Microfoams Based on Castor Oil Polyurethanes and Vegetable Fibers

Mirta I. Aranguren,[1] Ilona Rácz,[2] Norma E. Marcovich[1]

[1]Chemical Engineering Department, INTEMA-UNMdP-CONICET, Juan B. Justo 4302, Mar del Plata, Argentina
[2]Bay Zoltán Institute for Materials Science and Technology, Fehérvári út 130, Budapest, Hungary

ABSTRACT: This work was focused on the production and characterization of microcellular polyurethane (PU) composites reinforced with pine wood-fibers or with hemp, which can be applied to the manufacture of car interior panels, or acoustic insulation panels for the construction industry. The polymers selected for the study were crosslinked PUs, synthesized from a castor oil-based polyol, with the formulations adjusted to obtain different foaming levels. Microfoamed composites with preferential orientation were prepared from long hemp fibers. Also, samples with random arrangement of short hemp and wood fibers were obtained. The morphology of the composites was analyzed by scanning electron microscopy. The mechanical performance of the reinforced foams was studied through three point bending and dynamic mechanical tests. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2791–2800, 2007

Key words: polyurethanes; fibers; composites; mechanical properties; ageing

INTRODUCTION

Polyurethanes (PU) can be synthesized from an ample variety of reactants; the possibilities for their formulation are almost unlimited. Different materials can be prepared with properties ranging from those of flexible elastomers to rigid crosslinked PU that can be used as structural materials. The use of PUs foamed to different levels provide a wide range of possibilities for the fabrication of composite materials for low weight applications, as well as applications for acoustic or mechanical damping materials.

In particular, rigid polyurethane foams (PUFs) are materials used in different areas, construction, automotive, nautical, etc. They have a great adaptability to varying type of processes; they can exhibit high energy absorption, good thermal properties, and specific strength.[1] PUFs are obtained from the reaction of diisocyanate with polyol.[2–4] This is an exothermic reaction, and the released heat can be used to form a cellular structure by evaporation of physical blowing agents such as chlorofluorocarbons, although nowadays, its use is considered undesirable for the environment. Other alternative to generate the cellular structure of the PUFs is from chemical blowing agents. One of the widely used agents is water, which reacts with diisocyanate, releasing carbon dioxide bubbles, the initial step for foam cells formation.[2] The amount of water added determines the density and the mechanical properties of the foam.[5,6] These foams can also be modified incorporating solids such as metal, glass, and other powders. This addition modifies the walls of the foam cells[6,7] introducing changes in the mechanical and thermal properties of the materials.

During the last years there has been a constant growing interest from the academic and industrial sectors in the utilization of renewable resources for the manufacture of new materials. Thus, the use of resins based in natural products is being considered and the use of vegetable fibers is already installed in the market. Vegetable fibers are not only widely available around the world, but they also offer large aspect ratio, relatively high tensile strength and modulus, low density and low cost. All of these characteristics that contribute to increase the interest of the manufacturers to produce low-cost, light-weight composites.[8–10] Besides, these reinforcements are biodegradable and fit easily into the earth–ecological cycles. Thus, new materials and composites derived from natural sources rich in cellulose, and offering environmental and economic benefits, are being developed by the automotive, construction, household furniture, and packaging industries. Therefore, it is important to improve these materials for better and more effective use.[11] To obtain a good load transfer from the matrix to the fibers, it is essential that matrix and reinforcement are compatible and/or that they can react with each other, to ensure a strong

Correspondence to: N. E. Marcovich (marcovic@fi.mdp.edu.ar).

interface.[12] In particular, PU's are compatible with lignocellulosic reinforcements, which contain a high concentration of hydroxyl groups. However, vegetable reinforced PU's have not been systematically studied and there exist few references to this respect.[10,13,14]

On the other hand, currently most used polymers and polymeric composites are derived from petrochemical refining of crude oils and coals, both of which are rapidly diminishing natural resources.[15] As the number of applications of polymeric materials continues to increase, an alternative source for these materials is required.[15,16] Natural oils, which can be derived from both, plant and animal sources, are found in abundance in all parts of the world, providing an ideal petroleum-substitute from a chemical feedstock. Recently, renewable and natural plant products such as castor oil,[17] palm oil,[15] and rosin,[18] were used to synthesize polyester polyols, which were used as raw materials in the preparation of rigid PU foams.[19]

The present work is focused in the production and characterization of PU composites reinforced with pine wood-fibers or with hemp, which can be applied to the manufacture of car interior panels, or acoustic insulation panels for the construction industry. The polymers utilized are crosslinked PU's, formulated from a castor oil based polyol. The source of isocyanate groups utilized is a polymeric 4,4′-diphenylmethane diisocyanate (MDI) that has low vapor pressure and allows for easier handling of the reactants and reinforcements. Because of the chemical nature of the polymer chosen as matrix and the selected reinforcements, a very good interfacial adhesion is expected in these composites. Since the vegetable reinforcements are materials rich in hydroxyl groups, they can be reactive towards the isocyanate component and thus, become chemically linked to the polymeric matrix.

