CELLULOSE CHEMISTRY AND TECHNOLOGY

BIODEGRADABLE POLYURETHANES FROM SUGAR CANE BIOWASTES

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In a previous work, it was demonstrated that 70% of the molasses isolated from the biowaste generated by the agro-industrialization of sugar cane allow obtaining composite materials with adequate mechanical properties and bulk density. In the present research, these results were applied in the preparation of composite polyurethanes based on sugar cane molasses reinforced with bagasse fiber from the same biowaste.

Initially, milled fibers from bagasse were characterized both physically and chemically, according to their content of α-cellulose, moisture, ashes, hemicelluloses and lignin, as well as to their extractability in organic and aqueous solvents. The most representative values were α-cellulose (47.3%), lignin (24.4%) and holocellulose (66.1%).

Subsequently, polyurethane foams (PUF) were prepared using the natural fiber as a reinforcement, with 4 different percentages of fiber ground (5, 10, 15, 20% w/w) with an average particle size of 60 mesh; an extra PUF without fiber reinforcement was also synthesized as a reference. PUF synthesis was carried out with a PEG-molasses mixture in a 30:70% (w/w) ratio, diphenylmethane diisocyanate (MDI) and dibutyltin dilaurate as catalysts. Composite PUFs were characterized according to their bulk density, thermal (thermogravimetry-TGA) and mechanical (compression modulus) properties.

The results showed that the composite PUF sample with 10% sugar cane fiber added as reinforcement had the lowest bulk density. Also, its TGA thermal analysis showed a general trend towards reducing both the initial temperature of decomposition, as well as the temperature at the maximum rate of degradation, compared to the reference PUF without fiber added. Finally, its mechanical properties showed a maximum value for both effort to compression and compression modulus.

It has been concluded that the use of agro-industrial biowaste from sugar cane permits to develop composite materials with suitable properties for applications as foams. The PUF synthesized by partial replacement of PEG for molasses and reinforced with sugar cane bagasse fiber can be used in the packaging industry. In this case, the materials are used for short periods, and are usually very bulky, less dense. Thus, this novel type of PU foam could be useful in reducing the production costs and in improving the potential biodegradability of the polymeric matrix, becoming an interesting value-added application for this important source of agricultural biowastes, especially in Latin America.

Keywords: polyurethanes, foams, sugar cane, biowastes, biodegradation

INTRODUCTION

In Costa Rica, agriculture has been one of the major economic activities for many years, becoming an export-oriented activity and one of the most stable sources of foreign income, even if country has faced a relative decline in the importance of this sector in the national economy.[1] Moreover, the industrialization of agricultural products in our country, such as coffee, bananas, sugar cane, pineapple, etc., generates thousands of tons of agro-industrial waste, which explains why its biowaste production is currently taking a special interest, due to its multiple potential applications.[2]

Biowastes and residues produced during the industrialization of sugar cane are mostly bagasse fiber and molasses, reaching up to 25% of the total waste, consisting mainly of lignocellulosic materials. The most common use of the bagasse fiber is for producing energy, due to its caloric capacity, being currently involved in the sugar refining process.[1] However, there is an overproduction that accumulates in landfills without any treatment.[3]

Bagasse is a fibrous lignocellulosic residue obtained after crushing of sugar cane stalks during juice extraction. The most characteristic feature of the bagasse fiber is the abundance of large parenchyma cells and vessel segments. The dry bagasse is clear and varies in color – from white to light green and brownish, depending on the variety and age of the cane. The bone is white, consisting largely of parenchymatous tissue.[4,5]

Bagasse has a fiber content reaching 65%. The bagasse fibers are rigid and irregular in contour, as a result of the items subjected to mechanical stress during processing. On the average, the fibers are 1.7 mm in length, 20 μm in diameter, with a wall thickness of 4.0 μm, which classifies them as short fibers, comparatively with those of hardwoods.[5]

