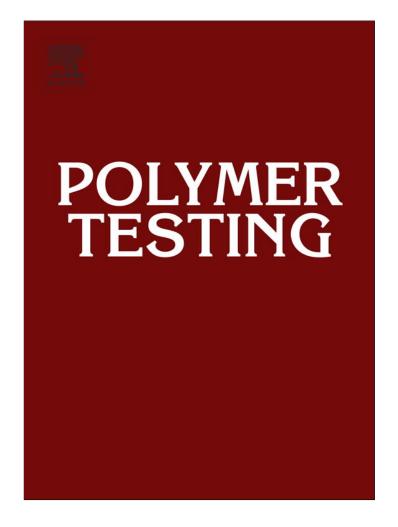
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Material properties

Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization



Virginia Ribeiro da Silva^{a,b}, Mirna A. Mosiewicki^c, Maria Irene Yoshida^a, Mercês Coelho da Silva^d, Pablo M. Stefani^c, Norma E. Marcovich^{c,*}

^a Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil

^b CAPES Foundation, Ministry of Education of Brazil, Brasília, DF 70040-020, Brazil

^c Institute of Materials Science and Technology (INTEMA), University of Mar del Plata – National Research Council (CONICET), Mar del Plata, Argentina ^d Universidade Federal de Itajubá, Campus Itabira, Itabira, MG 35900-373, Brazil

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ABSTRACT

A chemically modified tung oil was used as the main polyol component in the formulation of viscoelastic (low resilience) polyurethane foams. Rice Husk Ash (RHA), a residue from the rice process industry, was chosen to be incorporated as rigid filler in these materials because of its high silica content. Water was used as blowing agent in order to increase the green nature of the reinforced foams. Physico-chemical and thermal properties of the neat and reinforced foams were measured and analyzed. RHA addition leads to noticeable changes in several properties, mainly thermal conductivity, density and foam morphology, even at the low filler content used in this work. Although the thermal stability was almost unaffected by ash content, a stabilizing effect of the inorganic filler was identified, since the residual char was higher than predicted from theoretical calculations.

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1. Introduction

Polyurethanes (PU) are polymers with a wide range of applications that can display quite different properties according to the chemical reagents used in their synthesis. In particular, polyurethane foams are materials with very interesting properties such as high energy absorption capacity, particularly useful for shock damping, and low thermal conductivity due to the presence of a skeleton made of more or less regular cells (open or closed) [1]. Rigid/viscoelastic polyurethane systems are obtained from highly functionalized polyols and polymeric isocyanates.

E-mail address: marcovic@fi.mdp.edu.ar (N.E. Marcovich).

Nowadays, environmental concerns stimulate the use of renewable resources for producing economically convenient applications to maintain or even improve life quality [2]. A current need of the polyurethane industry is to identify new sources of reagents for polymer synthesis to replace petrochemical raw materials by those obtained from renewable sources. In this sense, the use of polyols based/derived from natural oils is a very attractive alternative that can contribute positively to environmental protection [3]. Vegetable oils are abundant renewable sources available worldwide. They have relatively low cost and offer, a priori, possibilities of biodegradation [4]. Oils are triglyceride molecules composed of saturated and unsaturated fatty acids. These oils can be functionalized by hydroxylation of the carbon-carbon double bonds with a peroxy acid and/or by alcoholysis with a triol like glycerol or triethanolamine to reach a hydroxyl value useful for elastomeric or rigid polyurethane production [5,6].



^{*} Corresponding author. University of Mar del Plata – National Research Council (CONICET), Institute of Materials Science and Technology (INTEMA), Juan B. Justo 4302, 7600 Mar del Plata, Buenos Aires, Argentina. Tel.: +54 223 481 6600; fax: +54 223 481 0046.

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Among the different vegetable oils, tung oil (also called China Wood Oil), which is obtained from seeds or wood of the tung tree, has already proved to be a suitable raw material to produce high hydroxyl content polyols [5]. Its main constituents are α -eleostearic acid (77-82%), oleic acid (3-12%) and linoleic (8-10%), all of them being acids with double bonds in their carbon chains that can be reacted to introduce hydroxyl groups [7,8].

