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Use of Rice Husk as Filler in Flexible Polyurethane Foams

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Summary: In this study, flexible polyether polyurethane foams were synthesized by using two kinds of fillers: Inorganic filler and vegetal fiber obtained from agricultural waste. Structural, thermal and mechanical properties of the obtained foams were analyzed.

Keywords: foams; polyurethanes; vegetal; waste

Introduction

Use of Flexible Polyurethane Foams (FPUF) has been widely extended into a high range of applications: The bedding sector, for manufacturing mattresses and pillows, the upholstered furniture, as a resilient filling material, the packaging industry and the manufacturing of car seats and other pieces of the automotive industry are the most outstanding applications of theese cellular materials.

The main reaction that takes place during the synthesis of FPUF is the reaction between a polyether or polyester polyol with an isocyanate, which usually is Toluene Diisocyanate (TDI) and Methylene Diphenyl Diisocyanate (MDI). Those two reactives, with several catalysts and additives which support this polyadiction reaction, are vigorously mixed with several techniques resulting a cellular foam. Besides additives and catalysts, inorganic fillers, such as talcs, barium sulphate, and calcium carbonate are added in the foam formulation in order to enhance mechanical properties, like density or hardness and to decrease economical costs of the final product.[1]

The main target of this study was to analyse the posibility of replacing those inorganic fillers of the foams formulation by vegetal waste and to characterize structural, thermal and mechanical properties of the obtained foams. In this study, rice husk obtained from rice harvest, which have been use in several studies[2,3] as a reinforced filling material, had been used as a vegetal waste.

Materials and Methods

The following raw materials were used to synthesize FPF: (i) Polypropyleneglycol (PPG), Average Mw $\sim$ 4000, Hydroxyl value: 31 mg KOH/g (SIGMA-ALDRICH), (ii) TDI 80, NCO content: 52% (MERCK CHEMICALS), (iii) Blowing agent, Distilled water, (iv) Surfactant, NIAX SILICONE L-550 ® (MOMENTIVE Performance Materials), (v) Reaction initiator, Triethylene diamine, NIAX Catalist A-33® (MOMENTIVE Performance Materials), (vi) Catalyst, tin octoate, Dabco T9 (AIR products), (vii) Calcium Carbonate, and (viii) Milled rice husk, previosuly milled and passed through a 90 μm sieve.

All reagents, in absence of the fillers and TDI, were added in a polystyrene cup and mixed using a mechanical stirrer at 1000 rpm for 60 s, then the filler was added in continuous mixing, stirring was

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Table 1.
Foam formulations (Parts per hundred parts of polyol, pphp).

	FPUF	$CaCO_3$-FPUF	RH-FPUF	RH-$CaCO_3$-FPUF
PPG	100,00	100,00	100,00	100,00
TDI 80	48,00	48,00	48,00	56,70
Distilled water	2,80	2,80	2,80	2,80
Niax-Silicone L-550	0,91	0,91	0,91	1.35
Niax-Catalist A-33	0,65	0,65	0,65	0,65
Dabco T-9	0,85	0,85	0,85	0,85
$CaCO_3$	–	12,61	–	6,30
Rice Husk	–	–	12,61	6,30

continued for 60 s. Last step was adding TDI to the blend, stirring was continued for 10 s, the final mixture was poured into a rectangular mold impregnated with a release agent before the rising time started, the mold was locked and 45 min later, the foamed piece was release from the mold and stored for at least 24 h before their characterization.

