

# **SILICA FILLED PA6: A STUDY ON THE REINFORCING ROLE PLAYED BY NANOPARTICLES**

E. Reynaud<sup>1</sup>, J.Y. Cavallé<sup>1</sup>, C. Gauthier<sup>1</sup>, G. Vigier<sup>1</sup>, and J. Varlet<sup>2</sup>

<sup>1</sup> *GEMPPM UMR CNRS 5510, INSA, 20 av. A. Einstein, 69621 Villeurbanne Cedex, France*

<sup>2</sup> *CRIT Rhône-Poulenc Industrialisation, 85 av. Frères Perret, 69192 St Fons Cédex, France*

**SUMMARY:** A model composite system was synthesized through in-situ polycondensation of Polyamide 6 around nanoscopic inorganic particles, whose size and concentration were varied. The filler influence on the crystallinity of the composite and its state of dispersion were characterized. The mechanical characterization was carried out below and above the glass transition of the chosen matrix, from the elastic region up to the ultimate properties. This was completed by scattering experiments under synchrotron radiation, while the sample were deformed in-situ.

**KEYWORDS:** silica nanofillers, Polyamide 6, crystallinity, mechanical behaviour, X-rays Scattering.

## **INTRODUCTION**

Nanososcopic particles have proved to be of interest as polymer fillers [1,2]. In the particular case of thermoplastic matrices, they actually give rise to better engineering properties, such as higher rigidities or higher heat distortion temperature than the pure polymers do [3-5]. Questions remain on the mechanisms involved in the reinforcing process. In order to gain insight into these nanostructured composites, the following study was carried out on silica reinforced PA6, produced by in-situ polycondensation around the inorganic powder.[6,7]. Most of the work concerns the influence of filler concentration, the particle size and their consequences on the macroscopic behavior of the nanocomposites, from the glassy to the rubbery states, both in the elastic and plastic regions.

## **MICROSTRUCTURAL ANALYSIS**

The crystallinity appears to remain constant whatever the filler concentration or size. From Differential scanning calorimetry experiments, it was found that the filler presence did not lead to any change in the degree of crystallinity nor in the crystalline morphology of the composite systems. [8,9]. In the same way, the crystallization kinetics was not sensitive to the inorganic phase. Wide Angle X-rays Scattering experiments completed the study to attest the non-evolution of the crystalline phases ratio within the composites [10,11].

Use was made of Transmission Electron Microscopy to gain insight into the filler dispersion. The smallest particles (12nm) tend to form aggregates of random shape and size. On the contrary, the largest particles (50 nm) appear mostly as single entities embedded into the polymeric matrix.

## **MECHANICAL BEHAVIOUR**

Concerning the macroscopic properties, the viscoelastic behavior of the composites was first investigated through Dynamical Mechanical Thermal Analyses. As a matter of fact, no significant difference was noticed in the loss factors evolution of the various composites. In particular, the nature of the dissipation phenomena appears not to depend upon the filler presence : the damping capacity remains the same, with or without filler.

The study of the viscoelastic behavior was completed by determining the modulus evolution both below and above the glass transition temperature. Actually, the modulus was found to increase with respect to the filler concentration in the glassy state: the experimental data are rather well fitted by mechanical approaches based on homogenization techniques, such as the self-coherent scheme [12,13]. Moreover in the investigated size range, the particle diameter does not seem to affect the composites modulus. Our observations were slightly different on the rubbery plateau: the mechanical approaches fail to account there for the given reinforcement.

Experiments on the molten state lead to a limited but significant difference in the filler size effect [14]. In fact, the viscosity ratio appears to depend upon the filler developed surface area rather than their volume fraction.

A further insight into the mechanical behavior was obtained through compression tests, which enable to reach the beginning of the plastic region. The yield stress was found to increase with respect to the filler concentration [15], whereas the yield strain could be considered as constant whatever the tested samples, within the experimental errors. Though starting from different stress levels the plastic curves appear actually as parallel to one another. The fillers act as reinforcing agents in that they level up the composites modulus by mechanical coupling. They nevertheless do not seem to impede the polymer deformation around the yield point.

## **DAMAGE AND FRACTURE**

To obtain a closer insight into the mechanisms involved close to the yield point, we were given the opportunity to perform scattering experiments under synchrotron radiation. The composite spectra were recorded respectively under strain (corresponding approximately to the yield point) and once the strain has been released. The analysis was conducted along the traction axis, and perpendicular to it. The intensity increase with respect to strain suggested the possible occurrence of debonding between filler and matrix. The observed slight intensity decrease with the strain release confirms this possibility of newly created surface within the sample.

