Composites of Rigid Polyurethane Foam and Cellulose Fiber Residue

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ABSTRACT: Rigid polyurethane composite foams were prepared with cellulose fibers as a filler. The cellulose fibers were an industrial residue of blanched cellulose pulp production. The influence of the cellulose fiber concentration on the structural, thermal, mechanical, and morphological properties of the foams was investigated. We also studied the influence of the cellulose fibers on the foam's resistance to fungal attack by placing a suspension of known fungus in contact with the surface of the foam and following the morphological evolution as a function of time (for 60 days). The increase in the cellulose filler concentration in the foams, up to 16% w/w with respect to the polyol, changed their properties as follows: (1) the cell size decreased, (2) the thermooxidative stability and mechanical properties remained approximately constant, (3) the thermal conductivity decreased slightly, and (4) fungal growth was observed. Therefore, a cellulosic fibrous industrial residue was rationally valorized as a filler in classical rigid polyurethane foams; this yielded materials with mechanical resistance and a susceptibility to fungi in a wet environment. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3665–3672, 2010

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INTRODUCTION

Rigid polyurethane foams (RPFs) are crosslinked, three-dimensional polymers with closed cellular structures. Because of their low thermal conductivity and good mechanical resistance, RPF are used as insulating materials for pipelines and in automotive parts, domestic and commercial refrigeration, and building engineering applications. One obtains an RPF by mixing a polyol with an isocyanate and other processing additives (e.g., catalyst, surfactant, copolyol, dyes, blowing agent) and leaving the ensuing mixture to expand. The foam expansion is due to evaporation of the blowing agent when the exothermic reaction between the polyol and the isocyanate starts to happen. The blowing agent remains enclosed in the cells of the solid material at the end of the process and ensures the insulating performance of the foam.[1,2] Physical and/or chemical blowing agents can be used in the preparation of the RPF. Distilled water is one of the chemical blowing agents widely used in RPF because it reacts with the isocyanate and generates *in situ* carbon dioxide. The influence of water on the foam properties was studied in different systems of RPF.[3–5] Hydrochlorofluorocarbons are still used as physical blowing agents as substitutes for chlorofluorocarbons.[6] Cyclopentane and distilled water have been studied as alternative blowing agents with the aim of eliminating the use of chlorofluorocarbons and hydrochlorofluorocarbons in cellular material production.[7,8] As mentioned before, in addition to the isocyanate, polyol, and blowing agents, the synthesis of the RPF requires chain-extending agents, catalysts, surfactants, and in some cases, fillers.[1]

The fillers can be used as modifiers of the mechanical resistance, to decrease the cost, and/or to modify the biodegradability of the material. Yang et al.[9] studied the influence of silicon dioxide powder and glass, nylon 66, and polyacrylonitrile (Pan)-based carbon fibers on the tensile strength of RPFs. These authors observed that 3.5% (w/w) carbon fiber provided optimal reinforcement. Bledzki et al.[10] used woven flax and jute fabrics as reinforcements for polyurethane microfoams. Flax fiber composites showed higher mechanical strength than that observed for their woven jute fiber counterpart. The advantage of fillers from a vegetal origin in polyurethane foams is the presence of hydroxyl groups at their surface, which can react with isocyanate to yield covalent bonds in the matrix–filler interface.[11–13]

In this study, RPF composites with different concentrations of cellulose fiber were prepared in the presence of water and pentane as blowing agents. These fibers were an industrial residue of bleached cellulose pulp production, which our group investigated previously.[14] This industrial waste showed a high proportion of cellulose with preserved fibrillar morphology and low lignin and inorganic residue contents.

The impact of the filler on the morphology, thermal properties, and mechanical properties of the foams was investigated. Furthermore, the influence of the cellulose fiber on the biodegradability of the polyurethane foam was studied.

EXPERIMENTAL

Materials

The materials used in the foam preparation were obtained from commercial sources. The isocyanate IsoPMDI 92140 (4,4′-diphenylmethane diisocyanate, with an average NCO functionality of 2.5), polyether polyol Lupranol 3323 (OH value = 340 mg of KOH), tertiary amines dimethylcyclohexalamine and N,N,N',N'-tetramethyl-2,2′-oxybis(ethylamine) (NIAX A-1), catalysts, and SR-321 NIAX surfactant were supplied by Elastogram (Lyon, France). The glycerol and pentane used as a chain-extending agent and physical blowing agent, respectively, were commercial products purchased from Aldrich (Lyon, France). Distilled water was used as a chemical blowing agent. The cellulose fibers were unbleached screen rejects (USRs), previously studied by our group.[14] They were supplied by Celulose Nipo-Brasileira S. A. (Belo Oriente, Brazil), a producer of bleached cellulose pulp from *Eucalyptus grandis* by the kraft process.