Structural analysis according to the cell size and the filler distribution into the foam matrix of the obtained foams was carried out using an optical microscope Motic BA400 at 100 magnifications, a Tensor 27 spectrometer with a single reflection diamond attenuated total reflectance accesory MVP-Pro Star (Harric) was used to analyze chemical composition of filler and foamed

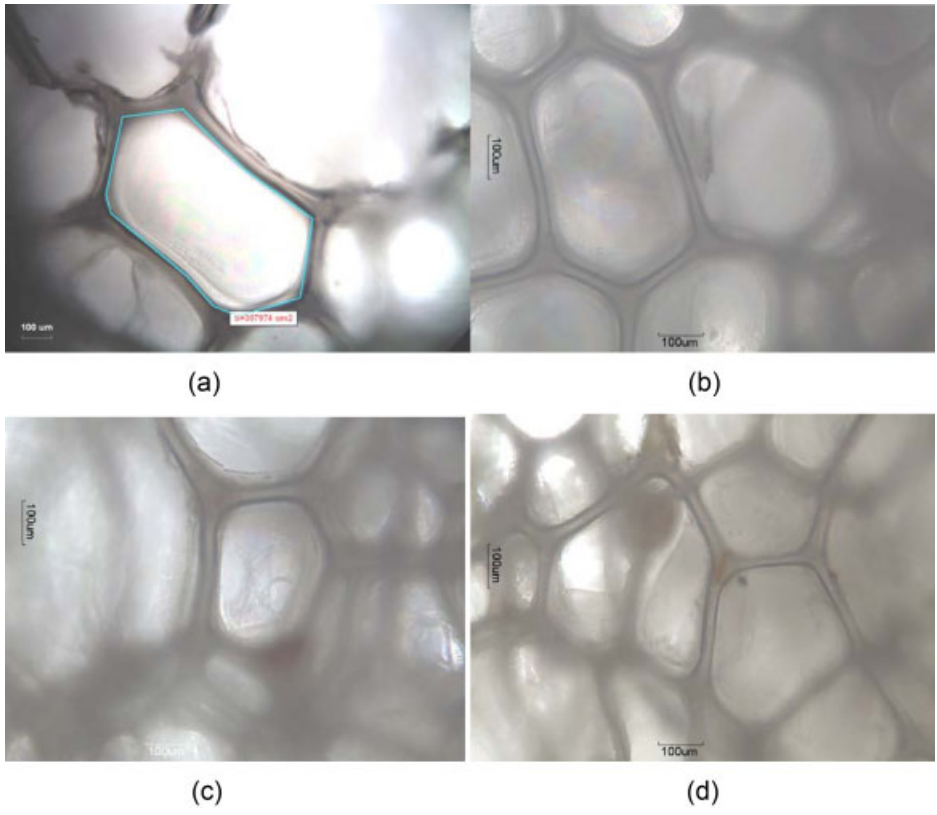

Figure 1.
Miscroscope images of (a) FPUF, (b) $CaCO_3$-FPUF, (c) RH-FPUF and (d) RH-$CaCO_3$-FPUF.

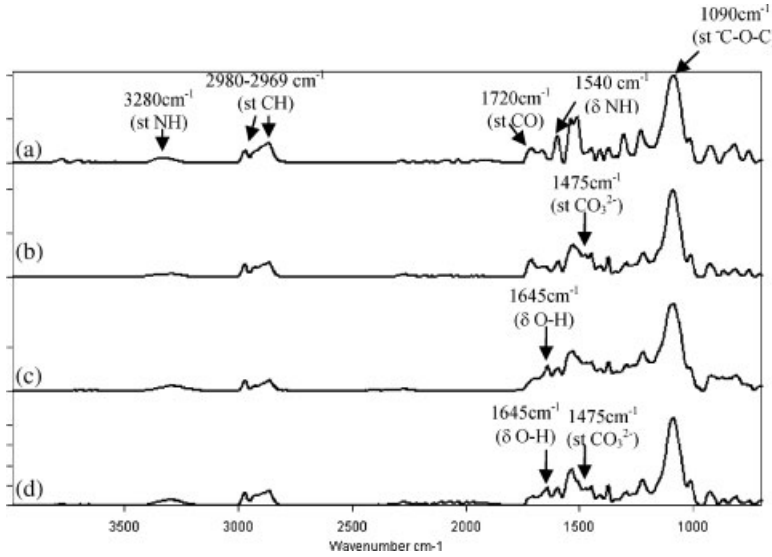

Figure 2.
Infrared Spectra of (a) FPUF, (b) $CaCO_3$-FPUF, (c) RH-FPUF and (d) RH-$CaCO_3$-FPUF.