Finely divided inert inorganic fillers are often added to foam formulations to increase density, load bearing, or sound attenuation [9,10]. All other foam physical properties are generally sacrificed. Typical results have been described in the literature [11–13]. Depending on the nature of the filler, the overall cost of the final foam may be reduced [9,10]. Among the commonly used inorganic loads, silica (SiO₂) is recognized as an effective flame retardant filler [14,15]. Several works in the scientific literature have reported studies about the behavior and the mechanisms of SiO₂ action as a flame retardant in polymers [16–19]. Different kinds of silica were also used as reinforcing filler in thermoplastic [20] and thermoset polymers [21] to increase their mechanical properties, such as the compression or tensile strength and toughness.

Rice husk is one of the main lignocellulosic residues of the agricultural industry and a natural source for silica production. World rice production in 2006/07 was ~600 million tons [22]. As a consequence, 145 million tons of husk residues were produced. An increasing application of rice husk in rice producing countries, such as Brazil and Argentina, is as fuel in the heat generation for drying rice operations, due to its high calorific power. However, in the combustion process, only the organic part can be burned, leaving the silica-rich ash as the residue. This large amount of silica residue can be reused, avoiding accumulation of solid material in the environment and adding value to a waste material [21].

Thus, the aim of this present work is to prepare and characterize polyurethane rigid foams based on hydroxylated tung oil, using water as blowing agent to enhance the green nature of the material. In addition, the feasibility of reinforcing the foam using rice husk ash (RHA) as inorganic load will be evaluated.

2. Materials and methods

The rice husk (RH) used in the present work was collected in from rice industries of Concepción del Uruguay (Entre Ríos, Argentina). Rice husk ash (RHA) was obtained from combustion of RH in air using a laboratory oven that was heated from room temperature to 600 °C at a rate of 10 °C min⁻¹. The sample was maintained at 600 °C for 90 minutes and then allowed to cool to room temperature inside the oven [21]. The obtained ash was further crushed using an analytical mill (IKA 50, Germany), for 10 minutes, and only ash particles with size lower than 100 mesh (U.S. Standard, <150 µm) were used. The physical-chemical characterization of the ash performed by X-ray fluorescence revealed that the RHA contains about 94 wt.% of SiO₂, and did not have residual char.

Tung oil (saponification value = 223 mg KOH/g, acid number = 2.11 mg KOH/g) was obtained from *Cooperativa*

Agrícola Limitada de Picada Libertad (Argentina) and conveniently modified to produce a highly functionalized natural polyol. The highly functionalized natural polyol was obtained in a two-step procedure that involves, first, the reaction of the tung oil with hydrogen peroxide solution and formic acid to produce and hydroxylated tung oil (HTO), then this intermediate product was reacted with dry triethanolamine to form the polyol through a transesterification procedure [1]. The final product was a mixture of different alcohols containing one or two hydroxylated fatty acid chains with high viscosity (at room temperature) and an average hydroxyl number of 450 mg KOH/g, as determined according the technique described elsewhere [23].

For the preparation of rigid polyurethane foams, 4,4diphenylmethane diisocyanate prepolymer, p-MDI (Rubinate[®] 5005, Huntsman Polyurethanes, USA) with an equivalent weight of 133 g/eq was selected as the isocyanate component. Also, different additives were incorporated to the formulation: surfactant agent (Tergostab[®] B8404 Hunstman Polyurethanes), catalyst (tertiary amine, n,n-dimethyl benzylamine, <98%, Aldrich) and ethylene glycol (Sigma). The replacement of a small part of the modified tung oil by a low molecular weight diol (etylene glycol) led to reactive liquid mixtures of adequate viscosity and facilitated the mechanical stirring of reactants. Distilled water was selected as blowing agent in order to avoid the use of materials such as HCFC and pentane that have undesirable characteristics such as high global warming potential or flammability.

