APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 435–439
DOI: 10.1002/aoc.168

Preparation methodologies of polymer matrix nanocomposites†

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Recently, as a result of developments in nanotechniques, there has been a growing interest in the field of nanocomposites. The use of inorganic nanoparticle-filled composites can provide high-performance materials that find applications in several industrial fields. In the present work, preliminary studies concerning the preparation of polymethylmethacrylate (PMMA)/$CaCO_3$ nanoparticles composites are reported. The preparation was performed by using an *in situ* polymerization methodology. In particular, the nanocomposites have been obtained by a modified radical polymerization of the MMA dispersing the nanoparticles directly into the acrylic monomer. Nanocomposites having 2, 3, 4 and 6 wt% of nanoparticles were prepared. The influence of the nanoparticles on the chemico-physical properties of the polymeric matrix and the mode of dispersion were investigated by performing thermal, mechanical and morphological analyses. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: nanoparticles; polymer matrix nanocomposites; *in situ* polymerization; interfacial adhesion; industrial applications

1 INTRODUCTION

The concept of polymer-based materials containing simultaneously an inorganic and an organic component has already been considered in the past.[1–3]

Many attempts have been made to introduce inorganic groups both along the polymeric backbone and as network units among different polymeric chains. Some systems, such as polydialchilsiloxane, polyidrazide, etc., have also found commercial importance.[4–7]

In the last 10 years, new methodologies to achieve materials containing organic and inorganic single phases have seen developed, giving rise to those materials called hybrid, ceramer or nanocomposites.[8–10]

These materials are different from the traditional ones because both the organic and inorganic parts are separately themselves materials.

The preparation methodologies of nanocomposites allow one to achieve two interconnected phases ranging between 5 and 100 nm. This morphology confers to the materials characteristics that are completely different from those of polymeric systems where the inorganic component is added to the polymer as a fiber or filler having micrometric dimensions.

Improved and unexpected properties, such as superconduction,[11] magnetism,[12,13] non-linear optics,[14–16] thermal stability[17,18] etc., can be achieved owing to the enormous interfacial adhesion region characteristic of nanoparticles.

Several methods are presently used to produce nanocomposites, such as the sol–gel route, *in situ* intercalative polymerization and *in situ* polymerization.

Particular attention is given to this latter preparation method, because it permits one to have nanocomposites with tailored physical properties while avoiding nanoparticles clustering and, at the same time, improves the interfacial adhesion between inorganic and organic phases. In the present contribution preliminary results concerning the *in situ* polymerization process of polymethylmethacrylate (PMMA) in the presence of $CaCO_3$

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† Based on work presented at the 1st Workshop of COST 523: Nanomaterals, held 20–22 October 1999, at Frascati, Italy.

Contract/grant sponsor: BRITE–EURAM; Contract/grant number: BRPR-CT96-024.
Contract/grant sponsor: COST Action 523.

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nanoparticles are reported. Precipitated $CaCO_3$ nanoparticles, commercialized under the trademark SOCAL® (Solvay & Cie) are currently added as fillers in paints, PVC films, rubber, paper, and toothpaste, but, to our knowledge, they have never been used to produce nanocomposites by an *in situ* methodology. The influence of the nanoparticles on the chemico-physical properties of the polymeric matrix were investigated by examining the thermal, mechanical and morphological properties of the nanocomposites prepared.

2 PREPARATION METHODOLOGIES TO OBTAIN NANOCOMPOSITES

Table 1 shows some recent polymer-based nanocomposite systems prepared via: (a) the sol–gel technique; (b) *in situ* intercalative polymerization; (c) *in situ* polymerization methodologies.

This paper deals with a novel nanocomposites preparation methodology called '*in situ* polymerization'. This methodology consists of dispersing the inorganic nanoparticles into a precursor of the polymeric matrix (monomer); then this mixture is polymerized by adding the appropriate catalyst under certain conditions.[19–21] The main parameters that allow one to obtain high-performance nanocomposites are the dispersion of the nanoparticles and the interfacial adhesion of the filler/matrix.

In order to promote the compatibility between organic/inorganic components and improve the homogeneous dispersion of the nanoparticles into the polymeric matrix, the nanoparticles can be further treated with a certain coupling agents.

Finally the materials, so prepared, can be processed by conventional molding technologies. The advantages of utilizing the *in situ* polymerization technology with respect to the other methods are:

- a direct and easier dispersion of the nanoparticles into the liquid precursor of the polymeric matrix, avoiding the agglomeration of nanopowders in polymer matrices and improving the interfacial interactions between the two components;
- the possibility of using less-expensive nanoparticles (e.g. $CaCO_3$ rather than silica particles) and conventional polymer processing technologies.