Sample preparations

The foams were obtained from a conventional formulation for RPFs containing polyol (90% w/w polyether polyol and 10% w/w glycerol). The concentrations of all of the other component, with respect to the polyol content, were as follows: 154% w/w isocyanate IsoPMDI, 1% w/w dimethylcyclohexalamine and 0.4% w/w NIAX A-1 as a catalyst mixture, 3% w/w SR-321 NIAX surfactant, 20% w/w pentane, and 2% w/w water.

The conventional procedure for foam preparation was adopted. It consisted first of vigorously mixing the polyol (or the mixture of the polyols), surfactant, catalysts, and water for about 60 s to form an emulsion. Then, the physical blowing agent pentane was added, and the mixture was stirred again for 30 s. Next, isocyanate was added with an additional 15 s of stirring.

The foam composites were prepared by the addition of the cellulose fiber in the first stage to the polyol and other components. The fiber concentrations used were: 0, 1, 3, 4, 8, 12, and 16% w/w, with respect to the total polyol mass. The composites obtained were designated as RPF0 (matrix foam), RPF1, RPF3, RPF4, RPF8, RPF12, and RPF16, according to their respective fiber content. The foams were prepared in a pot 10 cm in diameter and 25 cm in length before expansion started to take place. The prepared foams were cured for 24 h at room temperature before they were cut and tested.

Measurements

Fourier transform infrared spectroscopy was used to access the structural features of the sample foams with a Perkin-Elmer spectrophotometer (FTIR-GX, Waltham, MA). The samples were prepared with KBr pellets as a support for transmittance mode analysis within the range 4000–400 cm^{-1}, with a resolution of 4 cm^{-1} and 64 scans.

The structure of the polyurethane was confirmed by the presence of the main absorption bands characteristic of urethane moieties: 3307 cm^{-1} (NH), 1712 cm^{-1} (C=O urethane), and 1512 cm^{-1} (NH amide II groups).[15,16] The spectra of the composite foams showed the same absorption bands as those observed in the matrix foam, and no bands characteristic of the cellulose structure were observed; thus, the spectra were omitted.

The thermal stability was studied by thermogravimetric analysis with an SDT 2960 apparatus from TA Instruments (New Castle, DE) under a stream of air with a flow of 10°C/min from room temperature to 800°C.

The densities of the RPFs were measured according to ASTM D 1622. For this purpose, five cubes with the dimensions 50 × 50 × 50 mm^3 were measured for each formulation to determine the average values and the accuracy.

The morphology and cell size of the samples were studied on a Quanta (Hillsboro, Oregon) 200 FEI scanning electron microscope. The gold-coated samples were observed in the free-rise direction by scanning electron microscopy (SEM).

The mechanical properties of the foams were studied in the compressive mode. Samples prepared for density determination were used. The analysis was performed according to ASTM D 1621 with an Instron (Norwood, MA) 4501 universal testing machine with a speed of crosshead movement of 5 mm/min. All values are reported as the average value of the properties for five samples, and experimental errors were calculated.

The thermal conductivities of the polyurethane foams were determined according to ASTM C 177-97 with a guarded hot-plate device. Discs with a diameter of 9 cm and a thickness of about 3 mm were prepared and tested.

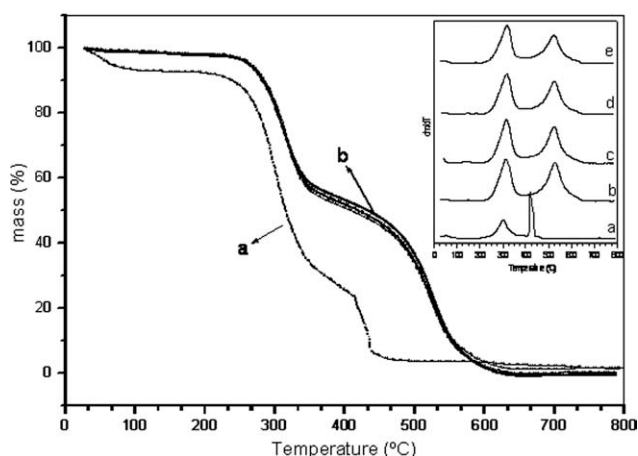The influence of the cellulose fiber on the biodegradability of the foams was also investigated. For