2.1. Preparation of polyurethane foams

Table 1

The index (moles of NCO groups/moles of OH groups) was adjusted for the system in order to obtain stable noncollapsing foams. The contributions of polyol and water were taken into consideration in the index calculation and the index was maintained at 1.1. Natural polyol and ethylene glycol were dehydrated under vacuum before their use. Similarly, rice husk ash was dried at 70 °C until constant weight in a vacuum oven before use. The adjusted foam formulation used to prepare unfilled and reinforced samples is shown in Table 1.

The foams were obtained by the free rise method at room temperature. The polyols, surfactant agent, catalyst,

Reactants used to prepare filled and unfilled polyurethane rigid foams.

Reactants	Reactant name/ company	Chemical composition	Mass (g)
Polyol	Polyol from tung oil	Modified tung oil	90
MDI	Rubinate [®] 5005/	4,4'-diisocyanate	210
	Huntsman	diphenylmethane	
	Polyurethanes		
Amine	DMBA*/Aldrich	dimethylbenzylamine	1
(catalyst)			
Silicon	Tegostab [®] B8404/	Protected patent	2.5
	Huntsman		
	Polyurethanes		
Water	Distilled water	H ₂ O	4
Chain	Ethylene glycol/Sigma	Ethylene glycol	10
extender			

foaming agent and rice husk ash were mixed together for 60 s in a container and then the MDI was added. The system was further mechanically mixed for 20 s and then the foam was allowed to freely rise. During the reaction, the cream time, the gel time and the end of rise time were recorded.

2.2. Characterization techniques

2.2.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained in a Genesis II Fourier Transform infrared spectrometer used in ATR (attenuated total reflectance) mode. The spectra were recorded at 2 cm^{-1} resolution and the reported results are the averages of 32 scans.

2.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed in a TGA-50 SHIMADZU Thermogravimetric Analyzer at a heating rate of 10 °C/min under air atmosphere.

2.2.3. Density measurements

The density of the foams was obtained as the ratio between the weight and volume of a cylindrical specimen. The weight was measured with a precision of ± 0.001 g and the sample linear dimensions with ± 0.01 mm accuracy.

2.2.4. Thermal conductivity

Was determined using the 'hot wire method' (HWM), a transient test performed using ad-hoc equipment [24].

2.2.5. Scanning electron microscopy (SEM)

Was used to obtain photographs of unfilled and RHA filled foams. Small specimens were cut from the foam blocks with a thin blade parallel to the foam rise direction and then coated with gold in preparation for the SEM study. A scanning electron microscope JEOL model JSM 6460LV was used.

3. Results and discussion

The green foams presented in this paper were prepared by the reaction of a polyisocyanate with two different polyols (a high-functionalized tung oil derivative and ethylene glycol). Water was used as blowing agent in order to further enhance the green nature of the foams. The reaction between the isocyanate and water produces both a substituted urea and the carbon dioxide blowing agent, which creates the PU foam [25]. Therefore, the foam structure depends on the relative rates of these two reactions. It is known that high water content produces more CO_2 during the foam formation, resulting in a low final

Table 2

Foaming characteristic times of unfilled and filled foams.

density [25,26]. Several groups [25-29] have studied the effect of the water content in the foam structure and they all found that an increase in the water content produced an expansion of the foam volume resulting in thinner foam cell walls and larger foam cells, changing the density of the foam and its morphology. Moreover, a typical effect of the addition of fillers to the reaction mixture is an increase in its viscosity [30]. In this work, it was observed that the dispersion of the rice husk ash became difficult as filler concentration increased, and the resulting foams presented a quite distorted structure of cells (large cell size distribution and density gradient in the foam rise direction), and undesirable mechanical properties added to a more granular surface texture when the rice husk content was higher than 5 wt.%. Hence, both the water and filler maximum content were optimized to lead to foams with an adequate performance and these values resulted fixed at 1.26 and 5 wt.%, respectively.