We applied this methodology to prepare PMMA filled with $CaCO_3$ nanoparticles composites. Also, in this case, the incorporation of nanosized inorganic particles into a polymeric matrix represents one of the most difficult problems in the achievement of the nanocomposites with good final properties.

To obtain the required homogeneous nanoparticles dispersion, the PMMA polymerization process has been modified.

The PMMA-nanocomposites, with nanoparticles content ranging between 2 and 6 wt%, were prepared by a 'reactive approach' that consists essentially of the radical polymerization of the acrylic monomer, methylmethacrylate (MMA), in the presence of nanoparticles. Surface-coated $CaCO_3$ nanoparticles (SOCAL®), insoluble in water, and with a mean size of about 40 nm, were supplied by Solvay & Cie.

The polymerization of an acrylic monomer is carried out in bulk, in suspension, or in an emulsion. Generally, a suspension is preferred over bulk polymerization of the acrylic monomers. In fact, owing to the exothermicity of the radical polymerization process, a better control of polymerization kinetics can be ensured by the reaction medium, the water. As a consequence, the polymerization yield is much higher and the molecular weight distribution is narrower. Of course, the presence of a suspending agent, like water, increases the volume of the reactant mixture; in addition, it is necessary to recover the aqueous phase at the end of the polymerization.

However, when using $CaCO_3$ nanoparticles as a filler, their insolubility in the water does not permit one to obtain their dispersion in the reaction medium and they become totally agglomerated. Thus, the radical polymerization of MMA in the presence of $CaCO_3$ was carried out in bulk. It was observed that the presence of the nanoparticles during the MMA polymerization is responsible for a higher rate of polymerization. So the time and the temperature are two important process variables.

The free-radical initiator selected was dicumyl peroxide (DCPO), whose $t_{1/2}$ is around 120 °C, which is 20 °C higher than the temperature of the process. In this way it was possible to obtain a better control on the rate of MMA polymerization, because the time necessary for thermal dissociation of the organic peroxide is greater. The DCPO concentration used was 1% by weight of the acrylic phase. Such a relatively high amount of peroxide is justified by the use of MMA in the presence of its inhibitor, so a higher amount of DCPO is required to deactivate the inhibitor. The acrylic monomer is

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Table 1 Recent polymeric-based nanocomposite systems prepared via the sol–gel technique, in situ intercalative polymerization, and in situ polymerization

Systems	Uses
Sol–gel technique	
Polycaprolactone (PCL)/silica (TEOS)	Bone–bioerodible polymer composites for skeletal tissue repair
Polyimide/silica (TEOS)	Micro-electronics
PMMA/silica	Dental application, optical devices
Polyethylacrylate(PEA)/silica	Catalysis support, stationary phase for chromatography
Polyethyleneoxide (PEO)/silica (TEOS)	Electrolyte and highly conductive polymer
Poly(*p*-phenylene vinylene)(PPV)/silica (TMOS)	Non-linear optical material for optical wave guides
Poly(amide–imide)/TiO_2	Composite membranes: gas-separation applications
Polycarbonate/silica (TEOS)	Abrasion-resistant coating
In situ interculative polymerization	
ε-PCL/Cr^{3+} fluorohectorite and montmorillonite	Biodegradable/biocompatible materials, packaging (enhanced barrier-properties)
Epoxy/organo-modified montmorillonite	Improved properties (aeronautics, …)
Polyimide/organo-modified montmorillonite	Materials for microelectronics with reduced thermal expansion coefficient and moisture absorption
Polystyrene/organo-modified montmorillonite	Improved properties
Copolymer butadiene/acrylonitrile/organo-modified montmorillonite	Rubber with enhanced barrier properties (H_2, H_2O)
iPP/organo clay	Improved properties
Starch/organo-modified montmorillonite	Enhanced barrier properties
Nylon/organo-modified montmorillonite	Improvement of structural, mechanical, thermal and barrier characteristics without significant loss in clarity or strength
In situ polymerization	
Nylon 6/silica and $CaCO_3$	Improvement of structural, mechanical, thermal and barrier characteristics without significant loss in clarity or strength
Polyimide/A1N	Materials for microelectronics with reduced thermal expansion coefficient and moisture absorption
Polystyrene–polyvinylbenzene/Fe_2O_3	Optical transparency and superparamagnetism (color imaging and printing)
PMMA/$CaCO_3$	Biocompatible materials and optical devices
PET/SiC	Improved properties

used without purification, because in this way it is possible to reach a better kinetic control of the polymerization rate.