Figure 1 TG and DTG curves in air between room temperature and 800°C for the (a) cellulose fiber, (b) unfilled matrix foam RF0, and the composite foams (c) RPF1, (d) RPF8, and (e) RPF16.

this study, suspensions of five fungi, *Syncephalastrum racemosum, Curvularia senegalensis, Rhizopus stolonifer, Aspergillus niger,* and *Rhizopus oryzae,* were cultivated with malt extract (20 g/L) and agar (18 g/L) supplied by Acumédia. These fungi are voracious, they were isolated from soil and have been previously applied to evaluate the biodegradation of paper and synthetic polymers.[17–21] After growth in solid media, fungal suspensions were prepared by the addition of sterile water to the test tube and the scratching of superficial mycelia. Before the test was begun, the middle of the culture, Petri plates, water, and samples were autoclaved at 120°C for 20 min to assure sterility. Two milliliters of each of the fungal suspensions was added to samples of the matrix foam and their composites. The samples were transferred to Petri dishes, and then, they were sealed with tape. After the first 15 days, no evolution of the tests was observed; therefore, the plates were opened, and an additional 3 mL of sterile water was added to them. The growth, or lack of growth, of the fungi on the surfaces of the foams and their composites was examined after 30 and 60 days by optical microscopy and SEM. The optical microscope was a Ken-A-Vision 3400, and the SEM apparatus was mentioned previously.

RESULTS AND DISCUSSION

Thermal characterization

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the cellulose fiber (USR) and the samples RPF0, RPF1, RPF8, and RPF16 in air between room temperature and 800°C are shown in Figure 1.

The fiber presented a mass loss corresponding to 8% between room temperature and 100°C [Fig. 1(a)], which could be associated with humidity loss. The sample was previously dried at 120°C for 12 h. After

the humidity loss, we observed that the USR sample decomposed into two stages, with temperatures of the maximum rate of degradation at 302 and 420°C, as shown in the DTG curve. At the end of the decomposition, the sample presented a residue that corresponded to 3% of the initial mass.

The sample RPF0 [Fig. 1(b)] displayed negligible mass loss below 200°C. The thermal degradation of polyurethane in volatile products occurs in two stages with mass losses of 46 and 51% and temperatures of the maximum degradation rate at 314 and 526°C. The thermal stability of RPFs was reported to show that the initial stage of weight loss is dominated by polyol component degradation, whereas the isocyanate component degradation governs the second stage.[22]

The TG and DTG curves for the composite foams RPF1, RPF8, and RPF16 [Fig. 1(c–e), respectively] showed that the presence of the cellulose fiber did not change the thermal stability and degradation process of the matrix foam. Furthermore, the foams did not show moisture uptake. These were indications that the chemical structure of the composites was not disrupted by the presence of fiber in comparison to the neat polyurethane foam. The cellulose fiber was probably not exposed to the environment on the pieces of foam because, in that case, moisture uptake would have occurred.

Density of the foams

The apparent density data for the foams (Table I) showed that incorporation of fiber in the 1–4% w/w range (composite foams RPF1, RPF3, and RPF4) did not lead to changes in the cellular material density. The composites obtained by increases in the fiber concentration in the range from 8 to 16% w/w (samples RPF8, RPF12, and RPF16) showed increases of 10–28% in the density value. A typical effect of the addition of vegetal fibers to the reaction mixture is an increase in viscosity. The filler can induce a decrease in the reactivity of the components in the system, affecting the foam expansion and increasing the density of the cellular materials.[16]

TABLE I
Average Density and Cell Average Diameter in the Vertical Direction for the Unfilled Matrix Foam and the Composite Foams