Table 2 shows the foaming behavior of the samples prepared with different percentages of rice husk ash. The characteristic times measured for the filled systems are, in general, higher than those measured for the neat foams, but still in the range of operation conditions for preparing rigid polyurethanes foams [29,31]. The differences are attributed again to the increasing viscosity of the reaction mixture as filler concentration increases, which complicates the processing step, slowing the polymer formation. It is found that the most affected time is the creaming, which is related with nucleation of gas bubbles and, from a macroscopic point of view, is evidenced by a change in color of the reacting mixture which adopts a creamy appearance due to the evolution of gas bubbles becoming big enough in size to scatter light. However, in the present case, this increase in the characteristic time is considered an advantage, because it allows mixing filled mixtures for some extra seconds, thus achieving more uniform mixtures.

3.1. FTIR analysis

Fig. 1 shows the FTIR spectrum of the unfilled foam (matrix foam - PU), from 4000 cm⁻¹ to 400 cm⁻¹. The signals corresponding to the stretching vibration of NH groups are clearly seen at 3297 cm⁻¹, indicating that the urethane linkages were successfully formed. A strong and wide band with maximum at 1704 cm⁻¹, characteristic of the carbonyl stretching vibration in the amide I (C=O) region, was also detected [32,33]. It is well known that the infrared absorbance of H-bonded carbonyl groups appears at lower wavenumbers than that of free urethane carbonyls [32,34]. Whereas non-H-bonded (free) carbonyl groups in

Characteristic times (s)	Rice husk ash concentration (wt.%)				
	0%	1%	2%	3%	5%
Cream	8.0 ± 0.7	16.0 ± 1.1	15.0 ± 1.4	20.0 ± 1.8	22.0 ± 2.0
Half cup	26.5 ± 0.7	21.0 ± 2.8	31.0 ± 2.8	30.0 ± 3.0	35.0 ± 3.1
End of rise	41.0 ± 1.41	$\textbf{32.0} \pm \textbf{2.2}$	$\textbf{42.0} \pm \textbf{2.8}$	41.0 ± 3.5	52.0 ± 4.2

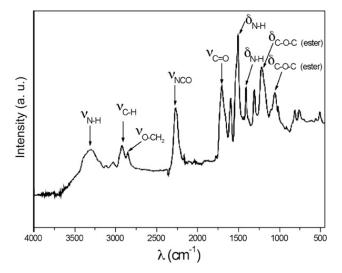


Fig. 1. FTIR spectrum of the unfilled foam, from 4000 to 400 cm^{-1} .

disordered (amorphous) conformations can be observed at 1714-1718 cm⁻¹ and H-bonded carbonyl groups in ordered (crystalline) hard domains are also observed at 1685-1706 cm⁻¹ [32,35]. Moreover, the carbonyl absorbances associated with soluble polyurea and hydrogen-bonded urea were reported to appear at 1715 and 1654 cm⁻¹, respectively [36,37]. Summarizing, in our case, this band can be assigned to the overlapped signals of the free species region, >1700 cm⁻¹, comprising both free urethane and free urea, and H-bonded species region, <1700 cm⁻¹ [38].

Other characteristic bands, the N–H deformation signal at 1519 cm⁻¹ of isocyanurate (resulting from reactions between isocyanate and urethane groups [39]), aromatic ester stretching at 1216 and 1064 cm⁻¹ and CH deformations of aromatic groups in the range of 800 to 600 cm⁻¹ are also noted in the spectrum. The main bands that characterize the urethane formation are summarized in Table 3.

The presence of a large signal at 2258 cm^{-1} indicates that residual (unreacted) isocyanate still exists in the system [32,40], which was expected, since an isocyanate index equal to 1.10 was used in the foam formulation.

The spectra of reinforced samples did not differ from the corresponding one for neat foam and, therefore, they are not shown. Due to the low rice husk ash concentration, silica signals (main chemical ash constituent) could not be detected. However, no interactions between the inorganic filler and the PU matrix were expected.

Table 3	
Main characteristic urethane bands.	

