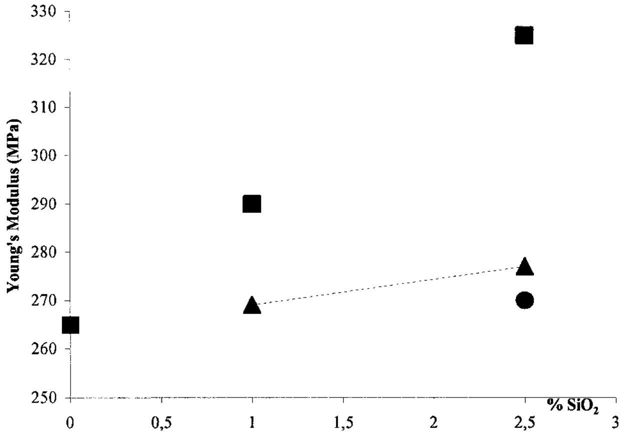

Fig. 9. Elastic modulus values of the nanocomposite containing: (■) 1, 2.5% of modified silica and (●) 2.5% of neat silica experimentally determined; and (……▲……) 1 and 2.5% of silica calculated with the computational approach

As can be noted from the figure, the elastic modulus of the computational approach is closer to the one of the unmodified silica particles composite than to that of modified silica particles one. This means that nanocomposite properties in the case of functionalised silica particles are more than the sum of the constituent bulk properties, while the properties of the unmodified one are slightly less. The last effect can be ascribed to some coalescence of the silica particles in the not modified nanocomposite, which is not taken into account in the model, but it is evident from SEM analysis. On the contrary, the influence of the grafted PCL chains onto silica is probably responsible of the surplus of elastic strength of the modified nanocomposite. As pointed out in literature[15], this can be explained with the formation of an interphase polymer layer near the inorganic surface, with properties differing dramatically from the bulk polymer. As a matter of fact, due to the large surface area of inorganic nanofiller, the interphase layer is expected to dominate the properties of nanocomposites.

Therefore, it can be concluded that the present model can be considered suitable for the description of the unmodified silica nanoparticles composites, where a simple perfect bonding in the finite element mesh was assumed. As regards the nanocomposite with modified nanoparticles, a more detailed model needs to be prepared, able to take into account the interphase layer surrounding the inorganic particle. This task is beyond the scope of the present work and will be the objective of a subsequent paper.

Conclusions

Innovative compatibilized PCL/SiO_2 have been prepared and characterised.

SEM analysis on fractured surface of the modified nanocomposites have shown a finer and more homogeneous distribution of the nanoparticles in the matrix together with a better interfacial adhesion between the two phases.

The mechanical properties of compatibilized nanocomposites display an improvement of Young modulus. A preliminary analysis performed in order to investigate the applicability to the mechanical behaviour of a modelling approach has shown a good agreement between the theoretical value with experimental data obtained for no-modified PCL/SiO_2, while in the case of compatibilized nanocomposites the experimental results are superior than the theoretical ones. Consequently a more detailed model able to account for the formation of an interlayer in the case of functionalised particles should be prepared.

[1] H. Smith in "Polymer Based Molecular Composites" editors, D.W. Schaefer, J.E. Mark, Pittsburgh: Material Research Society; 1990, p 3.
[2] B.M. Novak, *Adv. Mater.* **1993**, *6*, 422.
[3] A.V. Richard, K.D. Jandt, J.K. Edward, E.P. Giannellis, *Macromolecules* **1995**, *28*, 8080.
[4] M.D. Morse, *Chem. Rev.* **1986**, *86*, 1049.
[5] G.D. Stucky, J.E. MacDougall, *Science* **1990**, *247*, 669.
[6] V. V. Kresin, *Phys. Rep.* **1992**, *220*,1.
[7] X. Cao, Y. Koltypin, R. Prozorov, G. Katabi, A. Gedanken, *J. Mater. Chem,* **1997**, *7*, 2447
[8] S. Takagi, M. Koyama, H. Kameyama, Y. Tokiwa in Biodegradabile Plastics and Polymers, Eds., Y. Doi, K. Fukuda Elsevier Science B.V., 1994; p 237
[9] C.G. Pitt in "Biodegradable Polymers as Drug Delivery Systems" Eds., R. Langer, M. Chasin Marcel Dekker, New York, , 1990; p. 71
[10] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *1*, 62
[11] Y.J.Liu, X.L. Chen, *Mechanics of Materials*, **2003**, *35*, 69.
[12] D. R. Katti, K.S. Katti, J.M. Sopp, M.Sarikaya, *Computational and Theoretical Polymer Science*, **2001,** *11*, 397.
[13] W.C. Carter, S.A. Langer, E.R. Fuller. "The OOF manual: version 1.0", **1998.**
[14] www.mataweb.com
[15] D. Schmidt, D. Shah, E. P. Giannelis, *Current Opinion in Solid State & Materials Science*, **2002,** *6*, 205.