EXPERIMENTAL

Materials

The PU foam was synthesized from a polyol obtained through alcoholysis of castor oil (Parafarm®, Argentina). The castor oil (previously dried until constant weight), dry trietanolamine (1:3 mol ratio), and LiOH (catalyst, 0.2 wt % based on total reactants) were stirred together in a flask at 150°C during 180 min.[20,21] Figure 1(A) is a schematic of the polyol synthesis from castor oil, which consists of a mixture of the species shown in the figure and unreacted triglyceride, with a major concentration of the monoglyceride component.[22] The modification reaction allowed increasing the OH value from 169.3 mgKOH/g for initial castor oil to 449 mgKOH/g for the modified polyol after
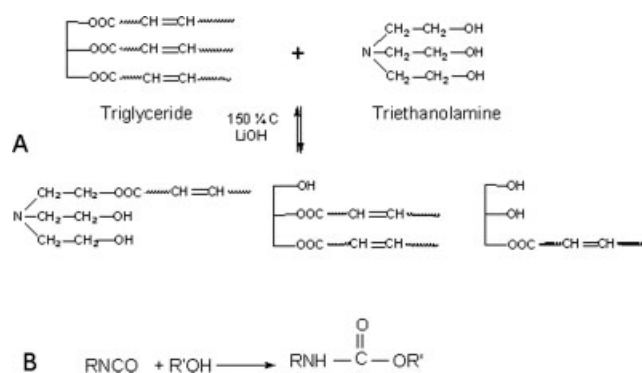

Figure 1 (A) Chemical pathway leading to castor oil derived polyol. (B) Chemical pathway leading to polyurethanes.

reaction. Both reported values were determined by analytical techniques.[23]

The isocyanate crosslinker was a 4,4′-diphenylmethane diisocyanate (MDI) prepolymer (Rubinate 5005, Huntsman Polyurethanes, USA) with an equivalent weight of 131 g/equiv. Figure 1(B) is a schematic of the PU synthesis from polyol and isocyanate.

Humidity present in the polyol and the vegetable reinforcements was enough to generate foaming. The samples prepared in these conditions are called throughout the text "foamed-1." In some samples, extra water (foaming agent, 0.25% respect to the total weight) was purposely added to the formulation to obtain a different foaming level. The samples prepared in these conditions are called "foamed-2" throughout the text.

The neat PU and reinforced samples (containing a 20 wt % of vegetable fibers), were formulated with an Index = 1.25 (equivalents NCO/equivalents OH from polyol). A relatively large imbalance was utilized for the reinforced formulations, because some isocyanate groups are assumed to be consumed in a heterogeneous covalent reaction with the surface OH groups of the vegetable fibers added. In all cases, the polyol was vacuum aid dehydrated during 2 h at 80°C with strong stirring before being used, to eliminate most of the absorbed moisture. A small amount of a commercial surfactant agent (Tergostab B 8404, Huntsman PUs, 1 wt % respect to the total weight) was added to the reactive mixture to control cell size distribution in the foam. Reinforcing fibers were dried overnight at 110°C prior to composite preparation.

The vegetable fibers utilized in the study were wood fibers from pine Sp. (Hungary) and hemp fibers (Hungary). The shape characteristics of the fibers are shown in Figure 2 (digital photographs). Hemp fibers were incorporated as short (cut to 20 mm length) or long fibers. In both cases, the fibers were forming threads (technical fiber), and in the
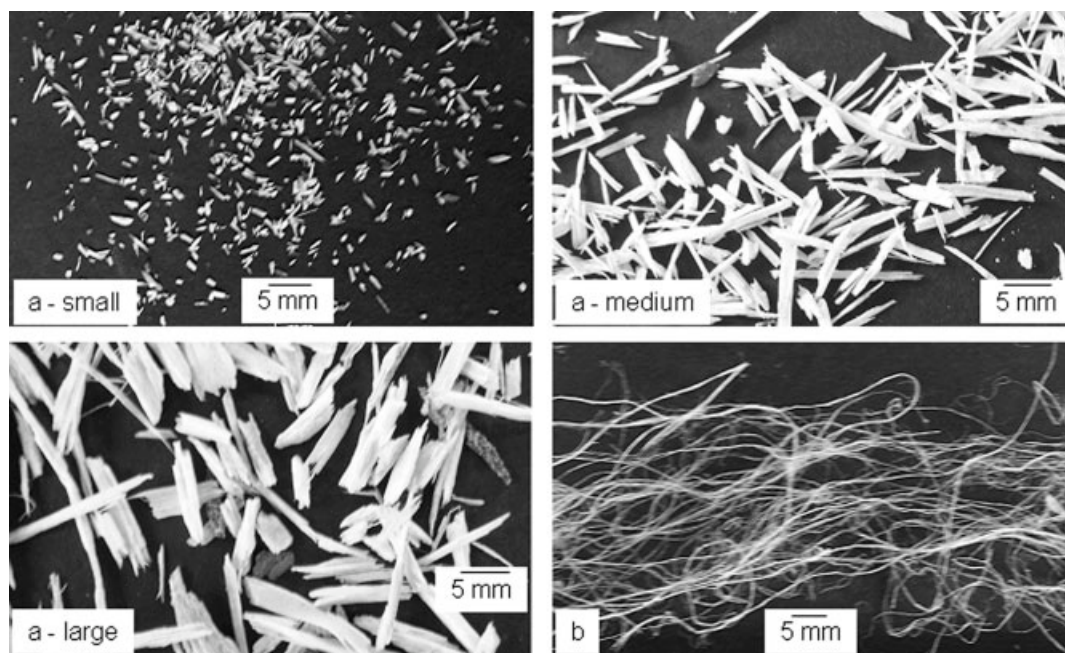
Figure 2 Images of the utilized reinforcing fibers, (a) pine wood fibers, (b) hemp fibers.

case of the long fibers the threads were long enough to behave as continuous fibers, they covered the whole length of the sample specimen ($\sim$ 15 cm). On the other hand, pine wood fibers were classified according to the following:

Small wood fibers: those that passed through a sieve number 20 (average particle size 840 μm),

Medium wood fibers: those that passed through a sieve number 10 (average particle size 2000 μm),

Large wood fibers: those that passed through a sieve number 6 (average particle size 3360 μm)

Sample preparation

Microfoamed PU samples were obtained by mechanically mixing appropriate amounts of MDI, polyol, and surfactant agent for 10 s. No catalyst was added to the formulation to have a processing time before reaction long enough for mixing and pouring the mix into the mold. As indicated, the unreacted mixture was poured into a metal mold (previously coated with a Teflon film to facilitate sample releasing) and closed. A relatively low pressure was applied on the cover lid of the mold, to avoid the opening of the mold by the internal pressure generated during foam raising. The crosslinking reaction took place at room temperature and 120 KPa, and was completed in about 1 h. No significant amounts of materials (fibers, particles, or liquid reactives) were lost during the reaction, thus the weight percentages of the different components in the composites were calculated on the basis of the initial weights added. Plaques of 150 mm diameter and

4 mm thickness were obtained. The same procedure was followed to prepare composite samples, but in this case the fibers were first placed into the mold and then the liquid PU mixture was poured onto them.

