Water-Blown Soy Polyol Based Polyurethane Foams Modified by Cellulosic Materials Obtained from Different Sources

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ABSTRACT: This article deals with the effect of cellulosic fiber from commercially available writing paper, bleached kraft pulp, and commercially available rice flour on the foaming of polyurethane based on polyol derived from soy bean oil. The presence of cellulosic materials was observed to have a notable influence on the density of the foams. Changes in the density of different foams were correlated with possible chemical structures generated in the presence of the fiber and were analyzed by Fourier transform infrared spectroscopy and thermogravimetric analysis. Furthermore, differential scanning calorimetry analysis was performed to lend support to possible changes in foaming behavior in the presence of refined fiber. Scanning electron microscopy observations were in line with the observation of structures generated in the presence of cellulosic fibers from different sources. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1974–1987, 2009

Key words: blowing agents; curing of polymers

INTRODUCTION

Soy polyurethane (SPU) foams are gradually gaining industrial importance for both economic and environmental reasons.[1–8] As documented in earlier communications,[3–6,8] soy-bean-oil-based polyurethane (PU) foams are produced via the reaction of soy polyol with an isocyanate (NCO). For water-blown PUs, foaming basically involves two basic reactions, where the NCO reacts with (1) polyol to generate the urethane linkage that leads to curing and (2) water to form urea and carbon dioxide, of which the latter expands the matrix polymer, that is

$$R-NCO + R'-OH \longrightarrow R-NH-COO-R' \quad (1)$$

$$2R-NCO + H_2O$$
$$\longrightarrow R-NH-CO-NH-R + CO_2^{\uparrow} \quad (2)$$
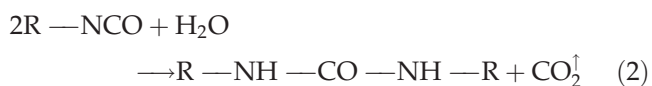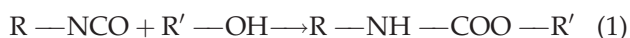
As mentioned earlier,[3–6,8] control of the previous two reactions offers ways to tailor the target morphology and the final properties of the foam. Catalysts, as well as the functionality and viscosity of the polyols, have been observed to have a considerable influence on the relative urethane and urea reactions and the final foam properties.[3] Recently,[4] a brief effect of a minute concentration of cellulose fiber from bleached kraft pulp (BKP) was reported on foaming. This study dealt with the modification of the properties of SPU foams with cheap, naturally available fibrous cellulosic materials (CMs), namely, commercial writing paper (WP), BKP, and rice flour (RF). Such modified foams may have applications in thermal insulation and other reinforced structures. Major studies have been done on foaming with fibers obtained from commercial WP. Kraft pulp has been used, in limited cases, to verify the observations made with fiber generated from paper. In addition, RF, a naturally abundant material, has been used to test its efficiency in the modification of the properties of SPU foams. In a previous study,[4] only a small concentration of minute fibers from kraft pulp was observed to lead to a considerable increase in the density of the foam, and the change in foam properties was understood to arise from the higher reactivity of the fiber at a small concentration. Higher fiber concentrations have not been considered then to prevent possible agglomeration effects,[9] which have been reported to deteriorate the beneficial properties obtainable at lower fiber levels. In this study, the effect of refined paper fiber at different concentrations on foam properties was verified.

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TABLE I
Formulation Used in the Foaming of SPU

Ingredient	Concentration (php)
Soy polyol	100.0
Water	2.0
Dabco-DC 5357	1.0
Dabco-T 12	0.4
Dabco-33 LV	0.4
Refined fiber/BKP/RF	0–8
RF	0–50
NCO index	Various

Similar attempts to modify the properties with paper have not yielded a notable change in the density of foams based on bifunctional polyol (BiSPUs), at lower NCO indices.

It was noted in a previous study[3] that the curing tendency of bifunctional polyol is lower than that of the trifunctional one. The reason was assigned to the lower hydroxyl number of the former, where the curing tendency is lowered. The main reason that we used RF was to see if it could modify the foaming behavior of the bifunctional soy polyol. Trifunctional polyol was also used to check the foaming characteristics compared to those of the bifunctional polyol. The chemical structures generated in the foaming process were analyzed by Fourier transform infrared (FTIR) measurements complemented by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) observations. Differential scanning calorimetry (DSC) analysis was used to determine the glass-transition temperature (T_g) of the different fiber-modified samples and correlated with the density changes of different foams.

EXPERIMENTAL

Materials

The trifunctional soy polyol, R3-170, was obtained from Urethane Soy Systems (Volga, SD). The hydroxyl number of the polyol was reported to be 170. The silicone surfactant, Dabco-DC 5357, and the tin and amine catalysts, Dabco T-12 and Dabco 33-LV, respectively, were procured from Air Products and Chemicals, Inc. (Allentown, PA). The role of these foaming ingredients have been reported in previous communications.[3–5] The aromatic diisocyanate, PAPI-27, was obtained from Woodbridge Foam Corp. (Ontario, Canada). It had a functionality of 2.7 and an equivalent weight of 134 g/equiv. To determine the effect of the cellulosic fiber on foaming, fibrous materials from Cannon-grade commercial WP, BKP, and commercially available RF were used.

A typical formulation with an NCO index of 120, as presented in Table I, was adopted to make a comparative study on the effect of paper fiber on the foaming process. The index here refers to the ratio of the equivalents of NCO to polyol used. For foaming with the bifunctional soy polyol, an index of 150 was used. The concentration of all ingredients was expressed in parts per hundred parts of polyol (php). The influence of the ingredients on foaming has been reported in earlier communications.[1–5] Different CMs, as mentioned previously, were identified by SEM and TGA measurements. Table II lists the TGA features of different CMs. WP was refined in a mechanical wood refiner with a Thomas–Willey laboratory mill (Philadelphia, PA). The fiber from BKP was obtained through refining in a Papirindustriens (PFI) refiner (Sweden) and used at different concentrations. RF was used as available without further processing. To prepare foams, polyol and all other ingredients were mixed in the required proportions under ambient conditions in a formable mold for 5 min, and then, the NCO was added and mixed for an additional minute. To see the effect of the refined fiber on foaming, WP was used at levels of 0.2, 1, 2, and 8 php, respectively. At the intermediate loading (5 php) of the fiber, the changes in the properties (e.g., density) of the foam were observed to be small. Although the influence of fiber from WP was mentioned in a recent communication, this article gives a more detailed analysis of the role of the fiber obtained from the paper. The time of stirring was observed to be important in affecting the changes in foam properties and varied from 5 to 20 min. As a prominent change was noted at a longer time of stirring (20 min), the same was maintained in this study when we processed foams with various levels of fiber from WP. However, for the control sample, a processing time higher than 5 min was observed to have no noticeable effect on the properties of the foam.[3] In the case of experiments with RF, the time of stirring was chosen to be 5 min. In this case, a higher time of mixing was observed to have no noticeable effect on the foam properties. For instance, the density of the foam obtained with 20 min of stirring was found to be around 440 kg/m^3, which was almost the same as that (437 kg/m^3) of the foam processed for 5 min. As no noticeable change in the foam properties was observed at a higher time (20 min) of mixing, a lower processing time (5 min) was followed for the RF-filled foam systems. Identical preparation conditions were followed for each system, and at least four foam samples

