Available online at www.sciencedirect.com

ScienceDirect

C. R. Mecanique 335 (2007) 702–707

COMPTES RENDUS
MECANIQUE

http://france.elsevier.com/direct/CRAS2B/

Experimental study and micromechanical modeling of MMT platelet-reinforced PP nanocomposites

Ludovic Cauvin [a], Naresh Bhatnagar [b], Mathias Brieu [a], Djimédo Kondo [a,*]

[a] *Laboratoire de mécanique de Lille, UMR CNRS 8107, boulevard Paul-Langevin, 59655 Villeneuve d'Ascq cedex, France*
[b] *Mechanical Engineering Department, Indian Institute of Technology, HausKhaz, New Delhi, India*

Received 18 June 2007; accepted after revision 27 July 2007

Presented by Évariste Sanchez-Palencia

Abstract

Nanocomposites with platelets reinforcements are emerging materials with strong potential for future engineering applications. The present study is a first step to characterize and predict the elastic behavior of Montmorillonite (MMT) clay reinforced Polypropylene (PP) nanocomposites. The pellets of nanoclay composites were made by first uniformly mixing the MMT platelets in a twin-screw extruder by the melt intercalation route. These pellets were then converted into tensile specimens as per ASTM 638 by injection molding process. From tensile tests it is shown that there is a significant increase of the Young modulus with the mass fraction (2–7%) of clay platelets. A first approach of homogenization allows to conclude that the Ponte Castañeda and Willis (1995) bound predicts the measured moduli provided that a suitable aspect ratio of the reinforcement is considered. ***To cite this article: L. Cauvin et al., C. R. Mecanique 335 (2007).***

Résumé

Étude expérimentale et modélisation micromécanique des nanocomposites à renforts plaquettaires. Les nanocomposites à renforts plaquettaires sont des matériaux émergents à fort potentiel. Cette étude est une première étape de caractérisation et de prédiction du comportement élastique de nanocomposites à matrice Polypropylène (PP) renforcée par des nanoplaquettes d'argile de Montmorillonite (MMT). Les granules du nanocomposite ont été préalablement réalisés en mélangeant de manière uniforme les plaquettes de MMT à la matrice dans une extrudeuse à double vis sans fin. Des éprouvettes de traction, conformes à la norme ASTM 638, ont ensuite réalisées à partir de ces granules à l'aide d'un procédé de moulage par injection puis testées en traction uniaxiale. Les modules d'Young, déduits de ces essais, montrent une augmentation significative avec la fraction massique (2–7%) des nanoplaquettes. Une première approche de modélisation micromécanique permet de montrer que la borne de Ponte Castañeda et Willis (1995) prédit ces modules à condition de considérer un rapport d'aspect adéquat pour les plaquettes. ***Pour citer cet article : L. Cauvin et al., C. R. Mecanique 335 (2007).***

Keywords: Solids and structures; Nanocomposites; Experimental study; Effective moduli; Homogenization

Mots-clés : Solides et structures ; Nanocomposites ; Étude expérimentale ; Modules effectifs ; Homogénéisation

---

[*] Corresponding author.
E-mail addresses: ludovic.cauvin@ed.univ-lille1.fr (L. Cauvin), nareshb@mech.iitd.ernet.in (N. Bhatnagar), mathias.brieu@ec-lille.fr (M. Brieu), djimedo.kondo@univ-lille1.fr (D. Kondo).

1631-0721/$ – see front matter © 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crme.2007.07.007

1. Introduction

Since the publication of the results obtained by Toyota Research on the dispersion of platelets silicate (Montmorillonite, MMT) in Polyamide 6 at the nanoscale fifteen years ago ([2,3]), worldwide a tremendous amount of research has been realized in the field of nanocomposites constituted of thermoset and clay platelet reinforcement, in order to enhance various physical properties. The remarkable mechanical behavior, for very low mass fraction of reinforcement (less than 5%), has induced a huge interest of industries and faculty communities (see for instance [4–7]). Still, there is a strong need of understanding the behavior of this new class of materials ([8,9]). This is specially crucial for their mechanical behavior for which experimental data, even in the elastic domain, are still rare. Moreover, the modeling of these materials in relation with their heterogeneous character are often limited to the Mori–Tanaka ([13]) and Halpin–Tsai ([14]) estimates (see for instance [10–12]). The present study is first concerned with experimental characterization of the mechanical behavior of platelet reinforced nanocomposites. A first approach of micromechanical modeling dealing with overall stiffness of the nanocomposite is proposed. Two homogenization schemes are considered: Mori–Tanaka ([13]) estimate and Ponte Castañeda and Willis ([1]) bound. The latter has the peculiarity of taking into account simultaneously the geometry of the reinforcements and their spatial distribution in the polymeric matrix. The predictions of the two homogenization models are compared to experimental results.