In a previous work, the advantages provided by natural fibers for polymer reinforcement, *e.g.* the technical, economic, ecological and environmental characteristics, were highlighted, together with their wide availability, diversity and renewability, as well as improved resistance, recyclability and appropriate mechanical properties.[6] In this respect, sugarcane bagasse is not an exception, being a material which, by its nature, could be used as a reinforcing material in the production of polymeric composite materials.[1]

On the other hand, the global sugar agro-industry is currently facing its lowest economical decrease in several decades, no significant positive change being predictable for the near future, and making multiple necessary efforts, especially oriented to the full utilization of the waste materials generated in this activity, as a possible novel source for value-added derivatives, which leads to diversified economic benefits for agribusiness, based on environmentally compatible initiatives. In this respect, one possibility is the use of biowaste and residues from sugar cane production for the development of alternative materials, such as composite polymers, specifically focused on the production of reinforced polyurethanes.

The use of natural fibers as reinforcements in polyester-type polymer matrices has been previously reported.[7] Also, sisal fibers have been used to reinforce polypropylene compounds as an ecological alternative to the automobile industry.[8] The use of short organic fibers as reinforcement for polyamide thermoplastic polymer matrices was also studied.[9] Regarding the polyurethane polymeric matrix, studies conducted by Arribas and Lopez tried to incorporate synthetic materials derived from renewable sources into other components from agriculture, for improving the properties of the resulting composite material and – at the same time – for increasing the biodegradability of the matrix, a desirable characteristic in many polymers.[8, 10]

Other studies have focused on the preparation and determination of the physical properties of polyurethanes derived from molasses,[11, 12] biodegradability of polyurethane foams synthesized by partial replacement of polyethylene glycol (PEG) for molasses from different agro-industrial substrates,[13-16] obtaining of biotechnological polyurethane from agro-industrial residues,[17] and synthesis and characterization of polyurethane foams from coffee pulp,[18] pineapple and corn cobs, among others.[19-22]

Recently, the Polymers Research Laboratory (POLIUNA) at the National University of Costa Rica has studied the incorporation of residual molasses from sugar cane agro-industry for the preparation of polyurethane foams (PUF).[23] In the present work, polyethylene glycol (PEG) was partially replaced by sugar cane molasses. This research shows the best results obtained in the synthesis of sugar cane-reinforced PUF, as an innovative value-added derivative for sugar cane biowastes (bagasse fiber and molasses).

EXPERIMENTAL

Raw materials

The sugar cane molasses and bagasse were kindly provided by sugar processing plant. Molasses were kept under refrigeration (<10 ºC), on adding zeolites as desiccant agents. The moisture content was determined[24] by the Karl Fischer method (Karl-Fischer Team Brand Coulometer Metrohm 684).

Bagasse fibers were placed in a circulating air oven (VWR brand FD 1350), at a temperature ranging between 50-60 °C, followed by milling (Yoshida Seisa Kusho mill Co., LTD 1029-B type) and particle size separation through a 40 to 60 mesh sieve (WAS Tyler Sieve, Sieve Shaker Type Incorporated Model RX-86).

Characterization of starting materials

1. *Sugar cane bagasse*. The ash content was analyzed[25] according to ASTM D 1102-56, at a temperature of 500 °C, and humidity was determined in a moisture balance O'Haus.[24] Solubility in cold and hot water was determined[26] according to ASTM D 1110-56, and solubility in organic solvents was analyzed[27] according to ASTM D1107-56, modified by replacing benzene with cyclohexane. The holocellulose content was determined[28] according to ASTM D 1104-56, the lignin content was analyzed[29] according to ASTM D1106-56 and, finally, the determination of α-cellulose was carried out[30] according to ASTM D 1103-60.

2. *Molasses*. The characterization of molasses was carried out according to the methods described in a previous work.[23]

3. *Other reagents*. Polyethylene glycol PEG-300 (Aldrich, 20.237-1) was used as a polyol source, showing a moisture content of 1.7%, according to the Karl-Fisher method (Karl-Fisher Team Brand Coulometer Metrohm 684).[24] The OH group content was calculated[31] according to ASTM D 4274-88. Commercial grade diphenylmethane diisocyanate (MDI) was used as an isocyanate source. The MDI isocyanate groups were quantified according to ASTM D 4666-8 (pH-meter Hanna Instruments, serial # 372887, Microprocessor pH Bench-Meter), modifying the amount of material used to 1 g, and changing dibutylamine with diethylamine. The temperature range was 40-45 °C, and dibutyltin dilaurate (DBTL, Aldrich 29.123-4) was used as a catalyst.