Microfoamed composites were prepared with random arrangement of short fibers (hemp or pine wood fibers), or with continuous hemp fiber-threads aligned in one, two (i.e., fiber placed at 0 and 90° with respect to the direction of the sample longitudinal axe), and four directions (i.e., fiber placed at 0, ±45, and 90° with respect to the direction of the sample longitudinal axe).

Characterization methods

Scanning electron microscopy

The fracture surfaces generated during flexural tests were analyzed by scanning electron microscopy (SEM) using a Philips Jeol 35 CF microscope. The samples were sputtered with gold prior to being examined.

Density measurements

The density of the samples was calculated as the ratio weight to volume of samples dried at 110°C. The specimens were bars of $50 \times 13 \times 4$ mm^3, with the linear dimensions measured to ± 0.01 mm, and the equilibrium weight of the dried samples were used in the calculations.
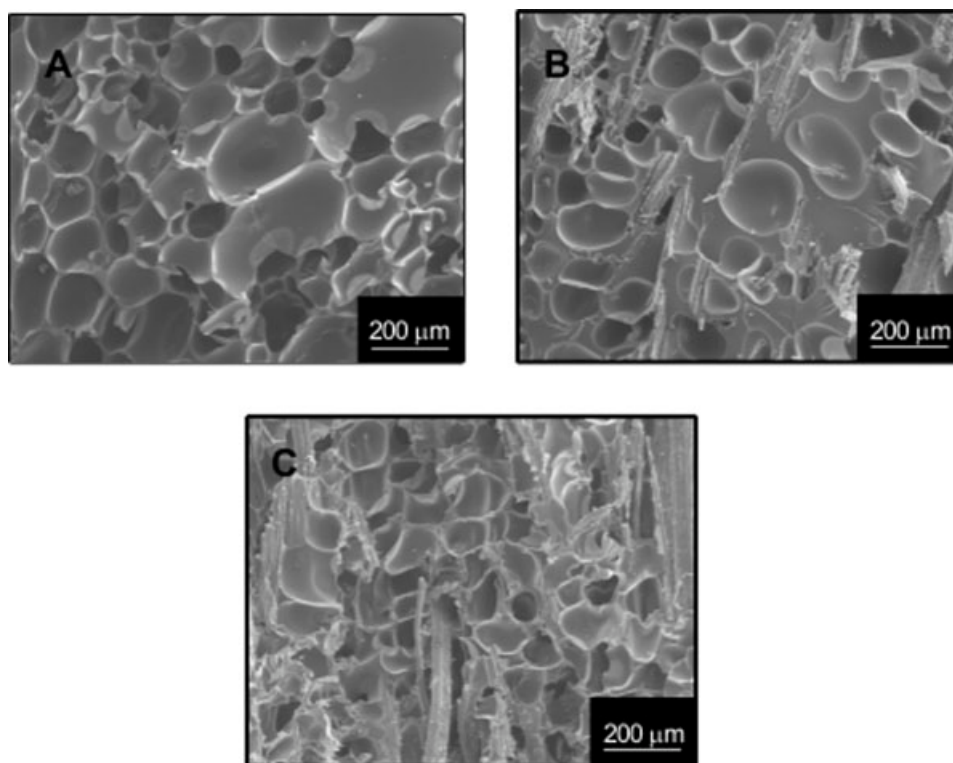
Figure 3 Scanning electronic micrographs. (A) Unreinforced foam (foamed-1); (B) Long unidirectional hemp fibers reinforced foam (foamed-1); (C) Long unidirectional hemp fiber-reinforced foams with added water (foamed-2).

Dynamic mechanical tests

A Perkin–Elmer dynamic mechanical analyzer (DMA 7) was used in these experiments to obtain the storage modulus (E'), and loss tangent (tan δ) of the samples. The tests were carried out using the temperature scan mode, and the three point bending fixture with a specimen platform of 15 mm length and under dynamic and static stresses of 4×10^5 and 8×10^5 Pa, respectively. The frequency of the forced oscillations was fixed in 1 Hz. The specimens were cut to $20 \times 4 \times 3$ mm^3, and the linear dimensions were measured up to 0.01 mm.

Flexural tests

The mechanical performance of the reinforced foams was studied using a three point bending fixture in a INSTRON 8501 Universal testing machine. A span of 60 mm (transversal area of 13×4 mm^2) and a crosshead speed of 1 mm/min were selected, according to the procedure A, ASTM 790 (rigid samples). Flexural modulus (E) and flexural yield stress (σ_y) were calculated from the stress–strain curves. Flexural toughness was calculated as the area under the stress versus strain curve.

RESULTS AND DISCUSSION

The morphology of the foams was analyzed by SEM of the fracture surfaces of samples tested in flexion. Figure 3 shows the features of an unreinforced foam [Fig. 3(A, foamed-1)] and unidirectional hemp foams prepared without (foamed-1) and with (foamed-2) additional water [Fig. 3(B,C), respectively], which are representative of the variations observed in all composites. The amount of open cells slightly increases when the reinforcement is added. The interfacial adhesion between fibers and matrix is very good, because the OH groups present in the fibers can react with the isocyanate groups to become covalently bonded to the polymeric matrix. The average cell size decreased as the concentration of foaming agent increases. Since the number of cells increases with the addition of water (which generates CO_2 blowing agent by reacting with the isocyanate) and the crosslinking reaction inhibits small cells to collapse into bigger ones, a larger number of smaller cells must result. This change in the morphology not only affects the mechanical performance of the foams but also their physical characteristics.