materials, and a TGA Q500 thermobalance (TA Instruments) was used for the thermal analysis of the obtained foams. For determining mechanical properties of the obtanied foams, standard test methods were followed in order to assess tensile properties,[4] indentation hardness[5] and thickness recovery after static fatigue.[6]

Results

Four flexible foams formulations were prepared (Table 1) which difference among them was the kind of filler: No filler (FPUF), Calcium carbonate ($CaCO_3$-FPUF), Milled rice husk (RH-FPUF) and mix of them (RH-$CaCO_3$-FPUF). In the

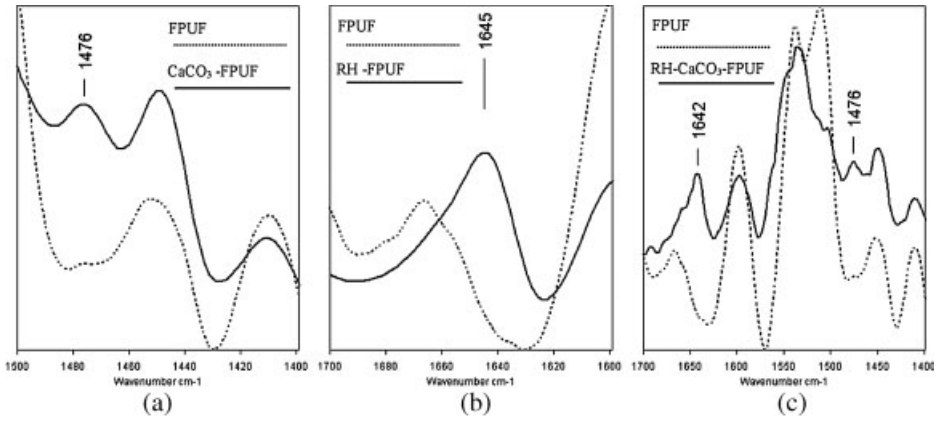

Figure 3.
Regions of the infrarred spectra of filled foams which can be observed the presence of bands which corresponds to the used fillers in (a) $CaCO_3$-FPUF, (b) RH-FPUF and (c) RH-$CaCO_3$-FPUF.