Eventually the fracture behavior was studied through three points bending tests. It was observed that the highest filler concentrations and the smallest particle sizes lead to the lowest fracture toughness. As a matter of fact, aggregates weaken the matrix, since they can be regarded as stress concentration points and their simple presence can give rise to flaws which reduce the fracture strength.

## CONCLUSION

Studying a model composite, with selected parameters, it was eventually noted that the classical mechanical approaches could account for the increase in modulus of the composite systems in the glassy state. This was no longer true above the glass transition temperature. Nevertheless, the molecular deformation within the composite systems appears as non sensitive to the filler presence up to the beginning of the plastic region. Debonding within the composites was thought to accompany the transition between the elastic and the plastic regimes. Further work needs to be carried out to follow their evolution with elongation. While the modulus in the glassy state was found to increase with the filler concentration, the fracture performance was noticed to decrease with respect to both the filler concentration and the particle size.

## ACKNOWLEDGMENTS

The authors want to thank Berriot Julien and Halary Jean-Louis (Laboratory PCSM, EPSCI, Paris, France) and Jouen Thierry for their contribution to this study.

## REFERENCES

1. Nielsen, L.E., Landel, R.F., *Mechanical properties of polymers and composites*, Second Edition, Marcel Dekker Inc, 1994.
2. Rother, R., *Particulate-filled polymer composites*, Longman Group Ltd, Harlow, 1995.
3. Becker, C., Krug, H., Schmidt, H., "Tailoring of thermomechanical properties of thermoplastic nanocomposites by surface modification of nanoscale silica particles", *Mat. Res. Soc. Symp. Proc.*, Vol. 435, 1996, pp. 237-240.

4. Enikolopyan, N.S., Fridman M.L., Stalnova I.O., Popov, V.L., "Filled polymers: mechanical properties and processability", *Advances in Polymer Science* , Vol. 96, 1990, pp. 1-67.
5. Sumita, M., Shizuma, T., Miyasaka, K., Ishikawa, K., "Effect of reducible properties of temperature, rate of strain, and filler content on the tensile yield stress of Nylon 6 composites filled with ultrafine particles", *Journal of Macromolecular Science- Phys.*, B22 (4), 1983, pp. 61-618.
6. Ou, Y., Yang, F., Zhong-Zhen, Y., "A new conception on the toughness of Nylon6/silica nanocomposite prepared via in situ polymerization", *Journal of Polymer Science* , Part B: Polymer physics, Vol. 36, 1998, pp. 789-795.
7. Yang, F., Ou, Y., Zhong-Zhen, Y., "Polyamide 6/silica nanocomposites prepared by in situ polymerization", *Journal of Applied Polymer Science* , Vol. 69, 1998, pp. 355-361.
8. Pfeil, ., Trafara, G., "Calorimetric and X-ray investigations of Polyamide-6 and its blends with a polyethyl acrylate elastomer. Part 1: phase transition behaviour of polyamide-6", *KGK Kautschuk Gummi Kunststoffe 50. Jahrgang*, nr. 10/97, pp. 685-695.
9. Keil, W., Trafara, G., "Thermoanalytical and X-rays studies of blends from polyamide-6 and polyamide-6,6", *Kautschuk Gummi Kunststoffe 46. Jahrgang*, nr 2/93, pp. 105-111.
10. Mateva, R., Mateev, M., Delev, O., "Structure and properties of polyamide 6 modified by N-trialkylsilylcaprolactam", *Acta Polymer*, Vol. 47, 1996, pp. 188-192.
11. Androsch, R., Stolp, M., Radusch, H.J., "Crystallization of amorphous polyamides from the glassy state", *Acta Polymer*, Vol. 47, 1996, 99-104.
12. Berveiller, M., Zaoui, A., "Modélisation du comportement mécanique des solides microhétérogènes", G'Sell, C., et Haudi edits, Nancy: INPL, J.M. 1995, pp. 225-250.
13. Shaterzadeh-Yazdi, M., "Etude et modélisation physique et mécanique du comportement viscoélastique et plastique de composites particuliers à matrice polymère", PhD Thesis from INSA-Lyon, 1997, pp. 142-147.
14. Kyu, T., Zhu, G.C., Zhou, Z.L., Tajuddin Y., Qutubuddin, S., "Novel filled polymer composites prepared from in situ polymerization via a colloidal approach. II. Blends of kaolin/Nylon-6 in situ composites with conventional Nylon-6 and -66", *Journal of Polymer Science: part B: Polymer Physics*, Vol. 34, 1996, pp. 1769-1775.
15. Voros, G., Pukanszky, B., " Stress distribution in particulate filled composites and its effects on micromechanical deformation", *Journal of Materials Science*, Vol. 30, 1995, pp. 4171-4178.