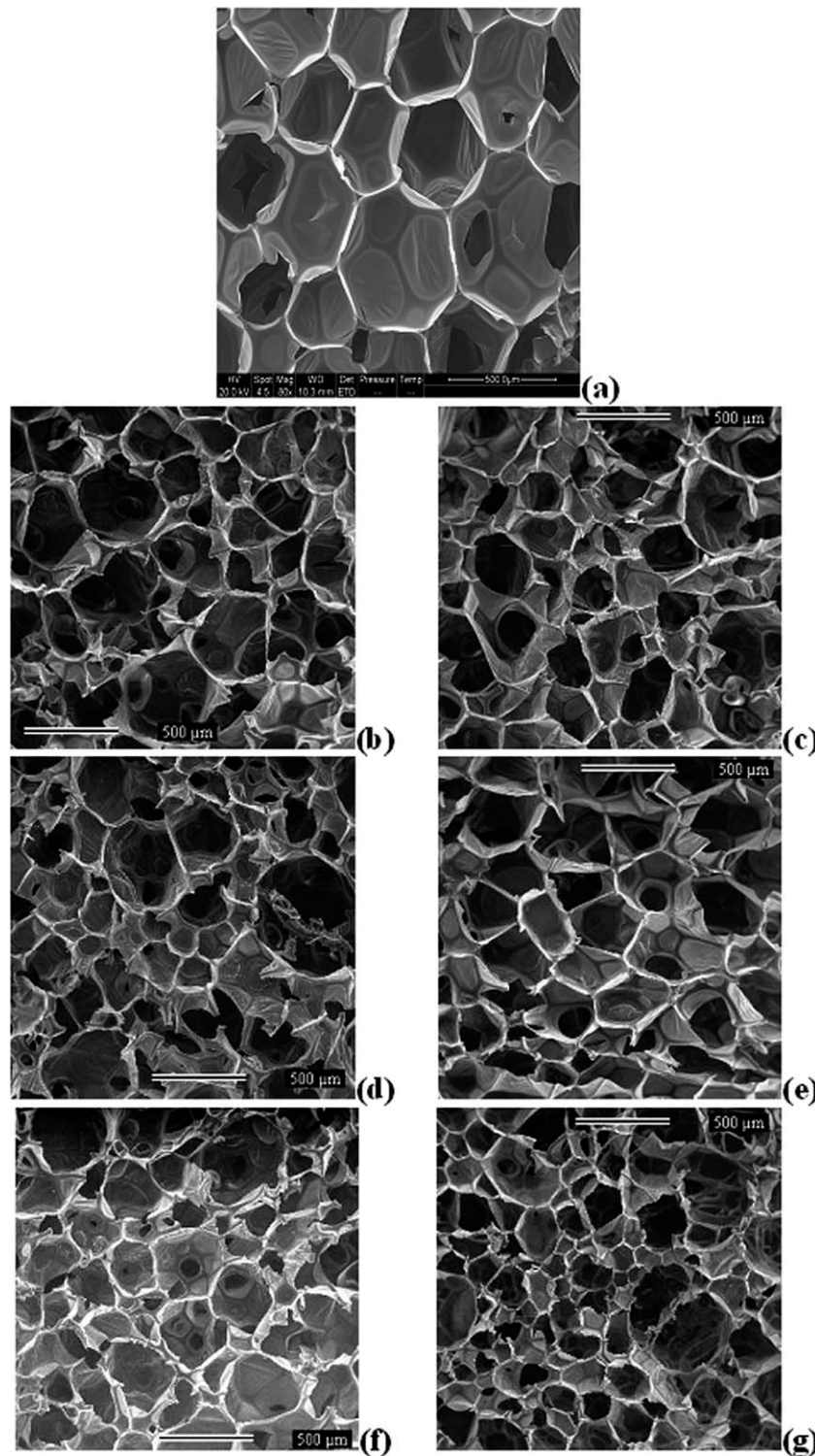| Sample	Average density (kg/m^3)	Cell average diameter (µm)
RPF0	29 ± 2	464 ± 126
RPF1	29 ± 2	348 ± 110
RPF3	27 ± 3	327 ± 89
RPF4	28 ± 2	342 ± 108
RPF8	32 ± 2	307 ± 96
RPF12	33 ± 2	368 ± 101
RPF16	37 ± 2	228 ± 81

Figure 2 SEM micrographs for the (a) matrix foam RF0 and the composite foams, (b) RPF1, (c) RPF3, (d) RPF4, (e) RPF8, (f) RPF12, and (g) RPF16 (the scale bar is 500 μm).

