

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

### Water Sorption of a Polyurethane/Bentonite Composite: Effects of Bentonite Content and Drying Conditions

M. R. O. Pinto<sup>a</sup>; S. M. de L. Silva<sup>b</sup>; L. H. de Carvalho<sup>b</sup>; J. R. M. d'Almeida<sup>c</sup>

<sup>a</sup> Department of Chemistry, Universidade Estadual da Paraíba, Rua Juvêncio Arruda s/n, Campus Universitário, Campina Grande, PB, Brazil <sup>b</sup> Materials Engineering Department, Universidade Federal de Campina Grande, Campina Grande, PB, Brazil <sup>c</sup> Materials Science and Metallurgy Department, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

**To cite this Article** Pinto, M. R. O. , Silva, S. M. de L. , de Carvalho, L. H. and d'Almeida, J. R. M.(2007) 'Water Sorption of a Polyurethane/Bentonite Composite: Effects of Bentonite Content and Drying Conditions', *International Journal of Polymeric Materials*, 56: 9, 885 – 892

**To link to this Article:** DOI: 10.1080/00914030601123351

**URL:** <http://dx.doi.org/10.1080/00914030601123351>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Water Sorption of a Polyurethane/Bentonite Composite: Effects of Bentonite Content and Drying Conditions

**M. R. O. Pinto**

Department of Chemistry, Universidade Estadual da Paraíba, Rua Juvêncio Arruda s/n, Campus Universitário, Bodocongó, Campina Grande, PB, Brazil

**S. M. de L. Silva**

**L. H. de Carvalho**

Materials Engineering Department, Universidade Federal de Campina Grande, Bodocongó, Campina Grande, PB, Brazil

**J. R. M. d'Almeida**

Materials Science and Metallurgy Department, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

*In the present work, compression molded polyurethane/bentonite composites were manufactured and their water sorption characteristics were determined as a function of filler content and drying conditions. The matrix was a polyurethane derived from castor oil and the filler was a commercially available sodium bentonite. Filler contents varied from 0 to 10% by weight. The effects of three filler drying conditions, that is, 1 h at 200°C; 1 h at 110°C, and 24 h at 110°C, on the water sorption behavior of PU/bentonite composites with 5% w/w filler loading were also analyzed. The experimental results show that the water sorption behavior of the composites could be satisfactorily modeled by the Fickian model, and that the amount of absorbed water increases with the filler loading. It was also observed that, within the first 200 h of immersion, composite water sorption was lower than that of the polymeric matrix alone. The data evince that although only minor differences were noted, water sorption is reduced when the filler was dried at higher temperatures.*

**Keywords:** bentonite, drying conditions, nanocomposite, polyurethane, water sorption

Received 25 October 2006; in final form 3 November 2006.

The authors thank Proquinor SA and Bentonit União Nordeste for providing the materials, and to RENAMI, PADCT/CNPQ, and CNPq for the financial support.

Address correspondence to J. R. M. d'Almeida, Materials Science and Metallurgy Department, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225 Gávea, Rio de Janeiro, RJ 22453-900, Brazil. E-mail: dalmeida@dcmm.puc-rio.br

## INTRODUCTION

In the last few years, polymer nanocomposites became an important research area because these materials exhibit excellent synergistic properties derived from both the reinforcement particles and the polymeric matrix [1]. One of the most promising systems of nanocomposite materials is based on organic polymers and clay minerals in the form of layered silicates [1–4]. Production of nanocomposites from layered silicates opens interesting possibilities because it improves the properties of traditional plastic resins, enlarging their field of application [5]. However, the properties of nanocomposite materials are highly dependent on the loading-matrix interaction, which can be significantly affected by surface treatments of the filler or by water sorption [6–7].

The present work deals with the water sorption behavior of compression-molded PU/bentonite composites made with industrial sodium bentonite clay as reinforcement and a polyurethane derived from castor oil as matrix. The water sorption behavior of these composites was analyzed as a function of the weight fraction of the bentonite clay, which was varied up to 10 % w/w. The effect of the clay drying conditions on the water sorption behavior was also analyzed.

## EXPERIMENTAL

The polyurethane matrix was obtained by combining a polyol (Garicin A230, with 230 KOH mg/g, provided by Proquinox, Brazil) and a modified isocyanate prepolymer (M25, with 15% free isocyanate, also provided by Proquinox, Brazil) in a 1:0.7 ratio by weight, as recommended by the resin manufacturer. Both materials were obtained from castor oil. The clay was an industrial sodium bentonite from Boa Vista, Paraíba (Brazil), commercially available under the name Brasgel. Composites with clay loadings of 0, 1, 3, 5, 7, and 10% by weight were analyzed. These composites were manufactured using bentonite dried for 1 h at 110°C.