Preparation of polyurethane foams

The methodology for the preparation of polyurethane foams is similar to that mentioned in previous articles.[11,20, 21] Table 1 shows the amounts used to synthesize polyurethane foams (PUF) and the nomenclature used to identify each mixture. Molasses blends with PEG-300 were prepared in plastic containers. The ratio MDI/OH used in the study was of 1.2 and that of the PEG-molasses mixture was of 30:70 (% per weight).

Four different percentages of fiber ground, namely 5, 10, 15 and 20% by weight (average particle size of 60 mesh) were used. MDI was added after the addition of fiber, followed by mechanical stirring until the mixture reaches the best possible homogeneity. When the foam started to grow, the propeller was removed.

Characterization of composite polyurethane foams (CPUF)

Thermogravimetric analysis (TGA Perkin-Elmer 6) was carried out under a nitrogen flow of 40 mL/min, heating rate of 20 °C/min and temperatures ranging between 70° and 675 °C, as described by Hirose.[11] To measure bulk density, the foams were cut into cubes with 2.00 cm sides, mass being determined with an analytical balance. The mechanical properties were analyzed according to the compression method described[32] by ASTM-D695M, yet changing the recommended sizes by 2 inches square cubes. The analysis was performed at room temperature, with a traverse speed of 10 mm/min (Orientec RTM-100). Compression stress at 10% strain and the values obtained for Young's modulus (E) were divided between bulk densities, to normalize the results of mechanical tests.[11]

RESULTS

Characterization of fiber sugar cane bagasse

The fiber is used as reinforcing polyurethane foam due to its mechanical properties and the possibility of reducing costs by adding a vegetable fiber waste from a highly accessible source. The intended uses of the foam could be located within the packaging line, in what is known as continuous rolling, which offers an economical method for obtaining insulating elements of different thickness, for the construction industry. Also, the sandwich panels may be used for the insulation of roofs and walls, false ceilings, floating floors, air ducts and constructions.[33]

The chemical properties of bagasse fibers are largely determined by the characteristics presented by their constituents, which in turn depend on the location within the structure. Generally, since it is a non-wood lignocellulosic material, sugar cane bagasse has a high content of parenchymal tissue rich in pentose, so that the ratios of chemical constituents that make it up will vary, depending on the parenchyma or spinal content.[5] The results of the analysis of their composition are presented in Table 2.

The value obtained in the determination of ash content of bagasse from sugar cane is high, compared to those reported by other authors,[5,34] with values between 2 and 3%. This difference is attributed to the amounts of mineral components of the fibrous plants, which vary considerably among the different species analyzed, as well as to the soil characteristics in which the plant was grown, or climatic conditions in which the species had developed, among others.[5] The main components of ash are potassium, calcium, magnesium, sodium, phosphorus and chlorine, as well as anions – such as carbonates, phosphates, silicates and sulfates.[5]

A moisture content of 11.67% is expected in natural fibers treated with a high content of hydroxyl groups, which gives them their hygroscopic characteristics. The aqueous extracts in hot and cold water were of 8.13 and 11.65%, respectively. The cold water extract corresponds to the extraction of tannins, gums, sugars and coloring material, while the hot water extracts starches. Extractable substances, such as terpenes, phenolic and aliphatic compounds (mainly waxes and fats), are also measurable by this method. The values are similar to those reported in literature.[34]

The extraction with organic solvents dissolves the polar substances, mainly terpenes, lignin, waxes and fatty acids, among others.[34] Solubility in the mixture of organic solvents was of 5.74%. As already mentioned, compared to literature values[34] differences higher than 6% are due to the different varieties of sugarcane bagasse analyzed[5] in different harvest or weather conditions, type of culture, etc. The lignin content obtained for the bagasse fiber was of 24.41%, which is close to the 20.3% value reported in literature. This component, a heterogeneous aromatic polymer which is part of the supporting tissues of the plant is, after cellulose, the most abundant element in plants.[5]