The incorporation of just a drop of water to the formulation produces the large changes observed by SEM and that are macroscopically measurable as a change in the density of the materials (Table I).

TABLE I
Density of the Samples

	Density (Kg/m^3)
Foamed-1 samples	
Unreinforced PU	954.5 ± 5.6
Small Wood fibers	969.1 ± 27.3
Medium Wood fibers	783.9 ± 10.8
Large Wood fibers	795.2 ± 3.8
Hemp Short fibers	782.5 ± 17.8
Hemp-1 direction	763.4 ± 31.4
Hemp-2 directions	722.2 ± 8.0
Hemp-4 directions	842.6 ± 28.4
Foamed-2 samples	
Unreinforced PU	672.3 ± 51.8
Medium wood fibers	611.1 ± 5.9
Hemp-1 direction	583.0 ± 20.5

Obviously, the stoichiometry of the reaction is also changed, because the isocyanate groups are consumed in the formation of ureas and CO_2 in a larger proportion than in the formulation without water addition. Comparison of the FTIR spectra obtained from both types of samples is shown in Figure 4. Infrared spectroscopy on recently prepared neat PU samples show some differences related to the addition of extra water. The main difference is on the consumption of the isocyanate groups at (2274 cm^{-1}); more NCO groups are consumed in the foamed-2 sample and thus the intensity of the peak is lower. A small difference appears in the region of soluble ureas at about 1660 cm^{-1}, a slightly larger concentration of these groups is formed in the foamed-2 sample.[24] As a consequence of the chemical and morphological changes induced by water addition, the materials can show different thermal and mechanical properties.

Besides, the materials can also show some aging which is the result of further polymerization of any originally unreacted isocyanate, and also of possible reactions of the unsaturations remaining in the chains of the castor oil based polyol. Because some of the unsaturations of the triglyceride chains in the polyol are not converted to OH and thus they remain in the crosslinked PU, a slow reaction initiated by oxygen is possible. This reaction is responsible for the solidification of drying oils and has been reported previously in the literature.[25–29] Since aging can result in changes in the chemical structure of the foams leading to changes in their physical and mechanical properties, only samples with similar aging times after preparation were compared. Therefore, in the following discussion, unless it is specifically indicated, the properties of the samples stored at room temperature during one year are reported and compared. Additionally, the density of the materials must be considered to discuss their final properties on a comparable basis.

Effect of the filler size and structure

Wood fibers

Thermomechanical (DMA) and mechanical (flexural) properties were measured for samples prepared with the pine wood flours of different sizes (and as previously discussed, different aspect ratios). No additional water was incorporated to the formulations so the little foaming observed in these samples is the result of the equilibrium humidity content of the fibers. The density of the resulting materials is not exactly the same, since it will depend on the nature of the fibers and the degree of microfoaming in the samples (Table I). These differences have been taken into account in the following analysis and discussion of the results.

Figure 5 shows the storage modulus and tan δ curves for the unreinforced PU, small, medium, and large pine wood fiber-composites. The analysis of the dynamic measurements shows that the temperature of the tan δ peak, which corresponds to the main relaxation of the matrix and is related to its glass transition, is in the range of 98–108°C for the composites, while it is around 70–73°C for the unreinforced sample.

All the samples show a decrease of E' with the temperature, but the drop in E' at the transition for the composites is of only about one decade, because the presence of the rigid fibers avoids a larger drop of the modulus. On the other hand, the difference between glass and rubber modulus is much higher in the matrix than in the composites, being the change for the unreinforced sample of about two decades.

The large differences between the dynamic mechanical behavior of reinforced and unreinforced samples are attributed to the combination of the hydrodynamic effects of the particles embedded in a viscoelastic medium and to the mechanical restraint
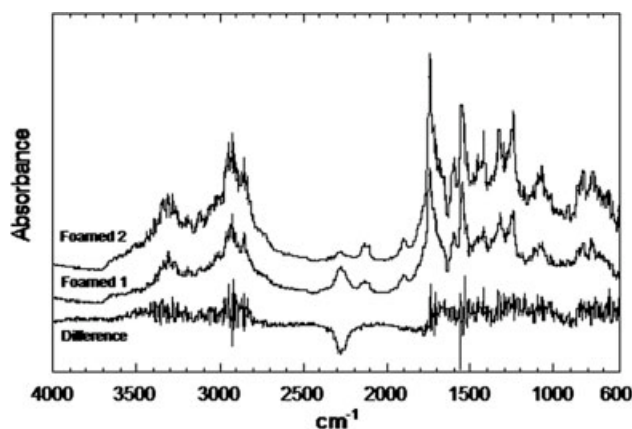

Figure 4 DRIFT spectra of PU foams. Difference spectrum corresponds to the subtraction: foamed-1–foamed-2 spectra.
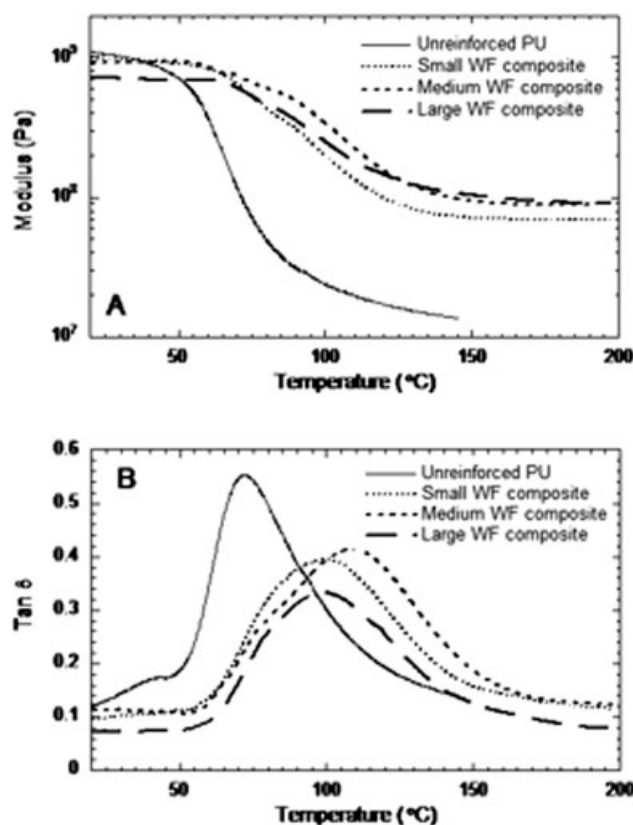
Figure 5 Storage modulus and tan δ curves for unreinforced PU, small, medium, and large pine wood flour-composites (foamed-1).