TABLE II
TGA Features of the Different CMs Used

CM	T_5 (°C)	T_{50} (°C)
WP fiber	231	354
BKP fiber	93	359
RF	124	314

were replicated for each experiment. To monitor the changes in the behavior of foaming, rise height (RH), which indicates the ease of foaming,[3] was used and noted 1 h after the gel point was recorded. To carry out the modification with RF, the level of RF was varied from 0 to 50 php. Wherever applicable, foams based on the bifunctional polyol are designated as BiSPU, whereas those based on the trifunctional polyol are designated as TriSPU.

Density

The apparent density of all of the foam samples was measured according to ASTM D 1621-94. At least three samples were considered for density measurements. The error in the measurement was ±5%.

Compressive strength (CS)

The CS values of the foam samples were measured, in limited cases, to verify the density changes in foams. CS was measured at a strain rate of 1.5 mm/min by a Zwick (Ulm, Germany) tensile tester in compression mode, according to ASTM method 1622-93. At least four samples were considered for each observation, and the error in measurement was ±10%.

FTIR analysis

To verify changes in the chemical composition of the foams in the presence and absence of fiber, FTIR measurements of the foam samples were carried out on the KBr pellets with a Bruker (Madison, WI) infrared spectrometer. The resolution of the spectra was 4 cm^{-1}, and 64 scans were recorded for signal averaging. We obtained a comparison of the spectral absorbances by constructing a base line and normalizing the absorbance of interest by dividing each absorbance by the phenyl absorption at 1602 cm^{-1}.[3–6] The apparent concentration of a functional group was expressed as the absorbance ratio, AR-x, where x denotes the absorption of a particular chemical functional group. The absorbance ratio of the urethane functionality, AR-1743,[3,4,6] was used to monitor the urethane reaction, whereas one related to AR-1664[3,4,6] was followed to check the blowing reaction. To describe the IR spectroscopic features, different foam samples were designated and are presented in Table III.

Gel fraction

Gel fraction measurement of the foam samples was performed to detect the solubility aspects of various foams. The process was carried through fraction measurements in the solvent toluene under ambient conditions and was expressed as the ratio of the weight of the dried sample after swelling and the swollen mass before swelling.

TABLE III
Designation of Different TriSPU Samples in the Presence and Absence of Fiber

Foam sample	System
0 php fiber, 5 min of stirring	S1
0 php fiber, 20 min of stirring	S2
0.2 php fiber, 20 min of stirring	S3
8 php fiber, 20 min of stirring	S4

SEM

The morphologies of the various foam samples were recorded with a Hitachi (Tokyo, Japan) S-2500 scanning electron microscope at a magnification of 400×. The void fraction of the foam was calculated from a knowledge of the density of the foamed and unfoamed sample with a relation reported in the literature.[10] The samples were fractured in liquid nitrogen and then coated with an alloy of gold and platinum with a sputter coater. The cell size and cell density were measured, the latter with the following relation:[10]

$$\text{Cell density} = (nM^2/A)^{3/2} \times \Phi \qquad (3)$$

where n is the number of bubbles in the micrograph, A is the area of the micrograph, M is the magnification factor of the micrograph, and Φ represents the expansion ratio. Φ is the ratio of the bulk density of the polymer to the measured density of the foam sample.

TGA

To complement the IR studies, TGA measurements were taken. They were carried out with a TA Instrument's (New Castle, DE) TGA analyzer (model Q 500) at a heating rate of 10°C/min in a nitrogen atmosphere. Decomposition temperatures of the foam samples at 5 and 50% weight loss (T_5 and T_{50}, respectively) were used to judge the thermal stability of the foam and correlate with the chemical structures detected by IR studies.

DSC

DSC studies were done to correlate the T_g values of different foams with density. The measurement was performed with TA Instrument's DSC analyzer (model Q 1000) at a heating rate of 10°C/min in a nitrogen environment over a temperature range of −80 to 140°C.

Wide-angle X-ray diffraction (XRD)