Bands (cm ⁻¹)	Attributions
3297	N—H stretching vibrations
2923	C–H stretching vibrations
2854	O–CH ₂ stretching vibrations
2258	NCO stretching vibrations
1704	C=O stretching vibrations
1510	N–H deformation
1411	CH ₃ deformations
1220 and 1058	C–O–C ester deformation

3.2. Thermogravimetric analysis

Thermal analysis was used to evaluate the dependence of the thermal stability of the polyurethane foams on the inorganic filler concentration. The thermogravimetric curves shown in Fig. 2 are quite similar for all the samples due to the low amount of ash used to prepare the reinforced foams, although some differences can be addressed. In all cases, there are two thermal degradation steps that are representative of the degradation pattern of polyurethanes, which is usually described as a very complex process that occurs as a result of a multitude of physical and chemical phenomena, and is not dominated by a single process [32]. Thermal stabilities of polyurethanes depend mainly on the equilibrium between polymerization and depolymerization of functional groups or linkages present in the polymer chains. It is known that the first stage of degradation is related to urethane bond decomposition, which takes place through dissociation to isocyanate and alcohol, followed by the thermal decomposition leading to the formation of amines, small transition components and carbon dioxide [5,32,41,42]. In this work, it can be noted that the first degradation step presents two maxima in degradation rate, clearly seen in the derivative thermogravimetric curves (not shown), which can be attributed to the degradation of soft segments (those derived from the reaction between the MDI and the longer chains that compose the natural polyol) and hard segments (derived mainly form the reaction between isocyanate and ethylene glycol), as indicated in related papers [32]. Furthermore, in the second stage it is possible to observe another weight loss step at higher temperatures, associated with degradation of substituted urea, isocyanurate and other thermally stable compounds [32,43,44], or might be due to C-C bond cleavage [32,45]. Table 4 reports the temperature corresponding to the onset of decomposition, the temperature at which 5 wt.% mass was lost and the residue formed at high temperature (800 °C) for the neat PU foam and the

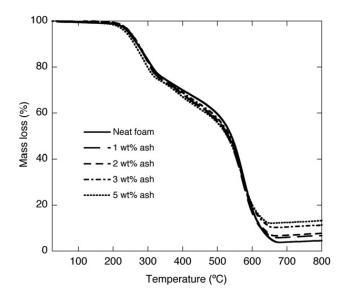


Fig. 2. Thermogravimetric behavior of unfilled and rice husk ash filled foams.

 Table 4

 Char mass values and temperatures corresponding to the onset of thermal decomposition and 5% mass loss of unfilled and rice husk ash filled foams.

RHA content (wt.%)	Onset of decomposition (°C)	Temperature 5% mass loss (°C)	Residual char (%) Experimental/ theoretical
0	228	245	3.74/3.74
1	231	249	6.03/4.69
2	229	249	8.40/5.63
3	227	250	11.55/6.54
5	224	238	14.12/8.32

reinforced samples. It is evident that the degradation temperatures are similar for all the samples, with the exception of the 5 wt.% filled one that exhibits lower values. As was previously commented, the dispersion of the rice husk ash in the reactive mixture become difficult as filler concentration increases and, therefore, 5 wt.% was selected as the maximum filler content. However, samples at this concentration are not as homogeneous as those produced with lower ash content due to dispersion problems and, therefore, presented a slightly lower resistance to thermal degradation. The stabilizing effect of the inorganic filler was further confirmed by analyzing the residue at high temperature. Even although the neat foam presented a non-zero value (3.74% vs 0% expected from the totally thermally degradable constituents), a synergistic effect may be inferred since the residue for the reinforced samples is higher than predicted from theoretical calculations (i.e. PU residual carbon content + all the inorganic filler mass, as indicated in Table 4). This behavior is attributed to the barrier effect of the inorganic filler, which slows down the escape of volatile compounds and the diffusion of oxygen, leading to a higher than expected char residue. This effect and was also noted by other researchers in similar systems [46]. Fig. 3 presents the dependence of the

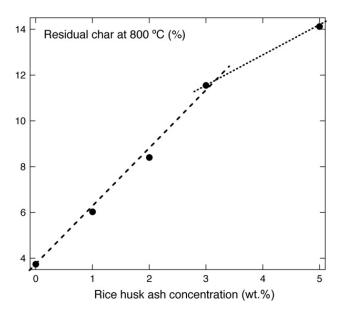


Fig. 3. Experimental residual char as a function of rice husk ash concentration.