introduced by the filler at high concentrations (which reduced the mobility and deformability of the matrix). This effect is even more important in the present system, where the —OH groups of the wood fibers can react with the NCO groups of the MDI, leading to the chemical bonding between matrix and reinforcement.

It is very interesting to notice that the width of the tan δ peak for all the composites covers a temperature range of almost 100°C, suggesting that these materials may have interesting damping properties.

Additionally, the materials were mechanically tested and thus, the flexural properties of the cross-linked reinforced samples were measured and are shown in Table II. As anticipated, the density of the samples was considered in the analysis. Table I shows that the densities of medium and large wood

fibers-composites are quite similar, which allows a direct comparison of the mechanical results obtained for those two samples. However, the small fibers-composite presented a higher density. A comparison is still possible by considering the modulus and strength of the samples per unit density. The results obtained in this way are presented in Figure 6.

It is clear that there is an overall trend of increasing properties (modulus and strength) as the size of the fibers decreases. Similar trends have been reported in the literature.[30,31]

Hemp fibers

The use of hemp fibers as chopped short fibers and as continuous threads in different oriented arrangements allowed obtaining materials with different final properties. Figure 7 shows the tan δ of the composites tested in DMA, three-point bending geometry. The temperature at the maximum of the main relaxation appears in the range of 90–118°C for all the materials prepared with hemp. In all cases, the relaxation covers a wide range of temperatures, from above 50°C up to 150–200°C. The width of the transition is larger for the composite prepared with short fiber hemp. This feature, as already indicated for wood fiber composites, may be quite interesting for applications that require materials with damping properties. The tan δ peak corresponding to the one direction composite is higher, and this effect is reduced as more directions are added to the composite. It looks like the polymer chains tested in flexion and perpendicular to the fiber length are less inhibited in their relaxation mobility than when matrix of the other composites is formed.

The static flexural properties of the hemp reinforced PU composites were also measured and are shown in Figure 8. It is clear that the best properties are obtained for the aligned one directional-fiber composite. The lowest properties correspond to the two directional-fiber composite, while the four directional materials have intermediate properties. When the material is subjected to bending, the lower face is under tensile loads, while the upper face is under compression. It seems that the lower face is more important in determining the observed trend. For that reason, the composite with longitudinal aligned fibers can stand higher stresses. The fibers on the

TABLE II
Flexural Properties of Wood Fibers Reinforced Foams (1 y After Preparation, Foamed-1)

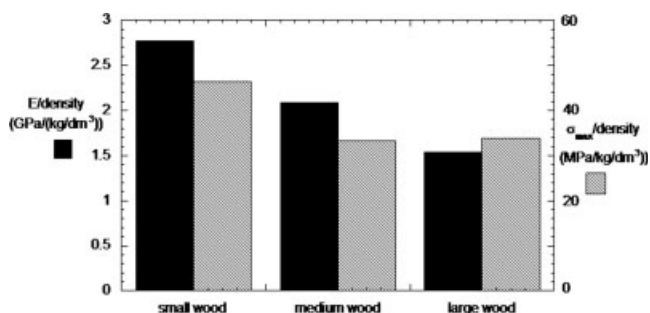| Composites made with	Maximum stress (MPa)	Maximum strain (mm/mm)	Flexural modulus (MPa)
Small wood fibers	44.94 ± 7.24	0.0285 ± 1.03 E −3	2684 ± 490
Medium wood fibers	26.05 ± 5.08	0.0248 ± 3.66 E −3	1635 ± 117
Large wood fibers	26.93 ± 0.13	0.0212 ± 4.06 E −3	1223 ± 485

Figure 6 Flexural modulus and strength per unit density, for pine wood flour composites (foamed-1).
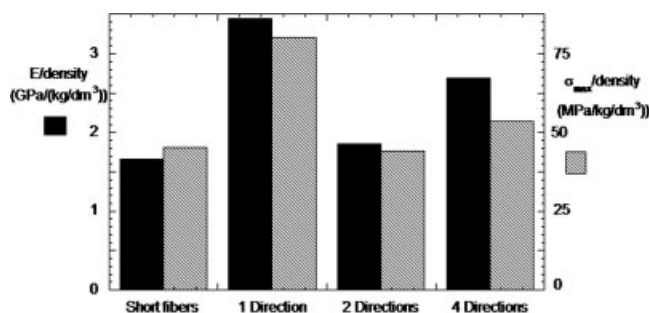

Figure 8 Flexural modulus and strength per unit density, for hemp composites (foamed-1).