Wide-angle XRD was used to characterize the fiber through measurements of crystallinity. It was done with a Philips (Westborough, MA) X-ray diffractometer (model PW 1830) equipped with a scintillation
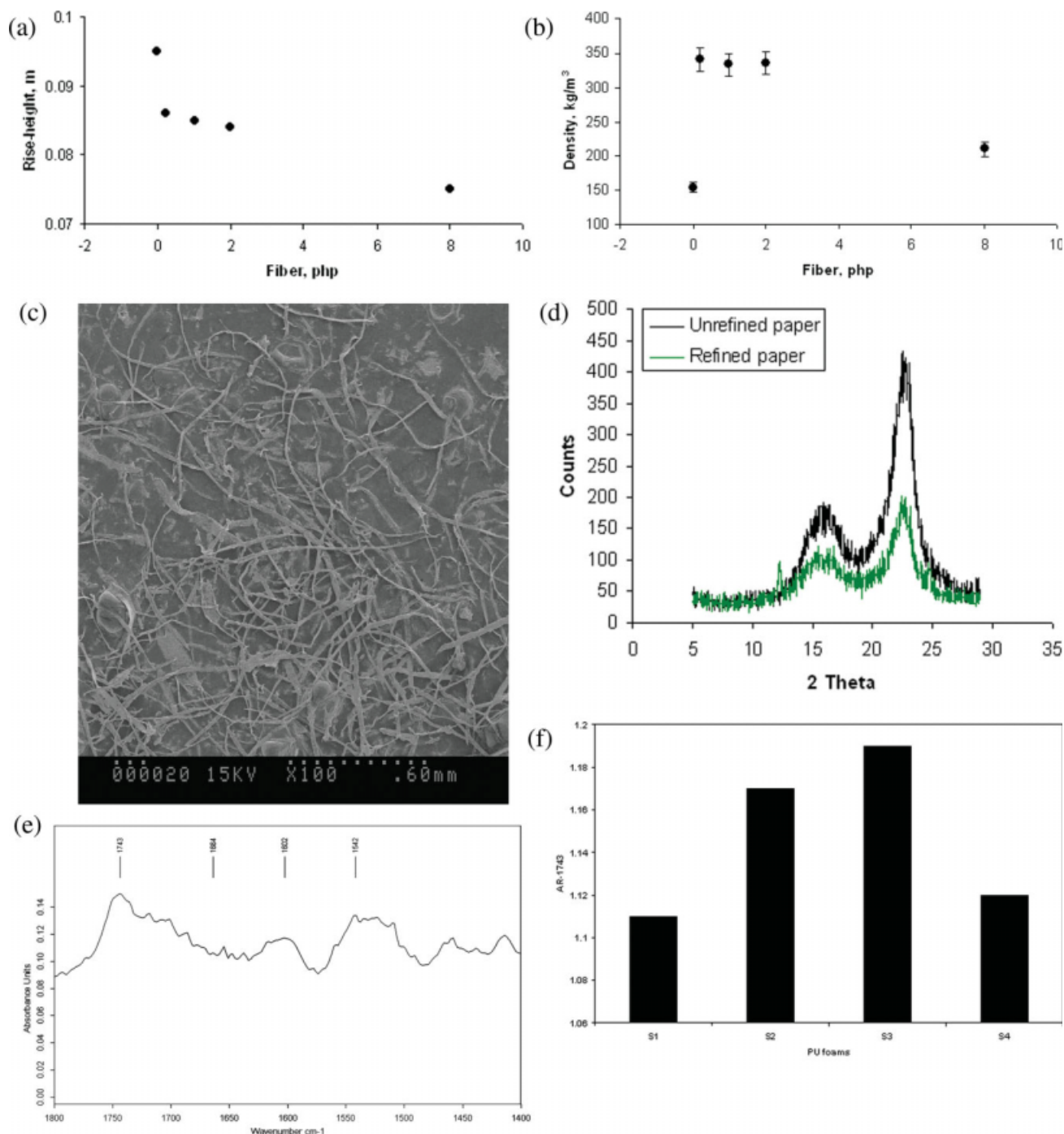
Figure 1 (a) RH of the TriSPUs at different levels of WP fiber, (b) density of the TriSPUs processed with various doses of refined fiber, (c) SEM micrograph of the refined paper fiber, (d) XRD patterns of the unrefined and refined paper, (e) typical IR spectra of an SPU foam, (f) variation in AR-1743 of the urethane group of the SPU foams mixed with different levels of the fiber, (g) variation in AR-1664 of the urea functionality of the PU foams based on soy polyol at various doses of the fiber, (h) CS of various TriSPUs, (i) gel fraction of the TriSPUs in the presence and absence of WP fiber, (j) typical TGA thermogram of a TriSPU, (k) DSC plot of a TriSPU, (l) SEM photograph of a TriSPU without fiber, (m) SEM picture of the TriSPU mixed with 0.2 php WP fiber, and (n) SEM micrograph of the TriSPU modified with 8 php fiber from WP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

counter. Diffraction intensities were recorded between 5 and 30° (2θ angle range). The crystallinity index (CI) was determined with the following relation:[11]

$$CI = [(I_c - I_a)/I_c] \times 100 \qquad (4)$$

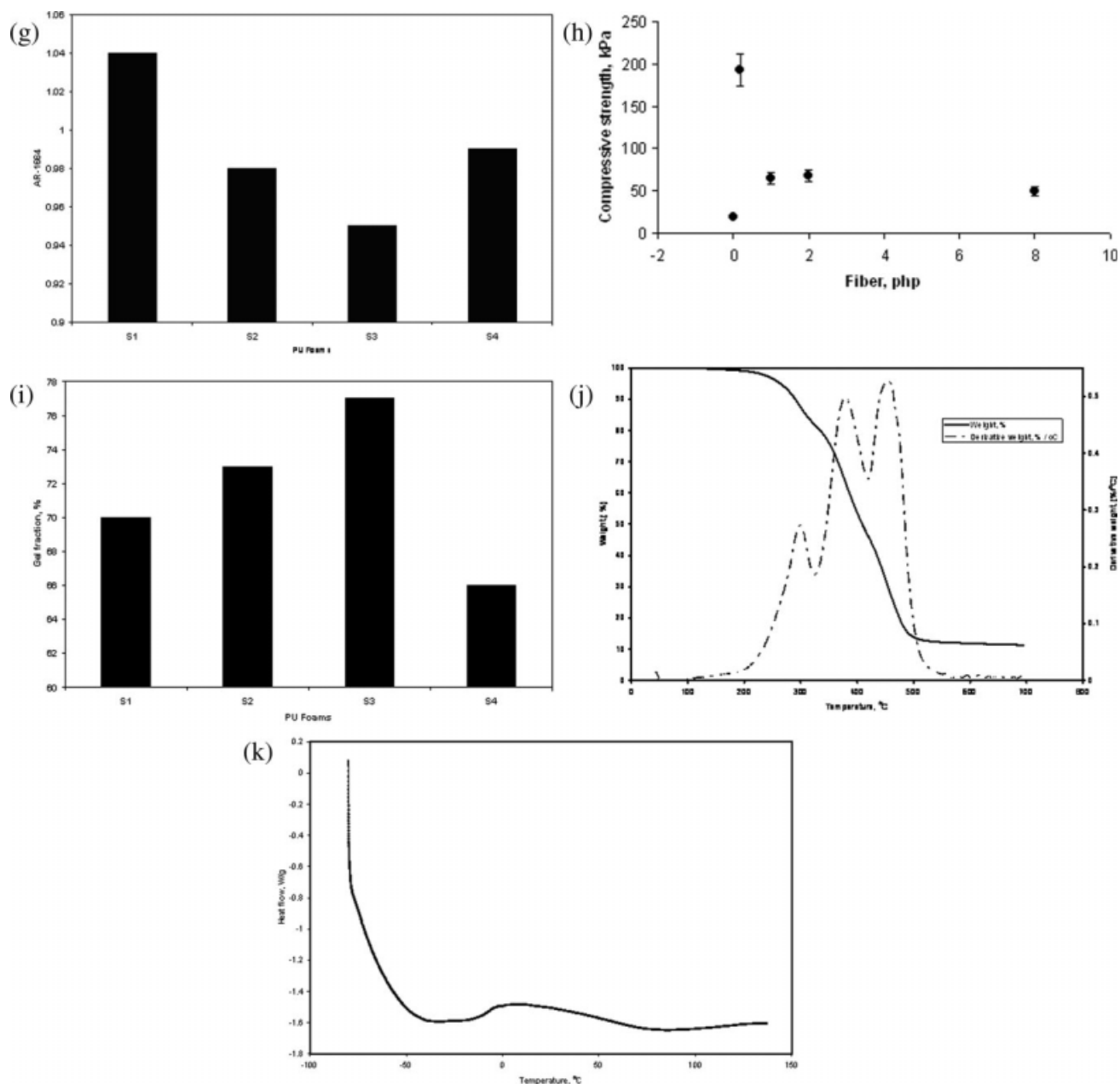where I_c and I_a denote the intensities of the crystalline and amorphous peaks, respectively.