The preparation of our nanocomposites was performed in two steps. The acrylic monomer, in which the organic peroxide was previously dissolved, and the nanoparticles were added to a cylindrical reactor equipped with inlets for a refrigerator and mechanical stirring. The reaction was carried out under vigorous stirring at 100 °C until the critical viscosity of the mixture (pre-polymer and nanoparticles) was attained: first reaction step. In this step, a pre-polymerization of the acrylic monomer in the presence of the nanoparticles occurs. It was observed that the time to the point of critical viscosity of the solution depended on the amount of nanoparticles. In the second step the mixture was put into a mold and kept in an oven at 100 °C for 24 h to complete the polymerization process. At the very least the material so prepared was kept for 4 h at 140 °C in order to ensure there was no residual monomeric fraction in the nanocomposites. The characterizations were carried out on samples prepared by compression molding in a common heated press at 200 °C for 5 min under maximum load.

3 RESULTS AND DISCUSSION

In order to study the nanoparticles dispersion in the polymeric matrix, the samples were broken after dipping in liquid nitrogen and the fractured surfaces

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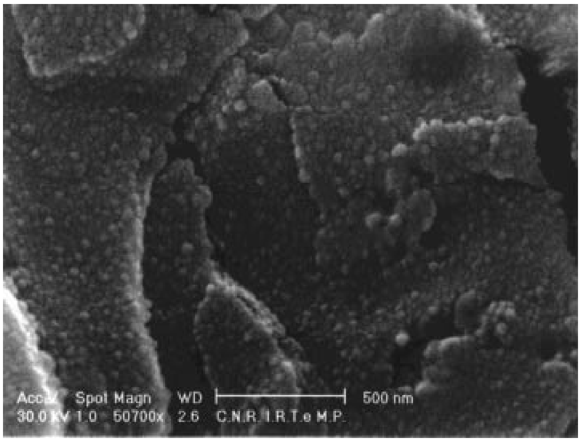

Figure 1 SEM micrograph of fractured surface of PMMA-based nanocomposite having 4% of $CaCO_3$ nanoparticles.

were observed using a scanning electron microscope (SEM). Figures 1 and 2 show examples of the morphology of the fractured surfaces of the nanocomposites having the 4 wt% and 6 wt% of nanoparticles respectively. It can be seen from the figures that the sizes of the nanoparticles range between 40 and 70 nm. Moreover, it is possible to see that the nanoparticles are quite homogeneously dispersed in the PMMA. This result permits one to assume that the preparation methodology used is able to obtain a good dispersion of the nanoparticles in the polymeric matrix even at relatively high amounts of nanopowder.

Finally, it can be pointed out that this uniform microstructure was produced owing to the specific dispersion coating agent present on the nanoparticles surfaces. As a matter of fact, the presence of an organic coating on the nanoparticles surface is necessary in order to render them hydrophobic and, consequently, to improve the matrix/nanofiller compatibilization.

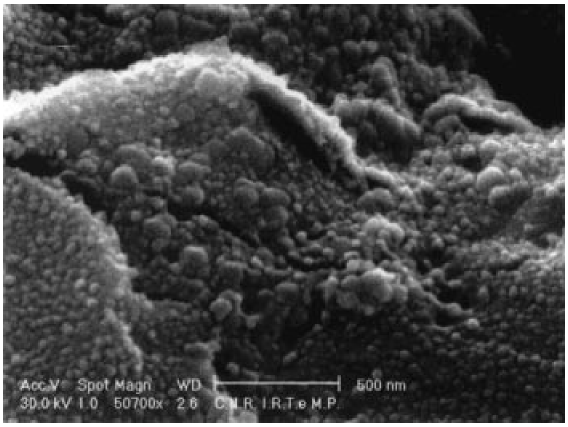

Figure 2 SEM micrograph of fractured surface of PMMA-based nanocomposite having 6% of $CaCO_3$ nanoparticles.