lower face are deformed under tensile forces, because of the orientation of the continuous hemp strands, and thus the modulus of the composite has a larger contribution from the fiber properties. The two directional samples has only half of the fibers aligned in that direction and consequently, the contribution of the fibers to modulus or strength is lower. Finally, in the four directional samples the fibers are ordered in 0, 45, and 90° with respect to the direction of the sample longitudinal axe. The fibers aligned at 45° contribute at least in part to the modulus and

strength of the material (the lower face of the tested specimen is considered for the analysis) and so the properties measured are intermediate between one and two directional aligned fiber-composites. Short hemp-fibers composites present comparatively low modulus and maximum stress. This is the expected output for a particulate material, where the short fibers contribute little to the strength of the material (they are below the critical length for effective stress transfer) and act mostly like a filler.
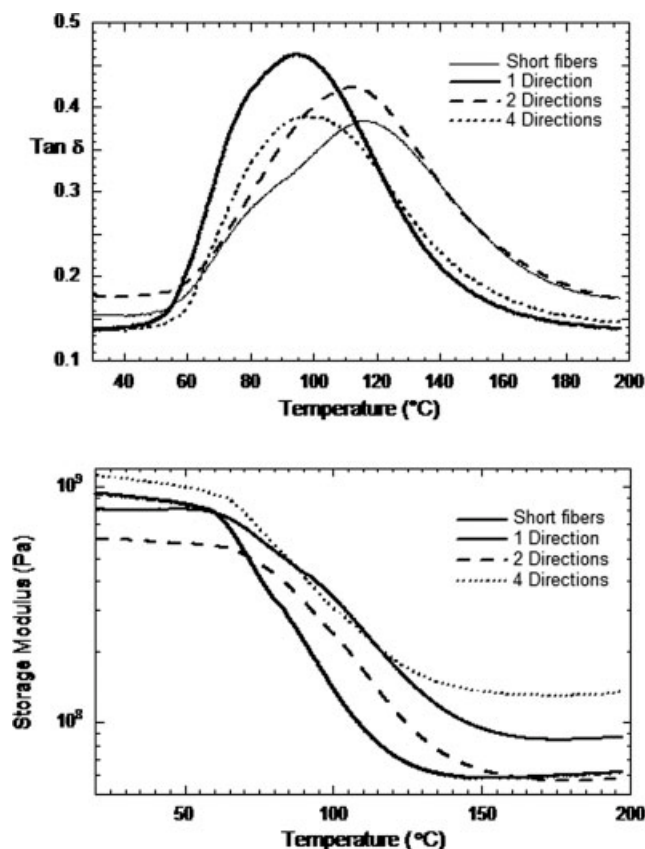

Figure 7 Storage modulus and tan δ curves for hemp composites (foamed-1).
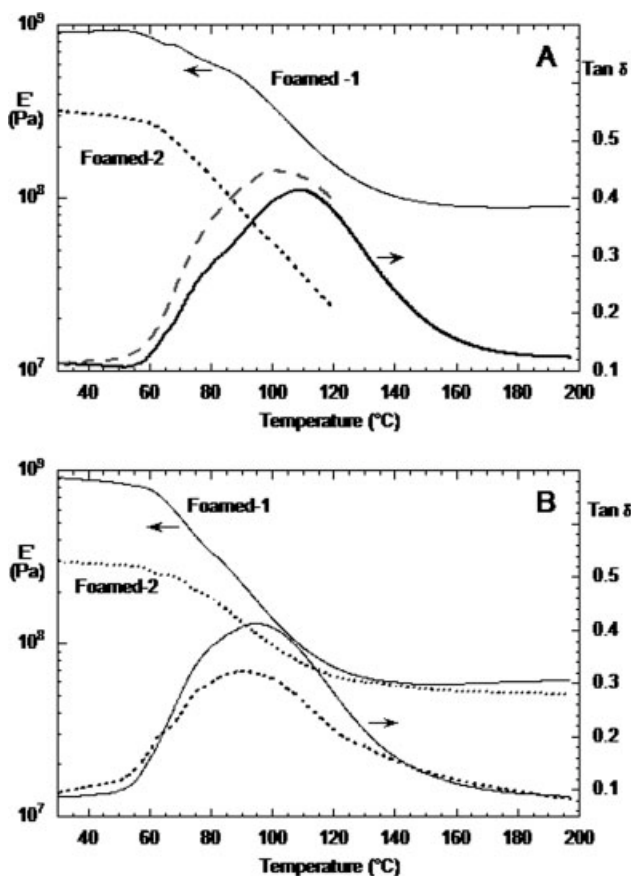

Figure 9 Thermomechanical behavior of reinforced foams with and without added water added, tested 1 year after preparation. (A) Pine wood flour composite; (B) Hemp composite.

TABLE III
Flexural Properties of Representative Samples

Composite sample	E_b (MPa)	σ_{max} (MPa)	Maximum strain (mm/mm)	E_b/ρ MPa/(kg/dm^3)	σ_{max}/ρ MPa/(kg/dm^3)
Wood fibers/foamed-1	1635 ± 117	26.05 ± 5.08	0.0248 ± 0.0037	2085 ± 149	33.23 ± 6.48
Wood fibers/foamed-2	638 ± 44	13.55 ± 1.51	0.0317 ± 0.0051	1045 ± 72	22.09 ± 2.47
Hemp-1 direction/foamed-1	2637 ± 520	61.16 ± 7.53	0.0449 ± 0.0020	3454 ± 681	80.11 ± 9.86
Hemp-1direction/foamed-2	1913 ± 290	39.02 ± 3.66	0.0470 ± 0.0036	3281 ± 497	66.93 ± 6.28

Effect of water addition

Figure 9(A,B) show the dynamic mechanical behavior (E' and tan δ vs. temperature curves) of medium wood fiber and unidirectional hemp composites prepared without and with addition of a drop of water and tested one year after preparation. The maximum in the tan δ peak appears at lower temperature in the samples prepared with added water, which is a consequence of the changes in chemical composition and consumption of extra isocyanate groups, as it was previously discussed. The storage modulus of the material at low temperatures depends strongly on the density of the material, and thus, E' is markedly lower in the foamed samples.

The flexural properties, modulus (E_b), deformation at break (ε_u) and ultimate stress (σ_u), of representative samples is presented in Table III. The flexural modulus and ultimate stress decrease when water is added to the formulations, as expected. When the properties are compared per unit of density the values become closer, but still some differences are observed between wood fiber and hemp fiber composites. The modulus of the foamed-2 wood composite is lower than the corresponding foamed-1 composite, even after density considerations. On the other hand, the properties of the hemp composites foamed-1 and foamed-2 are very similar when the effect of density is taken into account. Probably, the continuous fibers are long enough to ensure a good adhesion to the polymer through the contour length even in the microcellular composite.