The effect of the drying conditions of the bentonite clay upon the water absorption kinetics of composites manufactured with 5% w/w filler loading was also evaluated. Besides the basic drying condition of 110°C for 1 h, composites were also prepared using bentonite dried at 110°C for 24 h, and at 200°C for 1 h.

The clay was mixed with the polyol for 1 h hour at ambient temperature using a mechanical stirrer operated at 600 rpm. The mixture was dried under vacuum for another hour, with constant stirring, at a temperature of  $80 \pm 5^\circ\text{C}$ . The isocyanate prepolymer was also dried under vacuum for 1 h at  $80 \pm 5^\circ\text{C}$ , and then added to the polyol/bentonite

system, with manual stirring for 1 min. The resulting mixture was poured into the cavity ( $200 \times 180 \times 3$  mm) of a metal mold. The mold was closed, and the cure was performed under a pressure of 8 ton (2.2 MPa) for 4 h at ambient temperature. Test specimens 20 mm long, 20 mm wide, and 3 mm thick were machined from the plates and finished with grinding papers (#100 and 180 grits).

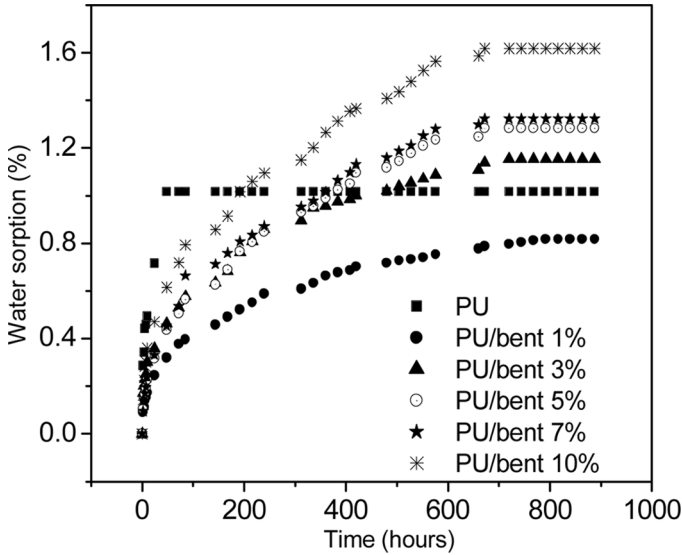
Prior to the water sorption test, the test specimens' sides were sealed with the same resin used as matrix. This procedure was adopted to avoid direct water contact with the filler. The test specimens were then dried in an oven for 24 h at  $105 \pm 5^\circ\text{C}$ . Water sorption was determined by comparing dry and wet weights, according to ASTM D570 standard. The test specimens were immersed in distilled water at ambient temperature, and at predetermined times (every 2 h at short times, 24 h at long times) were taken out of the water bath, quickly dried with low absorption paper towels, and weighted within  $\pm 0.1$  mg. Three test specimens were used per condition of analysis, and sorption measurements were made up to the apparent saturation (constant weight) of the samples. The experimental data were fitted to the simplified equation proposed by McKague et al. [8] that can model the complete absorption curve, namely:

$$\frac{M\%}{M_\infty} = \tanh\left(\frac{4}{h} \sqrt{\frac{Dt}{\pi}}\right) \quad (1)$$

where  $M\%$  is the mass of water absorbed in a time  $t$ ,  $M_\infty$  is the mass of water absorbed at saturation,  $h$  is the thickness of the sample, and  $D$  is the diffusion coefficient.

## RESULTS AND DISCUSSION

Figure 1 shows the experimental weight gain versus immersion time curves obtained for the composites manufactured after drying the bentonite for 1 h at  $110^\circ\text{C}$ . It can be seen that the water sorption increases with the bentonite weight fraction. For the larger clay loading (10% by weight) an increase of 60% over that of the matrix was observed. It was also observed that, within the first 200 h of immersion, the amount of water absorbed by the composites was lower than that of the polymeric matrix alone. This behavior can be attributed to the increase in the free path for water transport within the composite [9], That contributes to the steady decrease of the diffusion coefficient with the bentonite loading (Table 1). This initial behavior is, in fact, very attractive from a practical point of view. Moreover, when layered silicates are well dispersed inside a polymeric matrix, resulting in a