Morphological properties

The shape of the cells and the density of RPFs have, in general, a strong influence on their thermal and mechanical properties.[23,24] Foams constituted of isotropic cells have similar mechanical resistances in the horizontal and vertical directions, whereas those with anisotropic cells show higher mechanical resistance in the direction of growth.

Figure 2 presents SEM images for RPF0 and the composite foams, whereas the average diameters for the
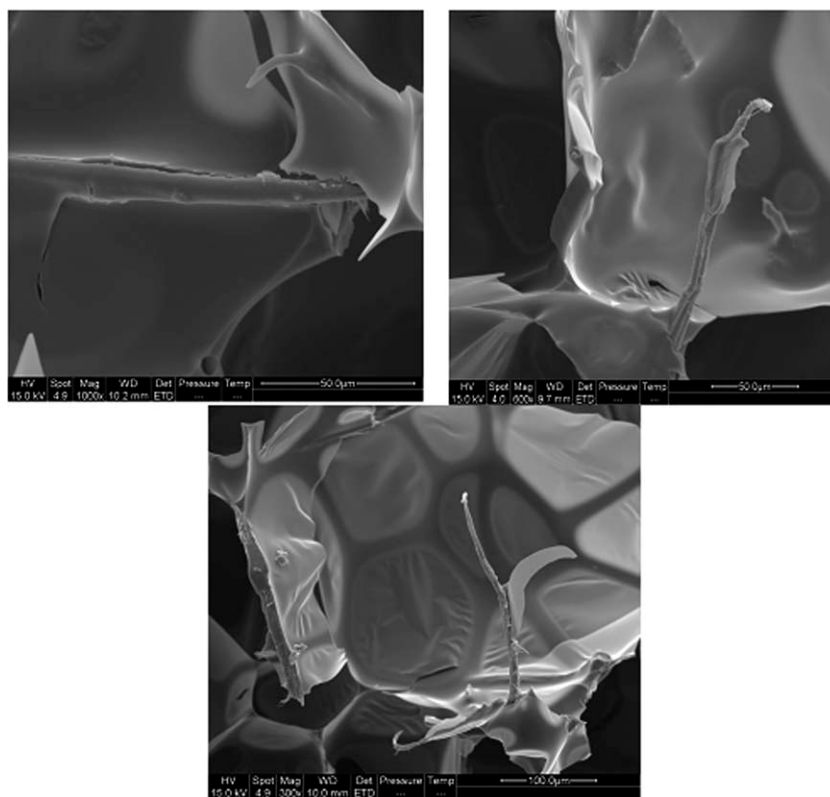
Figure 3 SEM micrographs of different fracture regions for the composite foam RPF16.

RPF cellular materials, in the direction of the growth of the foam, are shown in Table I. The SEM image of the foam matrix [Fig. 2(a)] indicated a slight anisotropic character for this foam. This characteristic was supported by the average vertical and horizontal diameters of the material, which were found to be around 464 $\pm$ 126 and 394 $\pm$ 93 μm, respectively. The introduction of the cellulose fibers into the composite foams did not alter the anisotropic characteristic of the foam, but the cells became more irregular and defective compared to those observed in the unfilled matrix foam, as illustrated in Figure 2(b–g). Table I shows that a reduction of about 30% in the average diameters of the cells was observed in the structure of the composite foams with the introduction of the fibers in the range 1–12% w/w (samples RPF1–RPF12). However, when the experimental errors were taken into account, the average diameter of the cells could be considered roughly similar. RPF16, shown in Figure 2(g), presented a smaller cell diameter, with a close to 50% reduction in the average diameter compared to the matrix foam.

Figure 3 shows the distribution of fibers in the structure of the composite foam for sample RPF16 in different areas of fracture. These micrographs clearly demonstrate that the cellulose fibers were distributed in the interior and in the borders of the cells recovered by the polymer. This observation was also related to the lack of identification of the absorption bands of cellulose by Fourier transform infrared spec-troscopy in the composite foams and the absence of moisture uptake by the foams from TG (Fig. 1). Independent and unattached fibers were not observed after fracture; this suggested the formation of good adhesion between the cellulose fiber and polyurethane.