Figure 1　(*Continued from the previous page*)

RESULTS AND DISCUSSION

Effect of the fiber from WP

Figure 1(a,b) shows the RH and density, respectively, of soy polyol based PU foam samples modified with refined paper fiber loaded at levels of 0, 0.2, 1, 2, and 8 php. The incorporation of refined fiber at a level of 0.2 php led to a large increase in the density of the foam. Thereafter, the foam density was observed to vary marginally and show a sharp drop at a very high concentration of the fiber used. On the other hand, RH showed a considerable drop at lower levels of fiber. However, at relatively higher levels of the fiber (8 php), the drop in RH was large.

This indicated an observed change in behavior of foaming in the presence of the refined fiber. The morphology of the refined fiber is presented in Figure 1(c). The dimension of the fiber was determined to be a few micrometers. Visible cells in the micrograph were related to the background. Although the foam density was observed to vary marginally at levels higher than 0.2 php, an increased resistance to stirring was noted, and the effect was observed to intensify gradually at fiber levels from 2 php. The XRD patterns of the unrefined and refined paper are depicted in Figure 1(d). The XRD curves revealed peaks close to 18 and 22°, which were characteristic of the amorphous and crystalline materials,
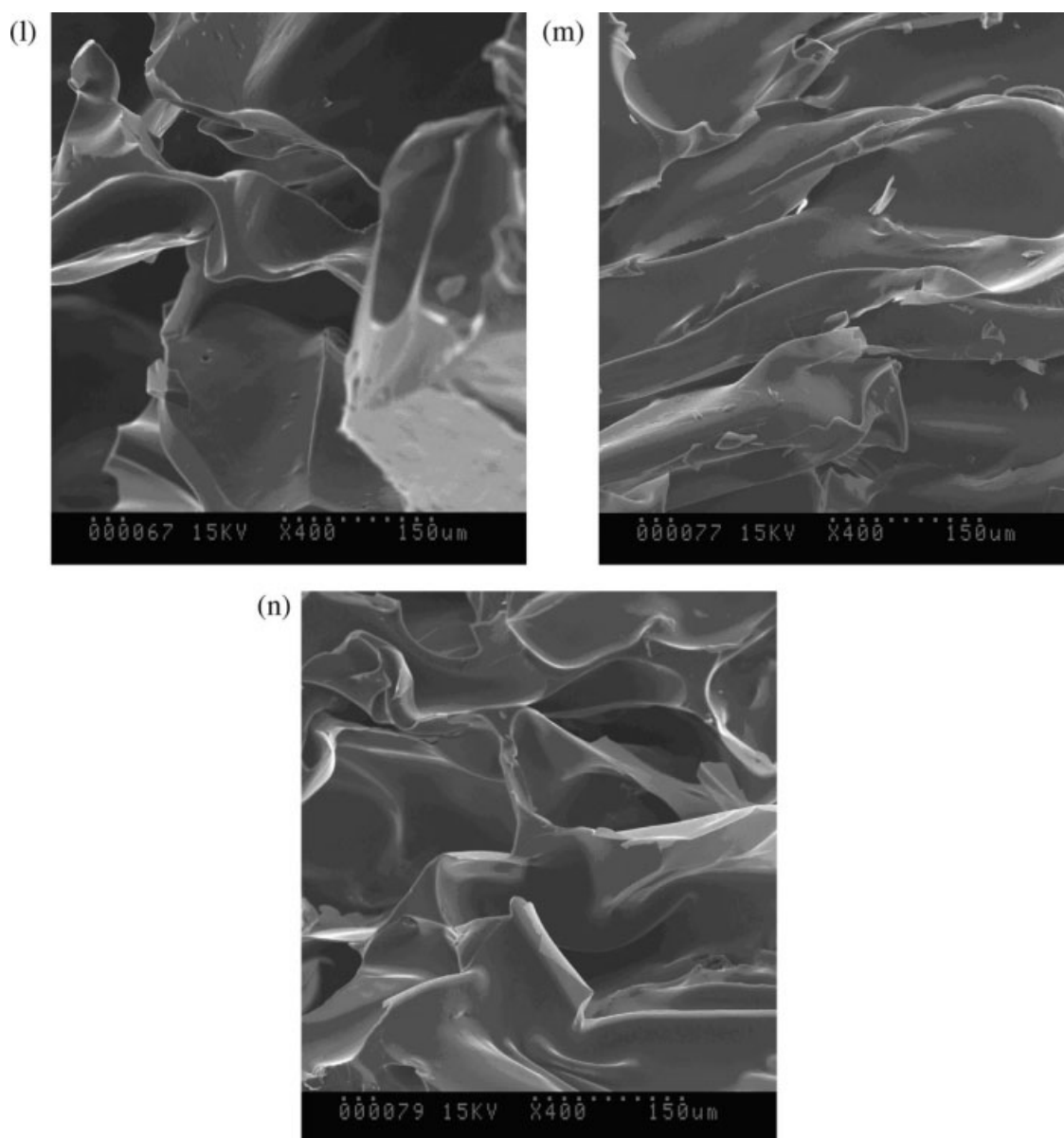
Figure 1 (*Continued from the previous page*)

respectively, of a cellulosic fiber.[11] The CI of the cellulosic fiber of the unrefined paper was calculated to be around 72%, and this was found to be reduced to nearly 54% on refining. Thus, refining was observed to reduce the crystallinity of the cellulosic fiber of the paper. Probably, the high shear force generated during refining damaged the crystalline portion of the fiber, which accounted for the observed loss in the crystallinity of the fiber. For clarity, the XRD curve of the refined fiber was not included with that of the unrefined material. A decrease in the crystallinity of alkali-treated natural fiber, resulting from the damage of the crystallites, was previously observed.[11]