2. Description of the studied material

The nanocomposite material under present study is polypropylene (PP) matrix (REPOL H020EG—Reliance make) with Montmorillonite (MMT) clay platelets (CRYSNANO 1010—Southern Clay make). The polypropylene (PP) and the clay (MMT) are first thoroughly mixed for different volume fractions of clay in a co-rotating twin screw extruder (Hake make). The extrudate is converted into granules for molding purposes. The tensile, flexure and impact samples are then obtained by injection molding of these nanoclay based PP granules. The size of the MMT nanoparticles are measured with a particles size analyzer (Brookhaven 90Plus). The nanoplatelets have ellipsoidal shape with a main diameter of 209 nm, a median diameter of 189 nm and a thickness of 50 nm. The polypropylene matrix (PP) Young's modulus is $E = 900$ MPa and Poisson's ratio $\nu = 0.4$ as per the manufacturer. Making use of X-Ray Diffraction (XRD), it is possible to highlight whether the obtained nanocomposite has an intercalated structure or not. According to the processing it is possible to get three kinds of material (Fig. 1). In the first case, the nanoclay particles/platelets are uniformly distributed and dispersed in an aggregate form. This two phase material is leading to enhancement in mechanical or thermal properties as in classical composite. So, it can only be called *micro composite*. The second case is an intercalated nanocomposite in which polymer chains gets into the space between thin platelets of nanometer dimensions thereby resulting into huge reinforcement. However, in such a case, platelets remain isolated in aggregates between which the matrix is intercalated. The last case is the nanocomposites with exfoliated structure. All the

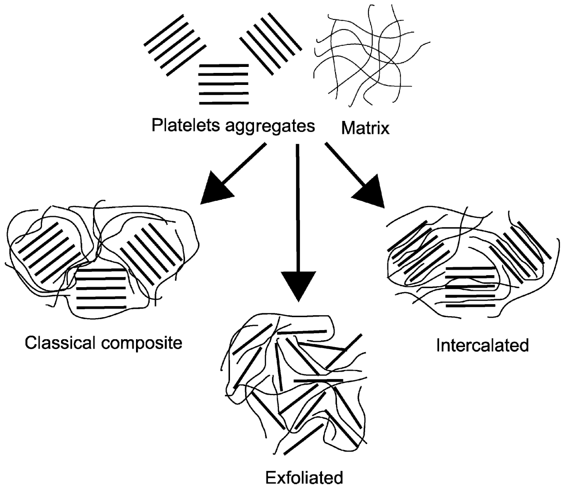

Fig. 1. Different types of nanocomposites.

platelets of the aggregates are separated and dispersed within the matrix. This results into quantum jump in the reinforced area which should ideally enhance the properties drastically. This can usually occur with very small fraction of nanoparticles in a matrix. The last two cases of materials are the true nanocomposites partially or fully intercalated and/or exfoliated, which are studied in this work.

3. Mechanical characterization of MMT nanocomposites

As the experimental data dealing with mechanical behavior of nanocomposites are not common, uniaxial tensile tests have been conducted on the PP based MMT nanocomposites. These tests have been performed on a conventional test machine (INSTRON 4302) with a load cell of 1 kN. The strains were measured without contact with a video extensometer (Apollor) that allows us to control the test at a constant rate of deformation. This one is kept constant for all experiments at $10^{-3}/\mathrm{s}$ in order to guarantee that the tests are quasi-static. All samples are based on ASTM D638-03 Type I test and are produced at optimized and constant processing parameters in a numerically controlled injection-molding machine (L&T Demag make). Mass fractions of 2, 3, 4, 5, 6 and 7% of MMT clay reinforcement in the PP matrix are considered in the present study to understand the elastic behavior (Young's moduli). Fig. 2 shows the evolution of the Young's modulus versus mass fraction of reinforcement. For general purpose, it is also convenient to represent the Young's modulus as function of volume fraction of reinforcement. The volume fraction is obtained knowing that the densities of Polypropelene (PP) and Montmorillonite (MMT) are $\rho_{\mathrm{PP}} = \rho_1 = 1\ \mathrm{g/cm^3}$ and $\rho_{\mathrm{MMT}} = \rho_2 = 2.83\ \mathrm{g/cm^3}$, respectively. Thus, the volume fraction of phase 2 (reinforcements) is $f_2 = 1 - \frac{\rho_2 wt_1}{\rho_2 wt_1 + \rho_1(1 - wt_1)}$ where wt_1 and wt_2 are the mass fraction of the matrix and the reinforcement, respectively. Fig. 3 presents the evolution of the Young's modulus as function of the volume fraction. A strong reinforcement effect due to the presence of the MMT platelets is observed.