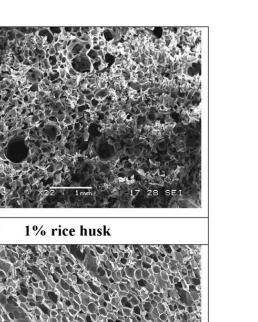
experimental residual char on the rice husk ash concentration. It is seen that the residue increases linearly with filler concentration for samples containing up to 3 wt.%, although the foam prepared with 5 w% deviates from this trend, exhibiting a lower than expected residual char. This is again attributed to the low degree of filler dispersion since it was reported that the effectiveness in promoting char formation is directly related to the degree of mineral filler dispersion [46].

3.3. Scanning electronic microscopy

Fig. 4 shows the scanning electron micrographs of the foams formulated with the tung oil derived polyol as a function of the rice husk ash content. The images show that the foams present mainly a closed cell structure and there is no preferential orientation in the cells for the neat foam (Fig. 4A). The cellular structure of the unfilled foams is almost spherical and evenly distributed, with few broken cells (Fig. 4B-E). The filled foams did not exhibit pronounced preferential orientation either; however, due the increase of viscosity of the reactant mixture with filler addition, the polymer expansion was partially damaged, causing the formation of cells with a more distorted structure and a larger cell size distribution (less uniform sizes) as compared to the unfilled samples. This effect increases with filler content, since rice husk ash particles are large enough to interfere with cell development (even particle size used was $<150 \mu m$, it is still large enough to perturb the growth). As was reported elsewhere [47], filler particles act as nucleation sites for cell formation and, since a higher number of cells start to nucleate at the same time, there is less gas available for their growth, and this leads to a decrease in the size of the cell. In addition, the incorporation of rice husk ash to the unreacted system leads to an increase in the viscosity, which hinders cell growth and results in smaller cell sizes when compared to the pure polyurethane foam. As the concentration of filler was kept quite low, there were sites left without filler and, therefore, the cells formed in those places were quite different from those nucleated on the particles. Moreover, Fig. 4F indicates that the filler particles locate both within cells and outside them, affecting the cell strut [48], which to some extent contributes to cell rupture.

3.4. Density and thermal conductivity

The Table 5 presents the density and thermal conductivity values for the unfilled and filled foams. It is seen that the foam density decreases as the concentration of rice husk ash increases. In general, the density of the foams depends on the mass of expanded polymer, which in turn is related, among other things, to the amount of blowing agent used. However, filler incorporation can affect foam density, due to the interference of the solid particles with the nucleation step. The nucleation process is related to the number and the homogeneity of the gas micro-bubbles formed during the mechanical agitation of the unreacted liquid mixture. The quantity and size of these blowing gas nuclei retained in the mixture, together with the surfactant, control and determine the number, the size and the



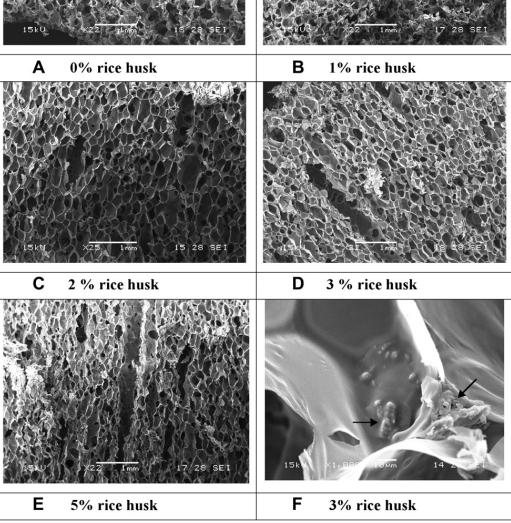


Fig. 4. Scanning electron micrographs of the natural foams as a function of rice husk ash concentration (A-E); location of filler particles in cell foams (F).

 Table 5

 Density and thermal conductivity of foams based on from tung oil and rice husk ash.