Table 1
Quantities used for the preparation of polyurethane foams BEPU from sugar cane molasses and the nomenclature used

Sample	Fiber (% w/w)	Weight (g)*			Nomenclature
		Mix	Fiber	MDI	
1	0	25.97	-	30.00	PU0
2	5	13.00	142	15.16	PU5
3	10	13.08	2.82	15.02	PU10
4	15	13.11	4.22	15.70	PU15
5	20	13.05	5.68	15.05	PU20

*Catalytic: 0.07 g

Table 2
Results of the analysis of sugar cane bagasse composition

Analysis	Results (%)
Ash	7.82
Moisture	11.67
Cold water soluble extracts	8.13
Hot water soluble extracts	11.65
Cyclohexane-ethanol soluble extracts	5.74
α-cellulose	47.29
Holocellulose	66.12
Lignin	24.41

Table 3
Results of (-OH) and (NCO) groups quantification for determining the isometric relationship, moisture, PEG-300 and molasses

Substrate	Groups OH meq – OH/g substrate	Groups COOH meq – COOH/g substrate	Moisture (%)	Groups NCO meq– NCO/g substrate
PEG-300	6.45	N/A	1.17*	-
Molasses	7.71	0.95	20.7**	-
MDI	-	-	-	7.50

* Karl-Fischer, ** Brix grades

The content of α-cellulose fibers from sugar cane bagasse was of 47.29%. The value obtained for holocellulose was of 66.12%, the term referring to the total holocellulose of carbohydrates cellulose and hemicelluloses (the latter being distinguished from the non-cellulose fibers).[5]

Overall, in the fibers of sugar cane bagasse, the main components are cellulose and lignin. Both macromolecules are polar, because they have a high content of hydroxyl groups, being therefore expected to produce an appropriate interaction with the polyurethane, through mainly hydrogen bonding.

Characterization of molasses, PEG-300 and MD

Such materials have been fully investigated in previous studies.[12,23] The quantification of these materials is summarized in Table 1. In the present study, a NCO/OH ratio of 1.2 was used, as previous researches[3,13,16] have shown that, generally, polyurethane foams show better properties when using this relationship. As listed in Table 3, molasses showed a total value of the OH groups of 7.71 meq/g, a free acid value of 0.95 meq/g, while the PEG-300 was of 6.45 meq/g (OH groups). Finally, the MDI showed 7.50 meq/g (NCO groups).

Moreover, the main component of residual molasses from sugar cane is sucrose, followed by glucose and fructose, with values of 30.6, 8.4 and 8.2%, respectively. The quantification of the sugars present in this material is important, since these components are a source of hydroxyl groups, which react with the isocyanate to generate the respective urethane linkage.

Finally, the determination of moisture in both molasses and PEG-300 must be known and controlled, because it depends on the polyurethane foam. The reaction in this process is the decomposition product of the isocyanate for producing carbon dioxide, which is trapped in the polymer matrix material during its synthesis. An excessive foaming polymeric material generates undesirable properties.[20,24,35]

Analysis of physical properties of polyurethane foams

Effect of bagasse fiber content on polyurethane foam density

As already mentioned, the density of foam is an essential feature, because it allows obtaining more low-weight material, especially if it is to be used as a packing material. Figure 1 shows the increasing tendency of density with increasing the fiber content of bagasse reinforcement. The samples with lower fiber content (PU5 and PU10) had the lowest bulk density. PU15 and PU20 showed higher density and lower resistance to mechanical traction, because they were fractured when handled, as probably due to the low fiber-matrix interaction.