To investigate the foaming behavior in the presence of fiber, IR spectroscopic studies were performed on different foam systems. Figure 1(e) shows the IR spectra of a TriSPU. The peak assignments were reported elsewhere.[3–7] The foams showed the presence of N—H bending absorption at 1542 cm^{-1}[7] and urethane and urea carbonyl absorptions at 1743 and 1664 cm^{-1}.[3–7] For simplicity, the curing tendency was mainly monitored by changes in the IR peak related to the urethane carbonyl functionality at 1743 cm^{-1}, whereas that corresponding to blowing by the urea carbonyl group was at 1664 cm^{-1}. Figure 1(f,g) denotes the variation in the absorbance ratios of the urethane and urea groups, AR-1743 and AR-1664, of different foam systems. With the incorporation of refined fiber at a small concentration of 0.2 php, there was a small increase in the apparent concentration of the urethane group accompanied by

a decrease in the absorbance ratio of the urea group. However, when a very high level of the fiber was used (8 php), the absorbance ratio of the urethane functionality was much reduced, whereas that corresponding to the urea group was raised compared to that of the foam mixed with a small concentration of the fiber (S3). For the latter, the increase was even higher than that in the system modified in the absence of fiber and processed for a longer stirring time (20 min, S2). These observations point to a possible change in the foaming behavior in the presence of the refined cellulosic fiber. As indicated in previous studies,[3,12] CMs have the possibility to modify a PU foam through hydroxyl functionalities present in the structure. The dimension of the fiber was found be a few micrometers. As the fibers were of small size and, therefore, of a high surface area, it appeared that the hydroxyl groups on the fiber surface somehow reacted with the NCO molecules to enhance the urethane formation. The reaction was possibly aided by an increased number of the hydroxyl groups on the fiber surface reacting with NCO functionalities achieved under agitation forces during processing, more so at longer mixing times. Because of this enhanced tendency toward curing, the blowing or expansion of the foam matrix was reduced, and this, then, led to the observed decrease in the RH of the foam mixed with small concentrations of fiber. This increased possibility of curing appeared to be responsible for the rise in the apparent density of the foam processed with lower concentrations of fiber. Reactive groups on the filler surface were previously reported to react with NCO and change the balance in an NCO–polyol reaction.[13] However, at high fiber levels, there are possible agglomeration effects,[9] which are expected to increase the viscosity of the foam system. As mentioned, the enhancement in the viscosity of the reaction mixture, particularly at fiber levels from 2 php, was indicated by an observed increase in the resistance to stirring. An increased viscosity of the foam reaction mixture was expected to decrease both the mobility and reactivity of the hydroxyl groups on the fiber surface during processing and to act as a barrier to curing reactions. This, then, accounted for the observed reduction in the urethane concentration of the foam system processed with a high level of the fiber (S4) used in this study. Because of this increased possibility of blowing, the sample S4 registered a reduced RH and apparent foam density. A decreased RH in this case was likely to be governed by the gelling reaction, involving formation of urea.[3,12] Intermolecular interactions of the filler with a PU foam[13] were previously reported to affect the final properties, such as density, of the PU foam.

Foaming behavior, as mentioned previously, was also verified by measurements of CS of the foam

samples. Figure 1(h) depicts the CS values of different fiber-modified SPU foam samples. The CS of fiber-modified samples was higher than that of the control sample, and the enhancement was sharp at a relatively low level (e.g., 0.2 php). A noted increase in the CS of foam samples pointed to a reduced tendency of blowing in the presence of fiber. As mentioned earlier, at levels higher than 0.2 php, probable agglomeration effects came into play, which hindered the reactivity of the fiber hydroxyl groups with the NCO molecules. Such an effect was noted in our previous studies.[9] At lower levels (0.2 php), molecules were free to move and caused possible enhancement in the state of curing through the reaction of the hydroxyl functionalities on the fiber surface with the NCO group. At levels higher than 0.2 php, probable agglomeration effects prevented the reaction of the hydroxyl groups of the fiber. As the formation of void structures were reduced, the increased rigidity of the system resulting from curing was indicated to explain sharp increase in the CS of the foam modified with fiber at a relatively lower level.

An indirect verification of the foaming reactions in the presence and absence of fiber was also obtained from gel fraction measurements. Figure 1(i) shows the variation of the gel fraction of different SPU foams. There was a considerable increase in the gel fraction of the sample incorporated with a low level (0.2 php) of fiber, but there was drop at higher levels of fiber. As indicated from IR studies, urethane formation was promoted with the addition of a small amount of fiber, which increased the degree of curing of the foam matrix. It was the formation of crosslinked network structures that enhanced the gel fraction of the foamed sample in the presence of a low level of fiber. However, at very high levels of fiber, possible urethane formation was hindered because of the agglomeration effects of the fiber. The blowing reaction was, then, understood to predominate over urethane formation and reduced the extent of curing. Because of this preponderance of the urea reaction over curing, the sample modified with a higher level of fiber registered a decrease in gel fraction. The incorporation of urea groups onto the backbone of PU polymer has been indicated to improve the solubility of PU.[14] Hence, the improved solubility of the foam matrix, due to the formation of urea groups, appeared to decrease the gel fraction of the samples, particularly at a high level of the fiber.