Table 2 Variation of PMMA glass transition temperature in the nanocomposites

Samples	T_g (°C)
PMMA	90
PMMA + 2% $CaCO_3$	120
PMMA + 3% $CaCO_3$	124
PMMA + 4% $CaCO_3$	127
PMMA + 6% $CaCO_3$	125

The variation of glass transition temperature of the PMMA was investigated using differential scanning calorimetery (DSC). Table 2 gives the DSC results calculated for all samples prepared are reported. These data show that the presence of nanoparticles shifts the glass transition temperatures (T_g) to higher values with respect to the homopolymer. It can be underlined that the T_g values increased as a function of the amount of nanoparticles used up to a plateau of about 125 °C for the sample containing 4 wt% of nanoparticles. These results can be attributed to the presumed interactions between the $CaCO_3$ surfaces and the PMMA macromolecules. As a matter of fact, the presence of nanoparticles and the existence of a good interconnection between the two phases (inorganic nanofiller and polymeric matrix) can justify the PMMA glass transition increasing because they hinder the chain mobility of polymer segments.

These nanocomposite materials exhibiting a good dispersion of the inorganic filler and high T_g values can find larger sector applications than unfilled polymers. In particular, PMMA-based materials can be utilized in optical and biomedical devices.

Finally, the optical and structural analyses, together with the biocompatibility studies, of these materials are in progress.

4 CONCLUSIONS

According to the results obtained, the following conclusion can be drawn.

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In situ polymerization technology can be successfully exploited to prepare PMMA-based nanocomposites with enhanced properties by utilising commercial, low cost, $CaCO_3$ nanofillers.

The nanoparticles surface coating appears to be a necessary requirement to obtain a homogeneous dispersion of the particle and a good adhesion with the polymeric matrix.

Both the surface coating and the polymerization process need to be optimized to take full advantage of the nanocomposite structure.

Acknowledgements This research has been partially supported by the European Commission under the BRITE–EURAM contract BRPR-CT96-024 and the COST Action 523 'Nanostructured Materials'. Dr R. Rosa, Dr A. Amodeo (MAGNESIA S.p.A.), and Dr K. Cavalier (SOLVAY & Cie) are gratefully acknowledged for many helpful suggestions and for having supplied the SOCAL® nanofiller.

REFERENCES

1. Payne AR. *J. Appl. Polym. Sci.* 1965; **9**: 1073.
2. Mullins L, Tobin NR. *J. Appl. Polym. Sci.* 1965; **9**: 2993.
3. Medalia AI. *Rub. Chem. Technol.* 1978; **51**: 437.
4. Novak BM. *Adv. Mater.* 1993; **5**(6): 422.
5. Schmidt H. In *Polymer based Molecular Composites*, Schaefer DW, Mark JE (eds). Materials Research Society: Pittsburgh, 1990; 3
6. Usuki A, Kojima Y, Kurauchi T, Kamigaito O, Kawosumu M, Okada A, Fukushina Y. *J. Mater. Res.* 1993; **8**: 1179.
7. Usuki A, Kojima Y, Kurauchi T, Kamigaito O, Kawosumu M, Okada A, Fukushina Y. *J. Mater. Res.* 1993; **8**: 1185.
8. Mark JE. *Polym. Eng. Sci.* 1996; **36**: 2905.
9. Novak BM. *Adv. Mater.* 1993; **5**: 839.
10. Schmidt H. *J. Non-Cryst. Solids* 1985; **73**: 681.
11. Nagaoka K, Naruse H, Shinohara I. *J. Polym. Sci.: Polym. Lett.* 1984; **22**: 659.
12. Palacio F, Maron MC, Garin J, Reyes J, Fontcuberta J. *Mol. Cryst. Liq. Cryst.* 1989; **176**: 415.
13. Sugano T, Kinoshita M, Shirotani I, Ohno K. *Solid State Commun.* 1983; **45**: 99.
14. Philipp G, Schmidt H. *J. Non-Cryst. Solids* 1984; **63**: 283.
15. Schimdt H, Krug H, Kasemann R, Tiefensesee F. *SPIE Submol. Glass Chem. Phys.* 1991; **36**: 1590.
16. Wung CJ, Yang Y, Prasaet PN, Karasz FE. *Polymer* 1991; **32**: 604.
17. Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. *J. Polym. Sci.: Part A Polym. Chem.* 1993; **31**: 2493.
18. Morikawa A, Iyoku Y, Kakimoto M, Inai Y. *Polymer J.* 1992; **24**(1): 107.
19. Usuki A, Kojima Y, Kowasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. *J. Mater. Res.* 1993; **8**: 1179.
20. Kess G. *Polym. Eng. Sci.* 1987; **27**: 410.
21. Ou Y, Yang F, Chen J. *J. Appl. Polym. Sci.* 1997; **64**: 2317.

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