Rice husk content (wt.%)	Density (kg/m ³)	Thermal conductivity (mW/m °C)
0	77.4 ± 1.3	44.1
1	$\textbf{77.4} \pm \textbf{2.7}$	44.6
2	65.4 ± 9.5	50.1
3	53.0 ± 5.5	50.7
5	56.2 ± 5.2	49.1

regularity of cell foams. Even low amounts of filler can interfere with the nucleation process, causing an increase of the cell number and a decrease of thickness of their walls. For higher concentrations of reinforcement, this interference occurs with more intensity. However, it is also quite common to find that the foam density increase with filler concentration, since the effect of adding a more dense material (filler) to the foam could prevail over the other effects [49,50].

Thermal conductivity (k) is the key property that governs insulation applications for PU rigid foams. Thermal conductivity value is closely related to foam density and cell morphology. Total k value consists of four parts: k-gas, k-radiation, k-solid and k-convection [51]. Foams with a high density have lower k-radiation, but a higher noncellular PU portion leads to higher k-solid. Although the PU solid only accounts for a small percentage of the whole foam, it has a much higher k value (220 mW $m^{-1} K^{-1}$) than the k value of the physical blowing agent CO₂ $(15.3 \text{ mW m}^{-1} \text{ K}^{-1})$ [51]. At a fixed foam density, k-radiation will decrease with decreasing cell diameter. The level of closed cell content should also be kept as high as possible. Open cells allow more convection, and even air to enter the foam, which has much higher k value $(24.9 \text{ mW m}^{-1} \text{ K}^{-1})$ than that of CO₂ [51,52]. Thus, a low k value results from a small average cell size and a high closed cell content. In this work, foams with k values between 44 and 51 mW m^{-1} K⁻¹ were obtained, which is considered satisfactory taking into account that the density of the obtained foams is in the higher limit of common polyurethane construction foams (thermal conductivities between 20 and 30 mW/mK for densities ranging from 30 to 100 kg/m³) [53], and that CO₂ was used as blowing agent (as opposed to the use of the more insulating chlorofluorocarbon liquids, CFC). However, it is noted that the addition of rice husk ash leads to slightly higher values (i.e. samples with worse insulation properties) than for the corresponding unfilled foam. Also, these results were achieved for samples with lower density than the neat foam, corroborating that the effect of this inorganic filler is not beneficial for thermal insulation. Modesti and Lorenzetti (2002) [54] attributed the increase of the thermal conductivity of their expandable graphite (EG) and redphosphorus (RP) filled polymeric foams (with respect to that of the neat ones) to the high viscosity of the foam formulation, which increases rising for both RP or EG amount and leads to a non-homogenous dispersion of EG. Badri et al (2005) [55] found the same behavior by reinforcing rigid polyurethane foams with empty fruit bunch fibers (EFB); they indicated that the inclusion of untreated EFB ruptured the cellular structure, leading to a higher rate of diffusion and increased the conductivity. In a previous work [1], we noted that the thermal conductivity of PU foams based on castor oil increases as the wood flour concentration (filler) increases, and explained that behavior considering the relative increase of small and/or clustered-small cells of the reinforced foams with respect to those of the neat sample. Any of these explanations can be applied to the present case.

4. Conclusions

Rigid PU foams and rice husk ash filled rigid foams based on a modified natural oil were successfully prepared. Reinforced foams presented larger characteristics times than the neat one, which was considered as an advantage, since filler addition increases the viscosity of the liquid reactive mixture and, therefore, more time is required for an adequate homogenization. FTIR analysis showed the typical bands expected for polyurethane foams while SEM images revealed a mainly closed cell structure for both the unfilled and filled samples. Although the reinforced foams showed a higher thermal conductivity than that of the unfilled samples, the increase was within 20% and they still behave well in the range of polyurethane foams for applications in construction. TGA analysis indicated that thermal stability was almost unaffected by ash content. However, a stabilizing effect of the inorganic filler was identified, since the residual char was higher than expected from theoretical calculations.

Summarizing, the tung oil based polyol revealed itself as a good alternative to replace petrochemical raw materials for polyurethane production. In particular, these tung derived foams can be used as substitute of petroleumderived formulations in semi-structural applications where low weight and insulating properties are desirable.

Acknowledgements

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