Mechanical properties

The compressive modulus and compressive strength values at 10% deformation for the matrix foam and the composite foams are presented in Figure 4. From these results, we observed that the introduction of fibers in the processing of the RPFs promoted a decrease in the compressive strength in the range 1–8% w/w of the cellulose fiber to the content of polyol (samples RPF1–RPF8). A slight increase was observed when high contents, from 12 to 16% w/w, of the cellulose fiber (samples RPF12 and RPF16), were added. For the composites RPF1–RPF8, which had densities similar to the matrix foam, the decrease in the compressive strength was associated with the presence of defects in the materials caused by a change in the morphology and the presence of more irregular cells. On the other hand, for composites RPF12 and RPF16, the increase in compressive strength, compared with the other composites, was related to the density of these foams, as shown in Table I.
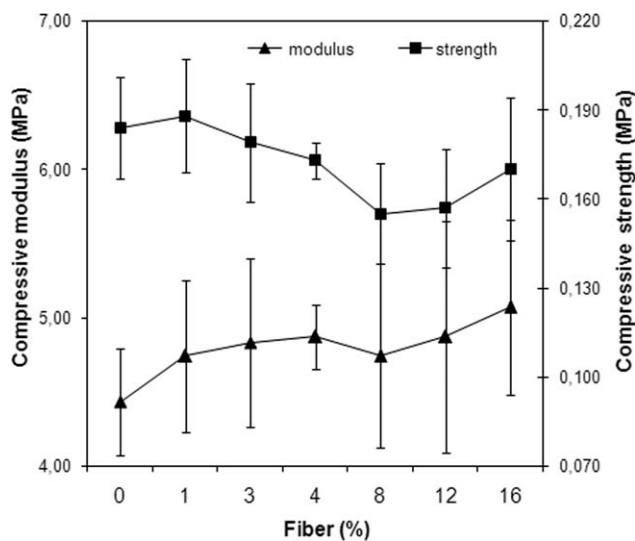
Figure 4 Effect of the fiber content on the compressive modulus and the compressive strength of the composite foams at 10% compression.

Figure 5 Thermal conductivity and cell average diameter in the vertical direction of the foam matrix and the corresponding composites as a function of fiber content.

Although the mechanical reinforcement of the cellulose-filled foams was not observed, the loss of compressive strength for these composites compared with the matrix foam was no greater than 7%. This was a satisfactory result, when we considered that the processing of the composites was more difficult in the presence of the fibers.

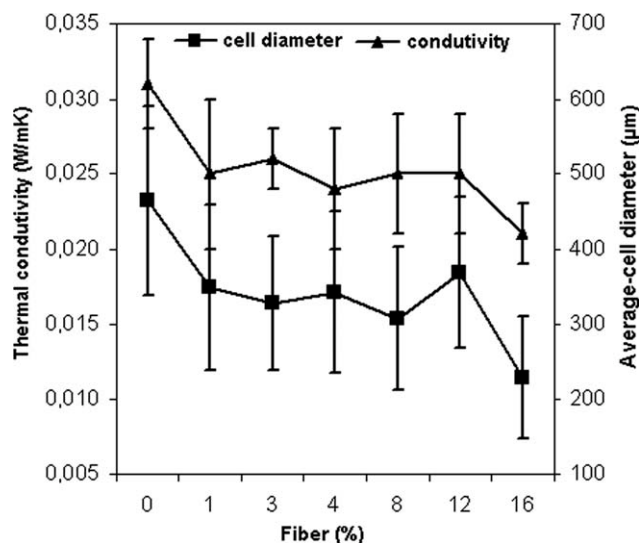On the other hand, an analysis of the modulus in the compression curve as a function of fiber content (Fig. 4) showed that the modulus of the composite foams tended to increase slightly compared with the matrix foam modulus. The stiffness enhancement was probably related to a higher rigidity of the foam solid phase due to the cellulose fiber contribution.