4. Micromechanical modeling and comparison with the experimental results

4.1. Principles of the considered micromechanical models

One of the micromechanical models commonly considered for the study of particles-reinforced materials is the one based on Mori–Tanaka (MT) estimate ([13]). The use of this model by few authors for nanocomposites (see [11]) revealed that it is not completely efficient for this class of materials. According to that observation, our purpose here is to consider, in addition to the MT model, the Ponte Castañeda and Willis bound ([1]) which allows to take into account not only the shape of the reinforcement as in the MT but also the spatial distribution of reinforcement.

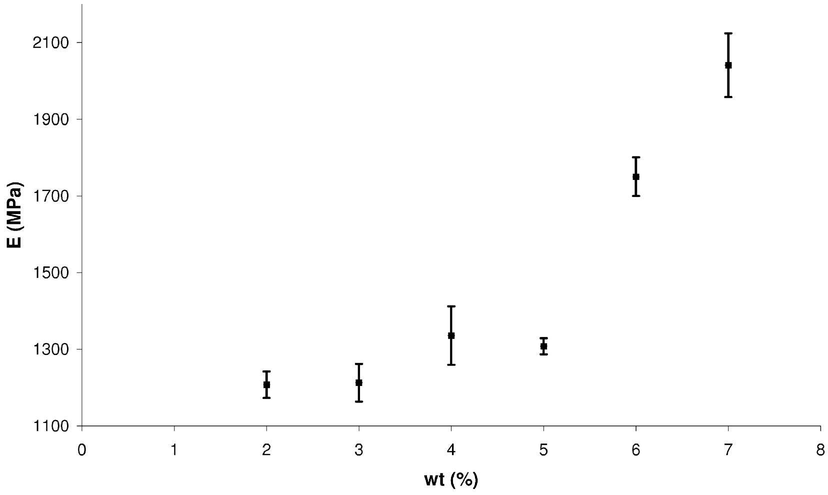

Fig. 2. Young's modulus of the nanocomposite versus the weight ratio Wt of reinforcement with standard deviations.

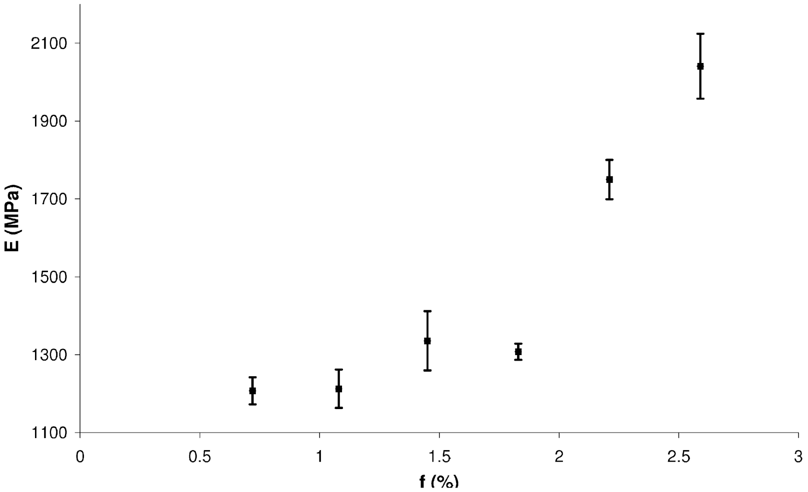

Fig. 3. Young's modulus of the nanocomposite versus the volume fraction f of reinforcement with standard deviations.