To complement IR observations, TGA measurements were taken on different foam samples. Figure 1(j) shows the typical TGA thermograms of the SPU foams. The thermal degradation features are presented in Table IV. As reported earlier[3,4,15] and as shown in Figure 1(j), the thermal decomposition of

TABLE IV
Thermal Degradation Features of Various SPU Foam Samples

SPU foam	T_5 (°C)	T_{50} (°C)
TriSPU, 0 php WP fiber, 5 min of stirring	276	408
TriSPU, 0.2 php WP fiber, 20 min of stirring	266	396
TriSPU, 1 php WP fiber, 20 min of stirring	267	395
TriSPU, 2 php WP fiber, 20 min of stirring	267	397
TriSPU, 8 php WP fiber, 20 min of stirring	268	397
TriSPU, 0 php BKP, 5 min of stirring	276	408
TriSPU, 0.5 php BKP, 20 min of stirring	258	405
BiSPU, 0 php RF	272	455
BiSPU, 10 php RF	248	452
BiSPU, 50 php RF	224	445
BiSPU, 50 php RF, 5 h dried	209	442
TriSPU, without RF	276	408
TriSPU, 50 php RF, 5 h dried	254	389

the foamed SPU polymer was characterized by multistage decomposition with the urethane bond decomposing around 260°C. The degradation temperature at 5% weight loss agreed more closely with the decomposition of the urethane bond.[3] Higher decomposition temperatures were reported to represent the decomposition of the polyol backbone. Both decomposition temperatures, T_5 and T_{50}, decreased with fiber loading of the foam, although the variation was small at different levels of fiber. This indicated a reduction in the thermal stability of the foam sample in the presence of fiber. The observed decrease in the thermal stability of the sample appeared to be in line with an increased extent of curing resulting from urethane formation. Urethanes have been reported to be thermally unstable, and this has also been verified in previous studies.[3,4,15] However, at high dosages of fiber, the foaming reactions were affected. As indicated earlier, this was understood to originate from an agglomeration effect at high fiber loadings, which was supported by an observed increase in resistance to stirring of the reaction mixture during processing. As curing was hindered, urethane formation was reduced. The blowing reaction, which led to the formation of urea, then predominated partly. This was also indicated

by a reduction in the apparent density of the foam, especially at high fiber levels. The urea group was observed to be thermally more stable than the urethane linkage.[3,4] Hence, despite the small variation in T_5 and T_{50} among the different fiber-modified foam samples, the formation of enhanced urea functionalities was indicated to be responsible for the marginal increase in the thermal stability of the foam at relatively high dosages of fiber.

To justify the effect of fiber on foaming, DSC analysis was carried out on the foam samples. Figure 1(k) depicts a typical DSC thermogram of an SPU foam. The transition temperatures, as observed from DSC analysis, are reported in Table V. The DSC trace showed two transitions,[7] the one at a lower temperature of −68.3°C was related to the β transition, and the other, at a higher temperature, corresponded to the primary transition or T_g at 51.9°C. The observed shifts were supported by the literature.[7] The β transition was reported to be related to the molecular motions within the polyol chain and other side groups on the polymer chain backbone. With the incorporation of fiber at a lower level of 0.2 php, the T_g shifted to a higher temperature. The observed shift was in line with an increased extent of curing, which resulted from the urethane reaction,

TABLE V
DSC Features of Various SPU Foam Samples

Sample	β-Transition (°C)	T_g (°C)
TriSPU, without fiber, 5 min of stirring	−68.3	51.9
TriSPU, 0.2 php fiber, 20 min of stirring	−73.6	56.2
TriSPU, 1 php fiber, 20 min of stirring	−71.2	51.9
TriSPU, 2 php fiber, 20 min of stirring	−72.7	51.8
TriSPU, 8 php fiber, 20 min of stirring	−72.8	48.8
BiSPU, without RF	−65.4	66.4
BiSPU, 50 php RF, 5 h dried	−61.8	66.6
TriSPU, without RF	−68.3	51.9
TriSPU, 50 php RF, 5 h dried	−65.3	59.6

TABLE VI
Cellular Characteristics of Different SPU Foam Systems

Sample	Cell size (µm)	Cell density (cells/m^3)
TriSPU, without fiber, 5 min of stirring	381	1.95×10^{24}
TriSPU, 0.2 php fiber, 20 min of stirring	85	0.11×10^{24}
TriSPU, 8 php fiber, 20 min of stirring	246	1.42×10^{24}
TriSPU, 0.5 php BKP fiber, 20 min of stirring	161	0.10×10^{24}
BiSPU, 0 php RF	307	1.95×10^{24}
BiSPU, 30 php RF	124	0.28×10^{24}
BiSPU, 50 php RF, 5 h dried	73	0.11×10^{24}
TriSPU, 50 php RF, 5 h dried	93	0.31×10^{24}

in the presence of fiber. The networking of polymer chains, which resulted from curing, provided a barrier to free segmental motions. This necessitated a higher temperature and caused inception of segmental rotation, which accounted for the higher T_g of the fiber-modified foam sample. However, other possible unknown intermolecular interactions of the foam matrix with the fiber[13] may have also restricted the movement of polymer chains and accounted for the observed enhancement in T_g. Cellulosic derivatives have been observed to modify the T_g of a PU foam.[12] The reason for the observed decrease in the β-transition temperature for the fiber-modified foam sample is not clearly known at this point. Probably, fiber modification led to conformational changes in the side groups of the polymer backbone,[8] which accounted for the noted change in the β-transition temperature. At very high loadings of the fiber used, T_g shifted to a lower value. The noted decrease in the primary transition appeared to match the reduced degree of networking, which resulted from a decreased extent of curing, as inferred from IR and TGA. However, a higher T_g of the control foam sample modified in the absence of fiber, as compared to one with a high level (8 php) of fiber, was possibly due to a greater amount of the hard urea phase, which resulted from a relatively increased blowing reaction for the former.

Finally, to correlate the TGA and DSC observations with the microstructure of the foams, SEM observations were made on a few selected foam systems. Figure 1(l–n), represents the morphologies of the foams modified in the presence and absence of fiber. The cellular parameters are reported in Table VI. The structure of the foam modified with 0.2 php fiber was relatively more dense, and the number of void structures generated was much lower than that of the foam without any fiber. However, when the fiber level was increased to 8 php, the morphology of the foam was more open, and the cellular structure approached that of the foam processed in the absence of fiber. The void fraction of the unmodified foam was around 78%, and this was reduced to nearly 50% in the presence of fiber at lower levels.