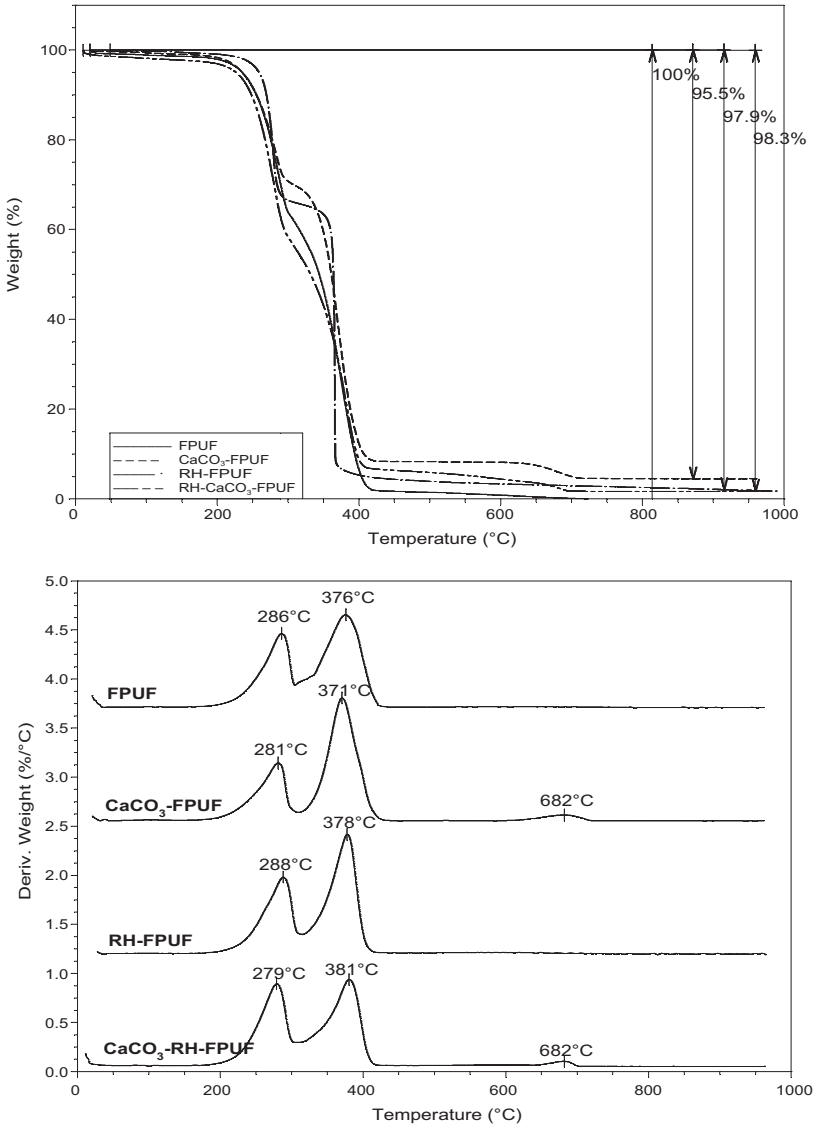

Figure 4.
TGA/DTG curves of obtained foams.

Table 2.
Indentation forces obtained according to ISO 2439:2008.

		FPUF	$CaCO_3$-FPUF	RH-FPUF	RH-$CaCO_3$-FPUF
Indentation force (N)	0%	5,0	5,0	5,0	5,0
	25%	13,8	16,0	14,2	8,3
	40%	19,0	26,0	21,2	12,5
	65%	32,4	61,0	47,5	30,0
S_f (F65%/F25%)		2,35	3,81	3,35	3,61

synthesis of fille foams, an 8 wt% of filler was used.

Images taken by optical microscopy, showed that filler addition produces a cell size reduction of the polyurethane matrix (Figure 1). It was observed that fillers can be placed whether inside of the cell or stuck in the branches that conforms the cell structure.

Infrared spectra of the four foams showed similar chemical structure which is characteristic of polyurethane polyether (Figure 2).

At 1090 cm^{-1} the intense peak produced by the vibrations of the aliphatic ether group can be observed. If the reaction is completed, no bands associated with N=C=O at 2260 cm^{-1} should be observed. There are absorption bands in the spectral region 2970–2869 cm^{-1} due to the stretching vibrations of C-H bonds. Bands assigned to stretching vibration of C=O bond in the urethane group at around 1700 cm^{-1} and also the stretching vibration of N-H urethane group at 3289 cm^{-1} can be observed. The band at 1540 cm^{-1} can be assigned to the bending vibrations of NH.

The infrared spectrum of $CaCO_3$-FPUF shows a low intensity band at 1475 cm^{-1} which corresponds to the asymmetric stress of carbonate group. This peak is not observed in the spectrum of RH-FPUF (Figure 3a). Rice husk is mainly composed by cellulose, hemicellulose and silica. The intense peak bands associated to Si-O-Si bonds 1100 cm^{-1} is overlapped by the peak produced by the alitphatic ether group. But it can be observed at 1645 cm^{-1} a low intensity band, which is a characteristic peak of cellulose according to OH bending of adsorbed water (Figure 3b). Infrared spectrum of RH-$CaCO_3$-FPUF shows the two peaks which evicende the presence of $CaCO_3$ and rice husk (Figure 3c).

Thermograms obtained for the formulated foams show two thermal decomposition stages (Figure 4). According to $CaCO_3$-FPUF and $CaCO_3$-RH-FPUF curves, there is also a third stage that belongs to $CaCO_3$ degradation. In the case of foams filled with rice husk no additional degradation stage related with rice husk is observed probably due to rice husk degradation occurs at the same time than second stage of polyurethane degradation.