Defining the matrix as phase 1 (whose stiffness tensor is denoted $\mathbb{C}^{(1)}$) reinforced by N-1 families[1] of inclusions, the Ponte Castañeda and Willis bound provides the following expression of the overall stiffness tensor $\widetilde{\mathbb{C}}$:

$$\widetilde{\mathbb{C}} = \mathbb{C}^{(1)} + \left[\mathbb{I} - \sum_{r=2}^{N} c^{(r)}\mathbb{T}^{(r)}\mathbb{P}_d\right]^{-1}\left[\sum_{r=2}^{N} c^{(r)}\mathbb{T}^{(r)}\right] \tag{1}$$

with:

$$\mathbb{T}^{(r)} = \left[\left(\mathbb{C}^{(r)} - \mathbb{C}^{(1)}\right)^{-1} + \mathbb{P}_i^{(r)}\right]^{-1} \tag{2}$$

$\mathbb{C}^{(i)}$ is the stiffness tensor of the phase i and $c^{(i)}$ the volume fraction of the same phase.

The fourth-order Hill tensor $\mathbb{P}_i$ is associated with the geometry of the inclusions of the considered family, while $\mathbb{P}_d$ is associated with the form of the spatial distribution of these inclusions.

Remark. As noted by ([1]), expression (1) allows us to retrieve the Mori–Tanaka estimate when the $\mathbb{P}$-tensors for the reinforcements geometry and their spatial distribution coincide: $\mathbb{P}_d = \mathbb{P}_i$.

As the distribution of the orientation of the spheroidal reinforcement is random for the considered materials, the determination of the overall properties requires to perform an average over the orientations. This leads to an isotropic macroscopic stiffness tensor from which can be determined the compressibility modulus K and shear modulus G which in turn allow the evaluation of the Young's modulus E.

4.2. Comparison to experimental data

The mechanical properties of the matrix as well as the size of the reinforcement considered have been defined in Section 2. As the MMT clay platelets are quite rigid as compared to the matrix, they are assumed to be elastically rigid. According to the dimensions mentioned in Section 2, the geometry of the platelets is assumed spheroidal of 200 nm of diameter and 50 nm of thickness, the aspect ratio being therefore $\omega = \frac{50}{200} = 0.25$. Furthermore, in agreement with the macroscopic isotropy of the nanocomposite, we assume for the Ponte Castañeda and Willis bound that the spatial distribution of reinforcement in the matrix is spherical. This assumption seems to be relevant for intercalated nanocomposites structures with an isotropic distribution of the intercalated aggregates. For the spherical spatial distribution of the reinforcements, the isotropic tensor $\mathbb{P}_d$ is classically the one associated to a sphere. The analytical

---

[1] Each family of inclusion is characterized by its orientation.

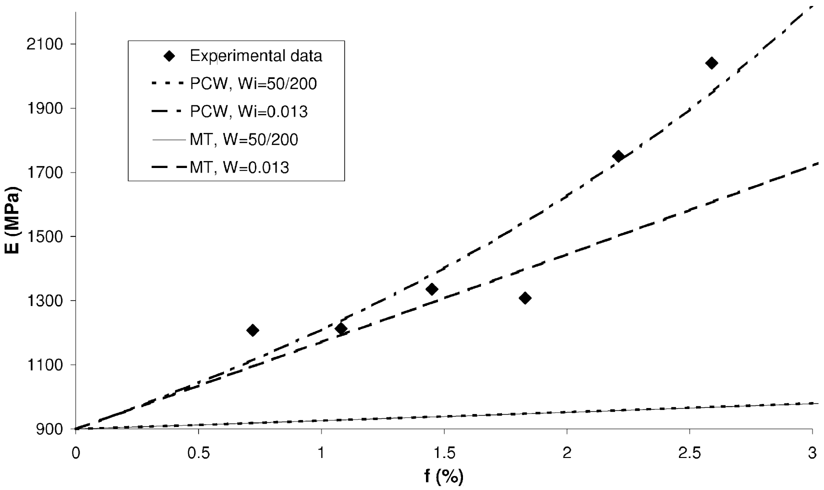

Fig. 4. Comparison between the experimental data and the predictions of the two homogenization bounds (Ponte Castañeda and Willis (PCW) and of Mori–Tanaka (MT)) for spheroid reinforcements with the aspect ratio $\frac{50}{200} = 0.25$ and 0.013.

and experimental results are presented in Fig. 4. From this comparison, it appears that, by considering $\omega = 0.25$, both the Mori–Tanaka (MT) scheme and Ponte Castañeda and Willis (PCW) bound predict a modest effect of the reinforcement due to platelets. These results clearly demonstrate that none of the considered model reproduce the experimental data. However, one should take care to measure the dimensions of these nanoplatelets carefully in the molded specimens which have intercalated structure. Indeed, the results might get affected if the dimensions of platelets in powder form are measured before processing and used for average estimate.