At a very high level of fiber used, the void fraction was raised to 69%, compared to that of the unmodified foam. Both cell size and cell density were reduced at the lower level (0.2 php) of fiber, beyond which there was an increase. As indicated by IR and thermal analysis, with the incorporation of fiber at a low level, the curing reactions were enhanced, and there was little room for the blowing reaction to occur. As the expansion of the polymer matrix was hindered in the presence of fiber, both the size and number of void structures formed were reduced; this led to the formation of a relatively rigid cellular structure. However, at very high levels of fiber, there was a barrier to the curing reaction because of an increased viscosity of the foaming mixture, which resulted from the possible agglomeration effects of the fiber. An enhanced viscosity of the reaction mixture was reported to affect foaming process.[13] As a result, foaming behavior at a very high level of fiber approached that of the foam system expanded in the absence of fiber. This led to increases in the size and number density of the void structure at the high level (8 php) of the fiber.

Effect of the fiber obtained from BKP

The purpose of using refined fiber from BKP was to verify the effects of fiber from paper on the foaming of PUs. A limited set of experiments was conducted to determine the foaming behavior in the presence of low dosages of refined BKP. The morphology of BKP fiber is presented in Figure 2(a). As with paper fiber, the dimension of the fiber was determined to be a few micrometers. XRD measurements yielded a CI of nearly 66. Figure 2(b,c) shows the influence of fiber on the density and RH of the foams at two fiber levels. Similar to the foaming in the presence of paper fiber, the density of the foam increased with a concomitant decrease in the RH of the foam in the presence of refined BKP at different fiber levels and at longer times of mixing. The observed results were in line with those obtained in the presence of fiber from WP and appeared to lend support to the fact that the tendency toward blowing was reduced in
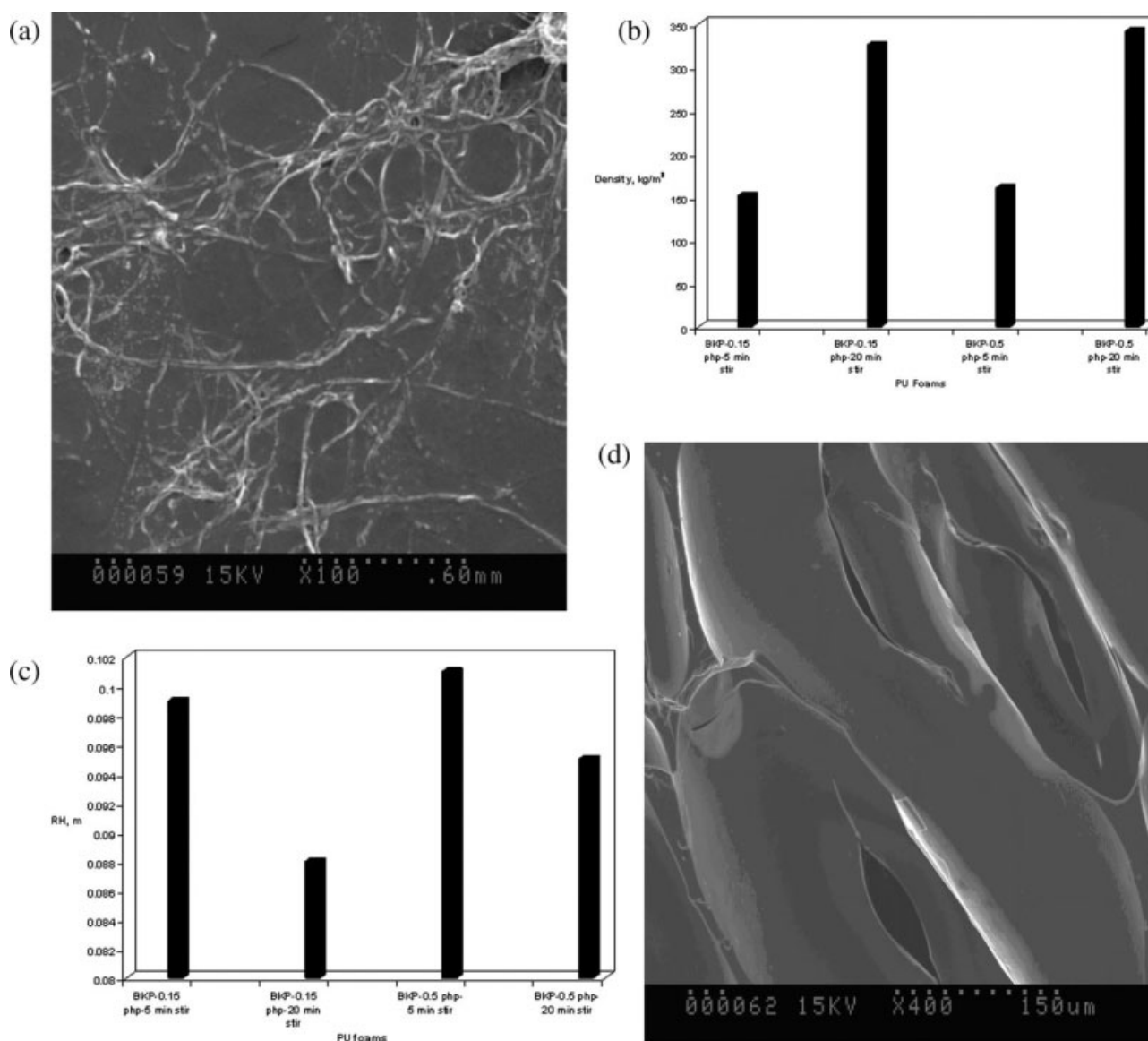
Figure 2 (a) SEM micrograph of the BKP fiber, (b) plot showing the density of different TRiSPUs modified with the BKP fiber, (c) RH of the TriSPUs mixed with different levels of BKP fiber, and (d) SEM picture of a TriSPU mixed with 0.5 php fiber from BKP.

the presence of refined fiber, more so at relatively lower levels of the fiber. A decrease in tendency toward the expansion of the polymer was expected to be accompanied by an enhancement in curing.