Effect of fiber bagasse ground on polyurethane foam thermal properties

Thermogravimetry (TGA) examines the weight change of a sample as a function of temperature. This analysis can determine the temperatures and kinetics of the decomposition of materials. In particular, it represents the temperature at which the process of substrate degradation begins, denominated as T_{d1}, and T_{d2}, corresponding to the temperature reached in the lowest point of the peak of the first derivative of curve analysis, which represents the average temperature decomposition or the temperature at the maximum decomposition rate. In addition, it is used to estimate the content of inert waste materials, generally obtained in the absence of oxygen.[36]

Figure 2 plots a thermogram, which includes derivatives for three different types of synthesized foams. Foam without molasses or sugar cane bagasse is the reference sample. PU0 is the foam with the mixture of PEG, molasses, MDI and catalyst. PUX is the sample synthesized with a mixture containing 70% molasses, MDI, catalyst and milled fiber bagasse.

The polyurethane foam PU0 and the samples containing sugar cane bagasse as reinforcement (PUX) showed T_{d2} and T_{d1} at lower temperatures, compared to materials with no molasses and not reinforced, as a result of the presence of a natural material. This effect is more pronounced in materials that also contain molasses and bagasse fiber.

Depending on the uses of this material (*e.g.*, packaging), a decrease in the thermal properties does not influence the use of these substrates. Hirose and colleagues[11] explain that the decrease in decomposition temperatures and the shape of the TGA curves reflect the decomposition of mono- and disaccharides present in the polyurethane. The decomposition temperature of these sugars is close to 200 °C. It also avoids the presence of reinforcement in samples with a high fiber content, the interaction between the polymer chains – probably hydrogen bonds, so that the material is thermally unstable.

If the results are evaluated in T_{d1} for fiber materials containing sugar cane bagasse, and then compared with the reference PU0 (Fig.

3), one may observe that the fiber content decreases the thermal stability of polyurethanes, as the T_{d1} value of the PU0 foam is higher than 320 °C, while the foam with sugar cane fiber decreases with increasing the content of fiber, up to 200 °C.

With respect to the values of temperature obtained at the maximum decomposition rate (T_{d2}) – as shown in Figure 4 – the same observation may be made, namely that the foam has a higher reference PU0 T_{d2}, which should be interpreted as a higher thermal stability. As in the case of T_{d1}, there was no significant difference in the T_{d2} value of the other molasses-containing foams.

Table 4 presents the results of the residual stand. As expected, the data show an increasing trend as residual weight increases the amount of sugar cane fiber incorporated into the polyurethane, the sample with 20% (PU20) recording the highest value.

Table 4
Effect of molasses content on residual weight of polyurethane foam (to 675 °C)

Sample	Residual weight (± 0.1 mg)
PU0	17.9
PU5	23.9
PU10	24.9
PU15	25.5
PU20	26.4

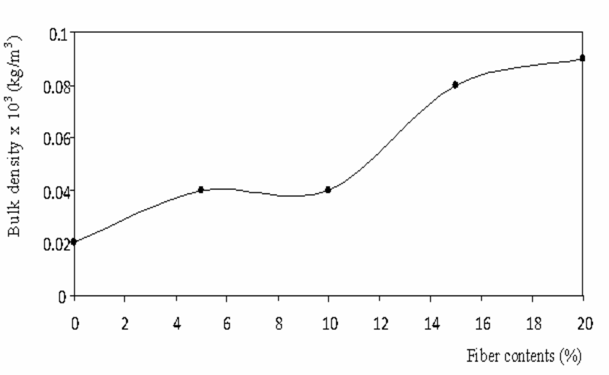

Figure 1: Effect of fiber ground sugarcane bagasse on the density of polyurethane foam with a PEG: 30%:70% mixture of molasses

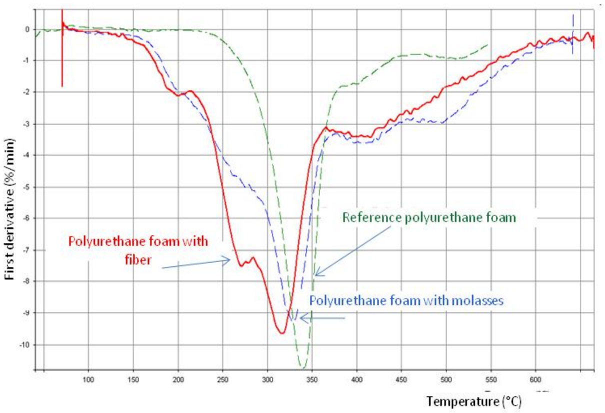

Figure 2: TGA thermograms showing the first derivative of the curves obtained for the synthesized polyurethane foams