Thermal conductivity

The thermal conductivity of the materials as a function of the fiber concentration is presented in Figure 5(a). The addition of a very small amount of
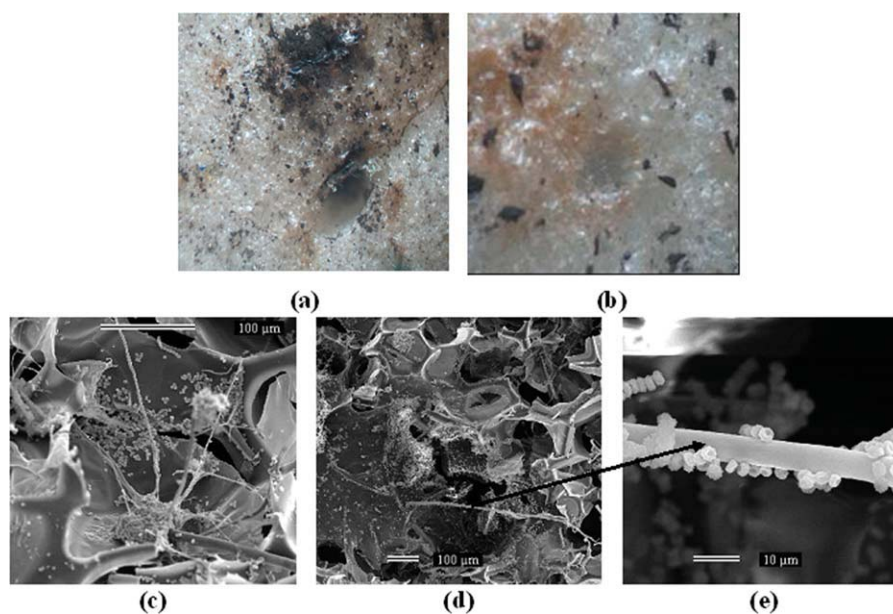

Figure 6 Optical microscopy images (120×) for the RPF16 foam: corresponding to the resistance to fungal attack test after 60 days with the (a) *A. niger* and (b) *R. oryzae* fungi and SEM micrographs corresponding to the resistance to fungal attack test after 60 days with the (c) *A. niger* and (d,e) *R. oryzae* fungi (the scale bar is 100 μm for images c and d and 10 μm for image e.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cellulose fibers (sample RPF1) induced a reduction in the thermal conductivity value by approximately 19% compared to that observed for the unfilled matrix foam. The decrease in the total thermal conductivity of the materials reached 32% for the RPF16 composite foam. This was a very interesting result because, usually, the application of RPFs as thermal insulating materials is favored by lower values of thermal conductivity.

The thermal conductivity of RPFs is influenced, among other factors, by their density, type of gases in their structure, and cell size.[25–27] Figure 5 shows the comparison of the thermal conductivity trend with variation of the average cell diameter in the vertical direction (data in Table I) as a function of the cellulose fiber content. The behavior of the two curves in Figure 5 was quite similar; this suggested that the average cell size had a strong influence on the total thermal conductivity of the composite materials, as observed in other similar studies.[4,24,28]

Resistance to fungal attack

Fungi have a vegetal body called a *talo* or *soma*, which is made of fine unicellular filaments named *hifas*. These hifas generally form a microscopic net near the substrate, which is called a *micelio*, from which the nutrients are absorbed. Although the matrix foam and all of the composites were tested, the results are discussed specifically for the composite with the highest cellulose fiber concentration (RPF16) in comparison with the matrix. This is because the experiment was a qualitative comparison, which was more informative in the case of the extreme compositions. For the same reason, only the results obtained with the fungi that induced stronger responses are discussed.

Figure 6 presents optical microscopy images corresponding to the assays of fungal after 60 days in a wet environment for the RPF16 foams containing *A. niger* [Fig. 6(a)] and *R. oryzae* [Fig. 6(b)] fungi at their surfaces. SEM images corresponding to the assays of fungal for the RPF16 foam are also shown in Figure 6. As shown in Figure 6(a,b), the formation of hifas agglomerates and the formation of a mass on the surface indicated the presence of micelios. The presence of hifas and the growing micelios in the foam cells was confirmed through electron microscopy images for the RPF16 foam containing *A. niger* [Fig. 6(c)] and the RPF16 foam containing *R. oryzae* [Fig. 6(d,e)]. For the matrix foam, after 60 days, fungal growth was not observed. Therefore, we concluded from this qualitative assessment that the sample containing the highest amount of cellulose fibers

(RPF16) was more susceptible to fungal attack than the matrix foam.

CONCLUSIONS

The introduction of cellulose industrial residue fibers in RPFs did not significantly alter the mechanical resistance and thermal stability of the composite foams. On the other hand, the thermal conductivity showed a small decrease. This set of properties indicates that typical applications, such as thermal insulating materials, should be considered for these materials. Moreover, the important result of this study is that these composite foams showed, because of the presence of cellulose fibers, a susceptibility to fungal attack in wet environments, which is a desirable attribute for decreasing the environmental impact after disposal.

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