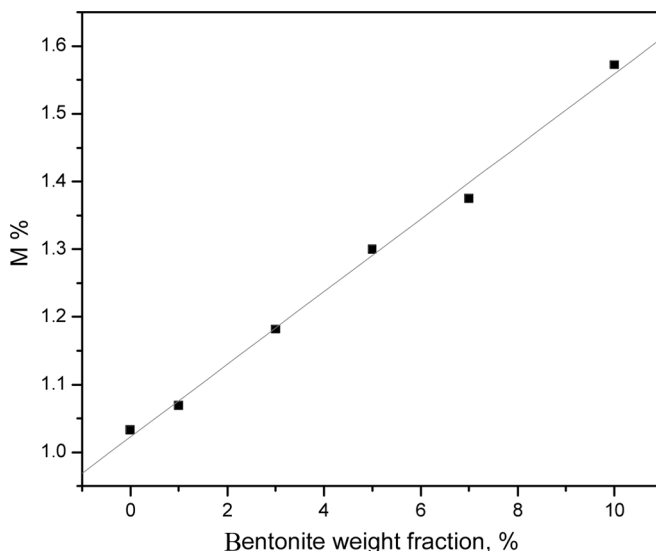


**FIGURE 1** Water sorption behavior of polyurethane/bentonite systems as a function of bentonite weight fraction.

considerable increase in the free path for water transportation, swelling of the matrix is also expected to decrease [10–11]. The results in Table 1 show that, in fact, the diffusion coefficient is leveling off to a constant value as the weight fraction of bentonite increases. This may suggest a change of the degree of exfoliation and, therefore, of the morphology of the composite as the fraction of bentonite is increased. In fact, an exfoliation to intercalation transition was observed as the amount of clay is increased for LDPE/clay nanocomposites [12]. A detailed microstructural investigation of these composites is, however, beyond the scope of this work.

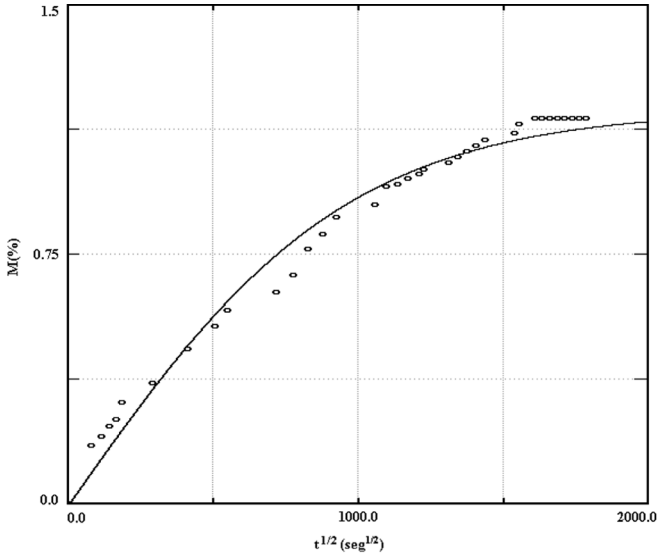
**TABLE 1** Water Sorption Parameters

%w/w bentonite	$D, 10^{-6} \text{mm}^2/\text{s}$	$M_{\infty}, \%$	$r$
0 (Matrix)	15	1.03	0.992
1	6.7	1.07	0.998
3	1.9	1.18	0.992
5	1.74	1.30	0.987
7	1.58	1.37	0.991
10	2.31	1.57	0.981



**FIGURE 2** Variation of the water saturation value,  $M_{\infty}$ , with bentonite weight fraction.

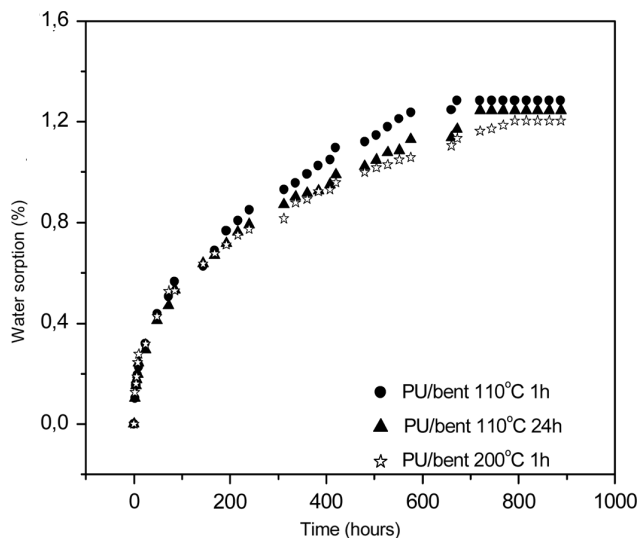
The values of  $M_{\infty}$ , obtained extrapolating the experimental data to Eq. 1, are also listed in Table 1, and are plotted as a function of bentonite loading in Figure 2. A linear relationship holds, highlighting the bentonite hydrophilic behavior. In fact, the polyurethane/bentonite composite manufactured is a multiphase system composed by hydrophilic regions (bentonite) dispersed in a hydrophobic matrix (polyurethane). The co-existence of phases with different water permeability characteristics results in complex water transport phenomena [13]. However, as shown in Figure 3, the experimental points for all formulations analyzed fitted well the theoretical Fickian model curve, Eq. 1. Table 1 also lists the high correlation coefficients found. Moreover, the value predicted for the diffusion coefficient of the polyurethane matrix is identical to previously reported values obtained modeling the water sorption using the Fickian model [14]. Therefore, and although the bentonite/polyurethane composite is a biphasic system, the evidence shows that a Fickian mechanism is driving water sorption. It is worth noticing here that for vinyl ester/montmorillonite nanoclay nanocomposites [15] considerable amount of deviation from Fickian behavior was observed, although the same trends of decrease of the diffusion coefficient and increase of equilibrium water