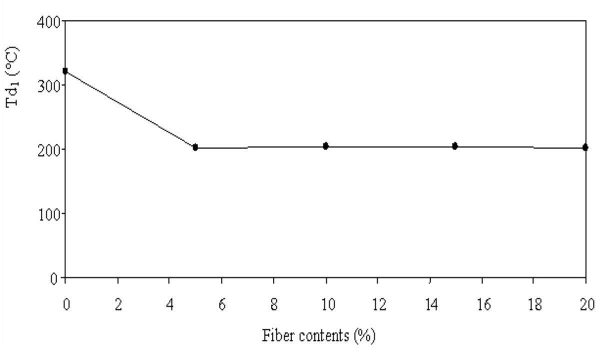

Figure 3: Effect of the fiber content of sugar cane bagasse on temperature, at initial decomposition temperature (T_{d1}) in polyurethane foam

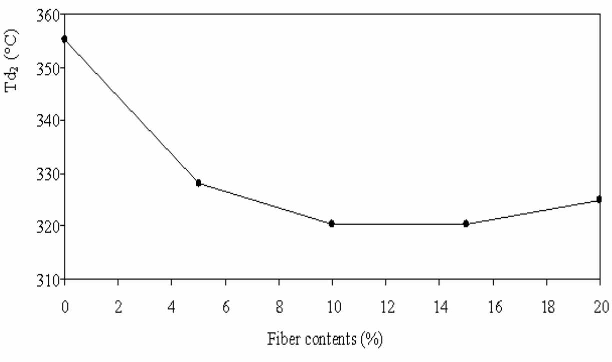

Figure 4: Effect of fiber content of sugar cane bagasse on temperature, at maximum decomposition rate (T_{d2}) in polyurethane foam

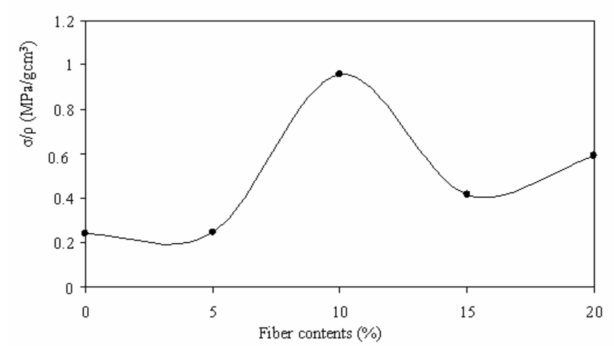

Figure 5: Effect of fiber ground sugar cane bagasse on the compressive strength of polyurethane foams

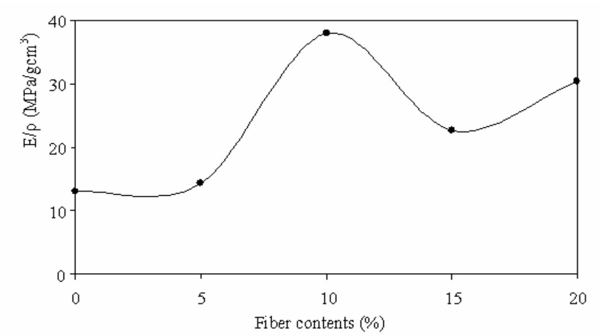

Figure 6: Effect of fiber ground sugar cane bagasse on the form of polyurethane foams

Effect of sugarcane bagasse ground fiber addition on polyurethane foam compression mechanical properties

Previous studies,[20] discussing, for example, the synthesis of polyurethane foam debris from the pineapple shell, indicated that the lignocellulosic materials incorporated as a reinforcement provide a polyurethane matrix, a greater ability to withstand compression tests and increase the modulus.