In a first step, it can be expected that a change in the aspect ratio can be used to describe the significant increase of the Young's moduli which also depends on the size of the platelets. From our computations, it was found that a value of $\omega = 0.013$ allows us to obtain a better result for the PCW model while the MT model still underestimates the overall elastic properties of the considered nanocomposite. In fact, it is known that the results provided by the PCW model for the bulk modulus K and shear modulus G of the composite have a certain range of validity depending on the concentration and shape of the platelets versus the shape of the spatial distribution of these platelets. Based on the constraints described in [1] (see their formula 4.6) and due to the spherical spatial distribution, it must be mentioned that for these two moduli the results provided by the PCW model are rigorous lower bounds only for platelets volume fractions $f \leqslant 1.3\%$ when an aspect ratio of $\omega = 0.013$ is adopted. Beyond $f = 1.3\%$ these results constitute simply estimates of the macroscopic properties. It can be readily verified that the above observations also applied to the Young's modulus.

5. Conclusions

To conclude, Polypropylene matrix reinforced by nanoplatelets of Montmorillonite has been elaborated for different volume fractions of platelets. The mechanical tests performed on specimens of the obtained nanocomposite showed a significant increase of the Young's modulus with very low volume fractions of reinforcement. The small size and the shape of the platelet-like reinforcement are mainly responsible for this increase. It is shown that the Ponte Castañeda and Willis (PCW) homogenization bound allows us to describe the experimental data when a spherical spatial distribution and a low aspect ratio (0.013) of the reinforcement are considered. Further developments will concern a specific analysis of the nonlinear behavior of the class of materials considered in the present Note.

Acknowledgements

The authors are grateful to an anonymous reviewer for useful comments on the modeling approach.

References

[1] P. Ponte Castañeda, J.R. Willis, The effect of spatial distribution on the effective behavior of composite materials and cracked media, J. Mech. Phys. Solids 43 (1995) 1919–1951.

[2] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito, Swelling behavior of montmorillonite cation exchanged for ω-amino acid bi ϵ-caprolactam, J. Mater. Res. 8 (1993) 1174–1178.

[3] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito, Mechanical properties of nylon-6-clay hybrid, J. Mater. Res. 6 (1993) 1185–1189.

[4] E. Chabert, Propriétés mécaniques de nanocomposites à matrice polymère: approche expérimentale et modélisation, Thèse de Doctorat de Génie des Matériaux de l'INSA de Lyon, 2002.

[5] J.M. Gloaguen, J.M. Lefebvre, Plastic deformation behaviour of thermoplastic/clay nanocomposites, Polymer 42 (2001) 5841–5847.

[6] J.-I. Weon, H.-J. Sue, Effects of clay orientation and aspect ratio on mechanical behavior of nylon-6 nanocomposite, Polymer 46 (2005) 6325–6334.

[7] V. Marcadon, Effets de taille et d'interphase sur le comportement mécanique de nanocomposites particulaires, Thèse de Doctorat de Mécanique et Matériaux de l'Ecole Polytechnique, 2005.

[8] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, Mater. Sci. Engrg. 28 (2000) 1–63.

[9] E.T. Thostenson, C. Li, T.W. Chou, Nanocomposites in context, Comp. Sci. Tech. 65 (2005) 491–516.

[10] F. Chavaria, D.R. Paul, Comparison of nanocomposites based on nylon 6 and nylon 66, Polymer 45 (2004) 8501–8515.

[11] T.D. Fornes, D.R. Paul, Modelling properties of nylon6/clay nanocomposites using composite theories, Polymer 44 (2003) 4993–5013.

[12] D. Shia, C.Y. Hui, S.D. Burnside, E.P. Giannelis, An interface model for prediction of Young's modulus of layered silicate-elastomer nanocomposites, Polymer Composites 19 (5) (1998) 608–617.

[13] T. Mori, K. Tanaka, Average stress in matrix and average elastic energy of materials with misfitting inclusions, Acta Metall. 21 (1998) 571–574.

[14] J.C. Halpin, S.W. Tsai, Environmental factors estimation in composite materials design, AFML TR, 67-423, 1967.