Chemical aging

The effect of chemical aging on the properties of the castor oil based-PUs and their composites was studied by the thermomechanical and mechanical characterization of samples recently prepared and those stored during one year. Because the castor oil based polyols have unreacted unsaturations, an oxidative process occurs during time, which leads to additional crosslinking of the polymer. This process is the cause of solidification of drying oils and, although the process has been recognized for long time, the complexities of the mechanisms involved are still under discussion.[25–29]

Dynamic mechanical measurements show that the main relaxation of the pine wood composites shifts from 72 to 82°C to 97–110°C, for the samples recently prepared and one year old, respectively. Figure 10 corresponds to medium wood fibers foams and shows that recently prepared samples have a tan δ peak, which is asymmetric with a tail in the region of high temperatures. After 6 months the tan δ peak not only shifts to higher temperatures but also becomes more symmetric. Significantly, the height of the peak is also reduced in the older samples because of the reduced mobility of the chains involved in the relaxation. The changes that occur in the subsequent 6 months (finally achieving 1 year of aging) are minor.

The flexural properties are also affected by the PU aging in all the composites tested, as it can be noticed from Figure 11(a-c), where the modulus, maximum stress, and deformation to rupture of recently prepared and one year old samples are compared. The bending modulus and the maximum stress of the materials increase with time. This was expected, as a result of the reaction of the triglyceride unsaturations, further contributing to the crosslinking of the matrix. It is quite interesting that the maximum
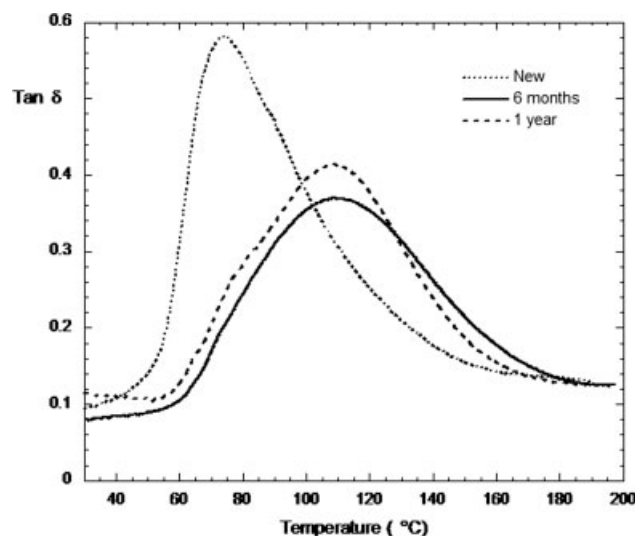

Figure 10 Tan δ versus temperature curves of medium wood fibers composite (foamed-1), as a function of aging time.
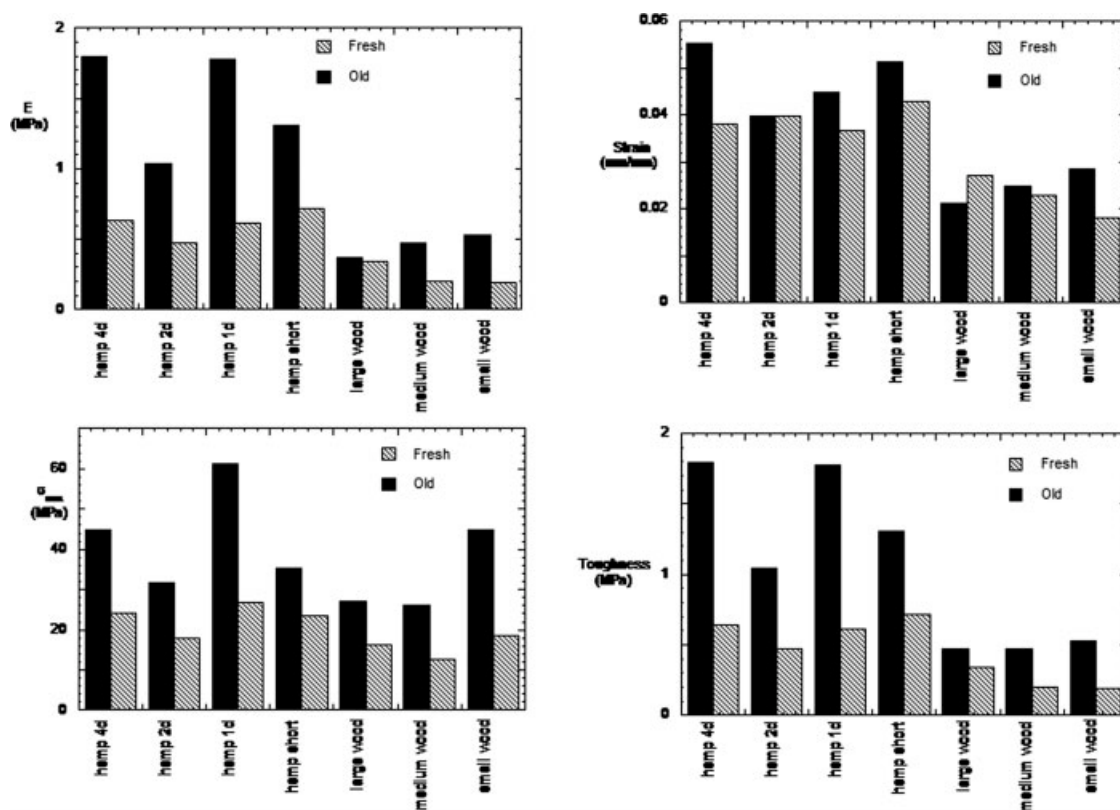
Figure 11 Flexural properties as a function of aging time. (a) Modulus; (b) Maximum stress; (c) Deformation at break; (d) Toughness.

deformation reached by the composites before breakage was not reduced. On the contrary, it increased in most of the composites investigated. This is a very interesting behavior since all the mechanical properties of the material improve through aging, included its flexural toughness [Fig. 11(d)].