Compression analysis, involving the exertion of a certain force on a sample, is aimed at observing its deformation under test conditions: it reveals the compressive stress (σ), *i.e.* the load per unit area, and the compression modulus (E), which involves splitting between compressive strength and deformation. The modulus provides information on the material's ability to withstand an applied load, before reaching the breaking point. The results obtained for the mechanical properties are illustrated in Figures 5 and 6. Effort data compression (σ) and the value obtained for modulus (E) were divided between bulk density (ρ), to normalize its effect on the results of mechanical tests.

A maximum value is reached in both compressive stress (σ) and modulus (E). It follows that the sample with better mechanical properties of compression is the one containing 10% bagasse fiber (PU10). At higher fiber concentrations, the synthesized materials show lower values of compressive strength and modulus, probably in response to the poor dispersion of fibers in the polymer matrix, generated by a poor interaction between fibers and the polymer chains.

Similarly, several studies[9,37] have concluded that the ends of the fibers incorporated into polymeric materials act as sources of stress concentrations, which produce cracks in the material, when subjected to stress. Other studies[38] have shown that composite materials contain voids, due to an incomplete impregnation of the fibers with resin, appearing as weak spots in the material, as a result of the high concentration of efforts that promote spreading of cracks. All this indicate that the addition of fiber can generate a larger percentage decrease in the mechanical properties, such as compression, as actually demonstrated in this study.

CONCLUSIONS

The study shows how to synthesize a low-density polyurethane foam with the addition of 70% of lignocellulosic material from agro-industrial activities (such as molasses), to be subsequently reinforced with 10% fiber ground sugarcane bagasse for obtaining foams with appropriate mechanical properties of compression and low bulk density, permitting their utilization in a large range of applications.

REFERENCES

[1] M. Moya, in "Development of Environmentally Compatible Polymers from Biowaste", Inform, San José, Costa Rica, 2001, p. 25.

[2] M. Durán, M. Moya and M. Sibaja, *Ingeniería*, **3**, 53 (1993).

[3] M. Chaves, in "Development of Environmentally Compatible Polymers from Biowaste", Inform, Costa Rica, 2001, p. 170.

[4] Grupo de Países Latinoamericanos y del Caribe Exportadores de Azúcar (GEPLACEA), "Manual de derivados de la caña de azúcar", 2nd ed., México, 1990.

[5] R. Sanjuán, "Obtención de pulpas y propiedades de las fibras para papel", México, Universidad de Guadalajara, 1997, p. 19.

[6] J. L. Gómez, C. Jarones and P. Gañán, *Plásticos Modernos*, **76**, 183 (1998).

[7] J. Vega-Baudrit, M. Moya, M. Sibaja, R. Pereira and P. Alvarado, *Química e Industria*, **51**, 572 (2004).

[8] J. M. Arribas, J. M. Navarro and J. M. Perea, *Plásticos Modernos*, **81**, 467 (2001).

[9] M. Arroyo and L. Ibarra, *Plásticos Modernos*, **465**, 226 (1995).

[10] M. A. López and M. Arroyo, *Plásticos Modernos*, **85**, 594 (2003).

[11] S. Hirose, K. Kobashigawa and H. Hatakeyama, *Sen-1 – Gakkaishi*, **50**, 78 (1994).

[12] S. Hirose, K. Kobashigawa, T. Tokashiki, H. Naka and H. Hatakeyama, in "Recent Advances in Environmentally Compatible Polymers", edited by J. F. Kennedy, G. Phillips, P. Williams, Woodhead, London, 2001, p. 229.

[13] Y. Asano, H. Hatakeyama, S. Hisose and T. Hatakeyama, in "Recent Advances in Environmentally Compatible Polymers", edited by J. F. Kennedy, G. Phillips, P. Williams, Woodhead, London, 2001, p. 181.

[14] K. Nakamuta, M. Iijima, E. Kinoshita and H. Hatakeyama, in "Recent Advances in Environmentally Compatible Polymers", edited by J. F. Kennedy, G. Phillips, P. Williams, Woodhead, London, 2001, p. 241.