In the test method for asess indentation hardness, compressive deflection coefficient (S_f) of each foam was measured, which is a parameter commonly used for the evaluation of indentation hardness for flexible foams and consisted in the ratio of the 65% indentation force deflection to the 25% indentation force deflection. RH-FPUF showed better compressive deflection coefficient than FPUF, but not better than the coefficient obtained by $CaCO_3$-FPUF (Table 2).

After summitting foam specimens to a static fatigue consisted on compress each sample up to 25% its initial thickness during

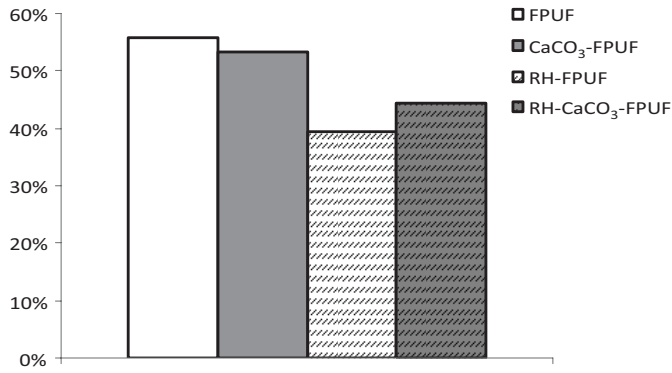

Figure 5.
Thickness loss of foams after static fatigue.

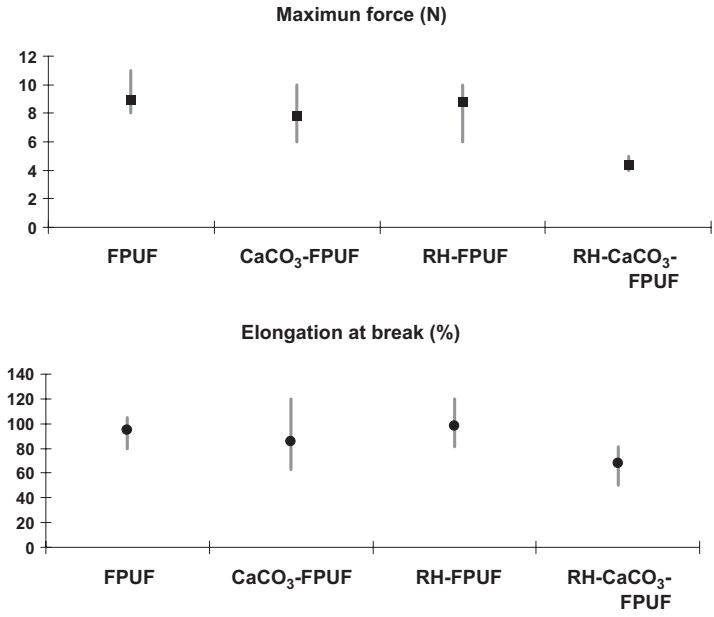

Figure 6.
Tensile strength and elongation at break obtained according to ISO 1798.

24 hours, it had been observed that RH-FPUF showed the best recovery results of all the obtained foams (Figure 5).

According to the test method for assess tensile properties of obtained foams, all filled foams showed lower results in tensile strenght and elongation at break than unfilled foam (Figure 6). This response is characteristic of materials reinforced with inert or non active fillers.[7]

Conclusion

In this study, flexible foams have been formulated using calcium carbonate and rice husk as fillers. Optical microscopy showed a good dispersion of the filler particles into the foam matrix. Typical infrared absorption bands of a polyether polyurethane and fillers were observed by infrared spectroscopic analysis of the obtained foams. The results obtained by thermal analysis showed, that filler addition does not affect the thermal decomposition of the foam. Mechanical test results indicate that rice husk is a suitable filler for flexible polyurethane foams in certain applications, where hardness of the foam is not important, but a good recovery of the foam is required, like manufacturing pillows for the bedding sector, or in the packaging industry for low weight devices.

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