CONCLUSIONS

It was possible to prepare microcellular PU composites reinforced with different wood fibers and hemp fibers and using a polyol synthesized from on castor oil.

In general hemp fiber composites showed better comparative properties, which was related to the larger aspect ratio of the hemp fibers. In this respect, one directional hemp composites offered the best bending behavior.

Dynamic mechanical studies of the composites showed very wide temperature transitions, which suggest that the materials could be used for damping applications.

Addition of just a drop of water to the formulations produced large variations in the morphology of the materials, which was directly related to their mechanical properties. This offers a possibility of

producing materials with very different properties by an adjusted control of the formulation.

The materials suffer important aging due to a secondary reaction of the unsaturations present in the vegetable oil-based polyol. As a result, the modulus and strength of the material are improved. It is very interesting that there was no decrease of the deformation to rupture, and for this reason aged materials showed improved modulus and toughness than original composites, under the test conditions reported.

References

1. Suh, K. W. Encyclopedia of Polymer Science and Engineering, Vol. 3: Cellular Materials. Wiley; New York, 1987.
2. Frish, K. C. In Polyurethane Technology; Bruins, P.F., Ed.; Wiley Interscience: New York, 1969; Chapter 1.
3. Recktenwald, G. W.; Andrews, W. R. In Polyurethane Technology; Bruins, P.F., Ed.; Wiley Interscience: New York, 1969; Chapter 3.
4. Stefani, P. M.; Moschiar, S. M.; Aranguren, M. I. J Appl Polym Sci 2001, 79, 1771.

5. Jung, H. C.; Ryu, S. C.; Kim, W. N.; Lee, Y.-B.; Choe, K. H.; Kim, S.-B. J Appl Polym Sci 2001, 81, 486.
6. Chang, L.-C.; Xue, Y.; Hsieh, F.–H. J Appl Polym Sci 2001, 81 2027.
7. Goods, S. H.; Neuschwanger, C. L.; Whinnery, L. L.; Nix, W. D. J Appl Polym Sci 1999, 74, 2724.
8. Nabi Saheb, D.; Jog, J. P. Adv Polym Technol 1999, 18, 351.
9. Bledzki, A. K.; Zhang, W.; Chate, A. Compos Sci Technol 2001, 61, 2405.
10. Soykeabkaew, N.; Supaphol, P.; Rujiravanit, R. Carbohydr Polym 2004, 58, 53.
11. Taniguchi, Y.; Okamura, K. Polym Int 1998, 47, 291.
12. Hilijanen-Vainio, M.; Heino, M.; Seppälä, J. V. Polymer 1998, 39, 865.
13. Chang, L.-C.; Xue, Y.; Hsieh, F.–H. J Appl Polym Sci 2001, 80, 10.
14. Teixeira, M. J.; Fernandes, A. C.; Saramago, B.; Rosa, M. E.; Bordado, J. C. Adhesion Sci Technol 1996, 10, 1111.
15. Chian, K. S.; Gan, L. H. J Appl Polym Sci 1998, 68, 509.
16. Khot, S. N.; lascala, J. J.; Can, E.; Shantaram, S.; Morye, S.; Williams, G. I. J Appl Polym Sci 2001, 82, 703.
17. Baser, S. A.; Khakhar, D. V. Cell Polym 1993, 12, 340.
18. Zhang, Y.; Shang, S.; Zhang, X.; Wang, D.; Hourston, D. J. J Appl Polym Sci 1995, 58, 1803.
19. Jin, J. F.; Chen, Y. L.; Wang, D. N.; Hu, C. P.; Zhu, S. J Appl Polym Sci 2002, 84, 598.
20. Hu, Y. H.; Gao, Y.; Wang, D. N.; Hu, C. P.; Zhu, S.; Vanoverloop, L. J Appl Polym Sci 2002, 84, 591.
21. Dell'Arciprette, G.; Aranguren, M. I.; Mosiewicki, M. A.; Marcovich, N. E. Polyurethane foams based on natural resources, In Proceedings of the ''III Argentine-Chilean Polymer Symposium'', ARCHIPOL III, Los Cocos, Argentina, 2005.
22. Mosiewicki, M. A.; Aranguren, M. I.; Borrajo, J. J Appl Polym Sci 2005, 97, 825.
23. Urbanski, J. In Handbook of Analysis of Synthetic Polymers and Plastics; Urbanski, J., Czerwinski, W., Janicka, K., Majewska, F., Zowall, H., Eds.; Wiley: Poland, 1977; Chapter 1, p 48–53.
24. Bellamy, L. J. The Infrared spectra of Complex Molecules, 3rd ed.; Chapman and Hall: Great Britain, 1975; Vol. 1.
25. Mosiewicki, M.; Borrajo, J.; Aranguren, M. I. Polym Int 2007, 56, 779.
26. Mosiewicki, M.; Borrajo, J.; Aranguren, M. I. Polym Int 2007, to appear.
27. Formo, M. W.; Jungermann, E.; Norris, F. A.; Sonntag, N. O. V.; Bailey's Industrial Oil and Fat Products, 4th ed.; Swern, D., Ed.; Wiley: New York, 1985; Vol. 1, p 701.
28. Lazzari, M.; Chiantore, O. Polym Degrad Stabil 1999, 65, 303.
29. Ioakimoglou, E.; Boyatzis, S.; Argitis, P.; Fostiridou, A.; Papapanagiotou, K.; Yannovis, N. Chem Mater 1999, 11, 2013.
30. Wong, F. C.; Ait-Kadi, A. J Appl Polym Sci 1995, 55, 263.
31. Ahamed, S.; Jones, F. R. J Mater Sci 1990, 25, 4933.