[15] H. Hatakeyama, D. Kamakura, H. Kasahara, S. Hirose and H. Hatakeyama, "Recent Advances in Environmentally Compatible Polymers", edited by J. F. Kennedy, G. Phillips, P. Williams, Woodhead, London, p. 191 (2002).

[16] H. Hatakeyama, S. Hirose, K. Nakamura and H. Hatakeyama, in "Cellulosics: Chemical, biochemical and material aspects", Ellis Horwood, Series in Polymer Science and Technology, 1992, p. 142.

[17] M. Lopretti, A. Montalbán, E. L. Martínez and H. Espino, *Indotecnia*, **6**, 25 (1993).

[18] M. Durán, H. Hatakeyama, M. Aikawa, S. Hirose and K. Kasuga, *Research of Polyurethanes from Lignocelluloses*, **9112**, 51 (1995).

[19] M. Moya, M. Sibaja, M. Durán and J. Vega-Baudrit, *Uniciencia*, **12**, 39 (1995).

[20] J. Vega-Baudrit, M. Moya, M. Sobaja and M. Durán, *Química e Industria*, **49**, 531, (2002).

[21] M. A. López and M. Arroyo, *Plásticos Modernos*, **85**, 594 (2003).

[22] J. Vega-Baudrit, P. Alvarado-Aguilar, R. Sibaja-Ballestero, M. Moya-Portuguez and S. Nikolaev, *Revista Iberoamericana de Polímeros*, **6**, 199 (2005).

[23] J. Vega-Baudrit, K. Delgado-Montero, M. Moya-Portuguez, M. Sibaja-Ballestero and P. Alvarado Aguilar, *Revista Iberoamericana de Polímeros*, **9**, 4 (2008).

[24] J. Vega-Baudrit, Graduation Thesis in Chemistry, Universidad de Costa Rica, San José, Costa Rica, 1994, 94 pp.

[25] American National Standard Institute, "Standard Method of Test for Ash in Wood", Designation D 1102-56, American National Standard 013.1-1960 (1974).

[26] American National Standard Institute, "Standard Method of Test for Water Solubility of Wood", Designation D 1105-56, American National Standard 013.9-1960. 349, 350 (1974).

[27] American National Standard Institute, "Standard Method of Test for Alcohol/benzene Solubility of Wood", Designation D 1107-56, American National Standard 013.6-1960. 346, 345 (1974).

[28] American National Standard Institute, "Standard Method of Test for Holocellulose in Wood", Designation D 1104-56, American National Standard 013.3-1960 (1974).

[29] American National Standard Institute, "Standard Method of Test for Lignin in Wood", Designation D 1106-56, American National Standard 013.5-1960. 342, 343 (1974).

[30] American National Standard Institute, "Standard Method of Test for Alphacellulose in Wood". Designation D 1103-60, American National Standard 013.2-1960 (1974).

[31] American Society for Testing and Materials (ASTM), "Standard Method of Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols", D 4274-88 (1991).

[32] American Society for Testing and Materials (ASTM) "Standard Test Methods for Compressive Properties of Rigid Cellular Plastics", D 1621-73, 488-490 (1991).

[33] J. M. Martín and A. C. Orgilés, Curso sobre poliuretanos, INESCOP, Alicante, España, 1994, 125 pp.

[34] R. Pereira, Despulpado etanol-agua de bagazo de caña de azúcar. Estudio cinético y derivatización de la pulpa obtenida. Proyecto de Graduación. Universidad de Sao Paulo, Brasil, 1995, 220 pp.

[35] G. Oertel, "Polyurethanes Handbook", Mc Millan Publishing, New York, 1993, 668 pp.

[36] T. Hatakeyama and F. X. Quinn, in "Thermal analysis", Wiley & Sons, London, 1999, p. 36.

[37] L. Pothan, S. Thomas and N. Neelakantan, *J. Reinf. Plast. Comp.*, **16**, 756 (1997).

[38] C. Salom, R. M. Masegosa and M. Prolongo, *Plásticos Modernos*, **80**, 661 (2000).