**FIGURE 3** Example of the fitting curve (solid line) obtained with the experimental data. The curve shown is for the bentonite/polyurethane system with 3 wt% of bentonite.

content with increasing amount of clay in the matrix polymer were found.

The effect of bentonite drying conditions on water sorption of the polyurethane/bentonite composite system is presented in Figure 4. Clay loading of 5% by weigh was employed in this test. Results show that, within the limits of time and temperature of drying investigated in this work (i.e., 110°C for 1 h, 110°C for 24 h, and 200°C for 1 h) the drying condition did not significantly affect water sorption, although small differences were observed. A decrease of 3.1% in the absorption of water when the bentonite was dried for 24 h at 110°C and a decrease of 6.2% when the bentonite was dried for 1 h at 200°C, compared with the composite where the clay was dried for 1 h at 110°C. These results may be attributed to a decrease of the water content in the load, contributing to a better bentonite/matrix interaction during the manufacture of the composite. Better load to matrix interfaces usually contribute to decrease the formation of defects, like voids, in the bentonite/polymer interface, leading to an effective decrease in the water absorption capability of the composite, as observed.



**FIGURE 4** Effect of clay drying conditions on the water sorption of polyurethane/bentonite systems.

## CONCLUSIONS

The water sorption behavior of bentonite/polyurethane composites was affected by the amount of bentonite. Although the diffusion coefficient was reduced if compared to that of the bare matrix—which was explained as being due to an increase of the water diffusion path with clay addition—the saturation value steadily increased with the loading, and a linear relationship was found between  $M_{\infty}$  and bentonite weight fraction. The overall sorption behavior could be modeled by the Fick model.

A comparative analysis of the results obtained for the composites manufactured with bentonite dried for 1 h at 110°C shows that longer clay drying times (24 h vs. 1 h, at 110°C) resulted in a 3.1% decrease in water sorption, whereas drying at higher temperatures (200°C vs. 110°C, for 1 h) caused a 6.2% decrease. Although small, these differences can contribute to reduce the number of defects at the load to matrix interface, and therefore, can contribute to better mechanical properties.

## REFERENCES

- [1] Jordan, J., Jacob, K. I., Tannenbaum, R., Sharaf, M. A., and Jasiuk, I., *Mater. Sci. Eng. A* **393**, 1 (2005).
- [2] Okada, A. and Usuki, A., *Mater. Sci. Eng. C* **3**, 109 (1995).



- [3] Giannelis, E. P., *Adv. Mater.* **8**, 29 (1996).
- [4] Ogawa, M. and Kuroda, K., *Bull. Chem. Soc. Jpn.* **70**, 2593 (1997).
- [5] Yao, K. J., Song, M., Hourston, D. J., and Luo, D. Z., *Polymer* **43**, 1017 (2002).
- [6] Zilg, C., Mülhaupt, R., and Finter, J., *Macromol. Chem. Phys.* **200**, 661 (1999).
- [7] Cavalcanti, W. S., M.Sc. Thesis, Universidade Federal da Paraíba, Campina Grande (2000) (in Portuguese).
- [8] McKague, E. L., Reynolds, J. D., and Halkias, J. E., *J. Eng. Mater. Tech.* **98**, 92 (1976).
- [9] Moon, S. Y., Kim, J. K., Nah, C., and Lee, Y. S., *Eur. Polym. J.* **40**, 1615 (2004).
- [10] Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Kurauchi, T., Kamigaito, O., and Kaji, K., *J. Polym. Sci. Part B: Polym. Phys.* **32**, 625 (1994).
- [11] LeBaron, P. C., Wang, Z., and Pinnavaia, T. J., *Appl. Clay Sci.* **15**, 11 (1999).
- [12] Wang, K. H., Lee, Y. H., and Park, C. B., In: Proceedings of the ANTEC 2004, Chicago, 2004, CD-Rom, 2510.
- [13] Karmaker, A. C., *J. Mater. Sci. Letters* **16**, 462 (1997).
- [14] Apicella, A., Egiziano, L., Nicolais, L., and Tucci, V., *J. Mater. Sci.* **23**, 729 (1988).
- [15] Shah, A. P., Gupta, R. K., Gangarao, H. V. S., and Powell, C. E., *Polym. Eng. Sci.* **42**, 1852 (2000).