To justify the previous observations, TGA was chosen to complement and verify the foaming behavior in the presence of refined BKP. Table IV lists the thermal degradation features of the foam modified in the absence and presence of 0.5 php fiber, with the latter processed for a longer time (20 min). Once more, the degradation temperatures of the foam, particularly, T_5, was reduced considerably in the presence of fiber. The results indicate that BKP had a small influence on the higher degradation temperature (T_{50}). As indicated in the previous section, curing is generally accompanied by an

increased formation of urethanes, and urethanes have poor thermal stability.[4,5,15] Thus, the observed decrease in the thermal decomposition temperature of BKP-modified foam seemed to be in line with an increased tendency toward curing, which resulted in the formation of thermally unstable urethanes.

Furthermore, to verify the foaming behavior in the presence of BKP, SEM observations were performed. Figure 2(d) shows a representative SEM picture of the foam mixed with 0.5 php fiber for 20 min. Cell size and density are included in Table VI. On comparison with the micrograph in Figure 1(l) obtained in the absence of fiber, we observed that there was restricted blowing in case of the BKP-modified foam. Both cell size and cell density were reduced in the presence of fiber. An increased tendency toward
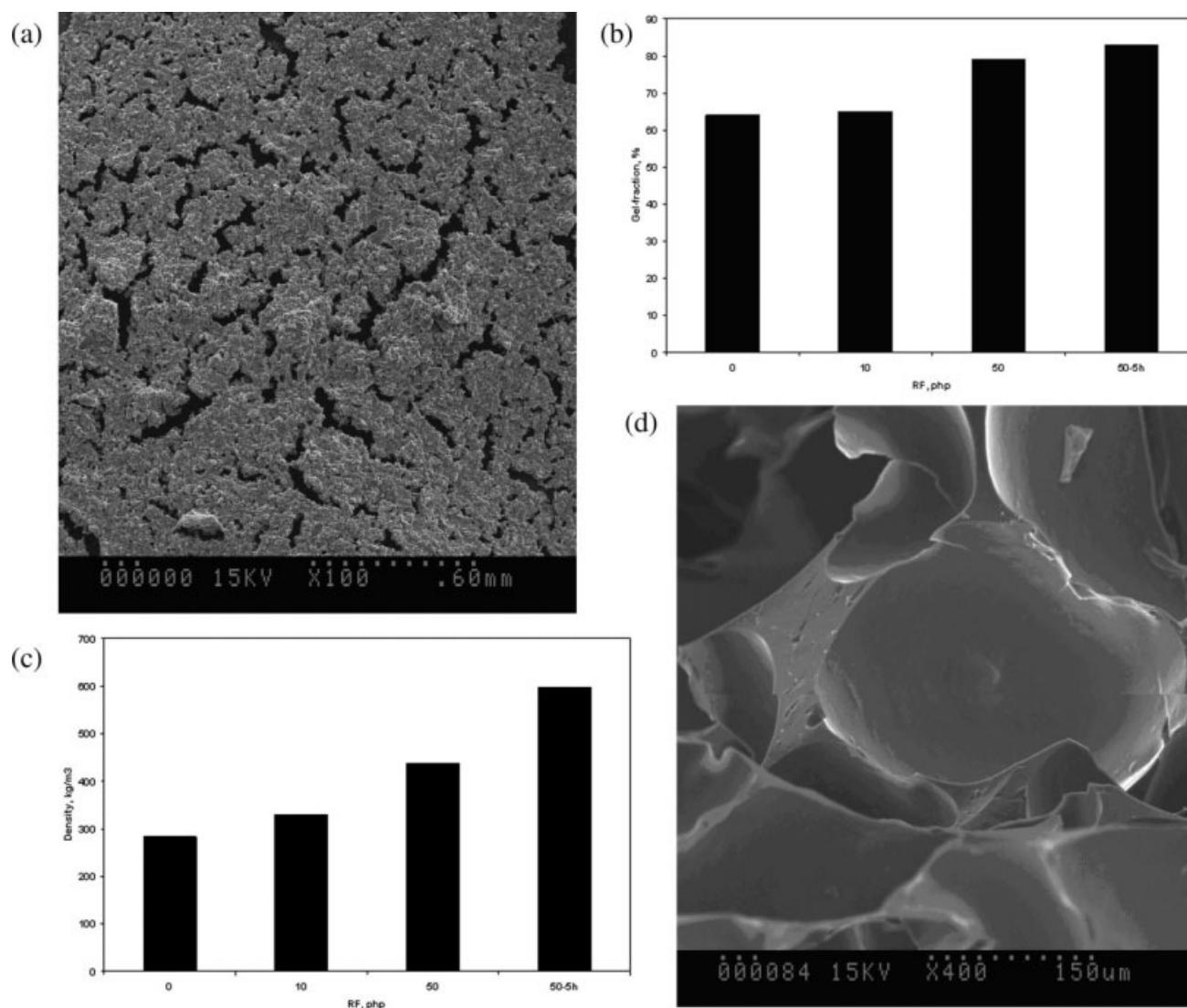
Figure 3 (a) SEM photograph of RF, (b) gel fraction of BiSPUs modified with RF, (c) variation in the density of BiSPUs modified with different levels of RF, (d) SEM photograph of a BiSPU without RF, (e) SEM micrograph of the BiSPU modified with 30 php RF, (f) SEM picture of the BiSPU mixed with 50 php RF and dried for 5 h, and (g) micrograph of the TriSPU modified with 50 php RF dried for 5 h.

curing in the presence of BKP was expected to lead to a reduced expansion of the polymer matrix, which was also consistent with the reduced void fraction of 0.50 in the presence of fiber from BKP. The reduced blowing tendency was also supported by a reduction in both the cell size and density.

Effect of RF on foaming

As indicated in the Experimental section, commercial RF, with and without drying, was used to study the modification of SPU foaming. Figure 3(a) depicts the SEM micrograph of RF. The picture shows an aggregated morphology of RF. A published report[16] revealed that RF has a considerable moisture content (∼ 9%) and contains chemical groups, such as carbo-

hydrates and proteins, bearing hydroxyl functionalities in their structure. Because of the presence of hydroxyl functionalities, it was of interest to determine whether RF could have any impact on PU foaming.

Figure 3(b,c) shows the influence of the level of RF on the density and gel fraction of the BiSPUs. Although the density of foam was increased with the level of RF, a large change was observed with the dosage of RF at the level of 50 php. Drying enhanced the density of the foam. The gel fraction of the samples showed a notable increase with RF at a level of 50 php. The RH of the system without RF was determined to be around 0.5 m, and this was reduced to 0.3 m for the foam mixed with 50 php RF. The results point to a possible reduction in
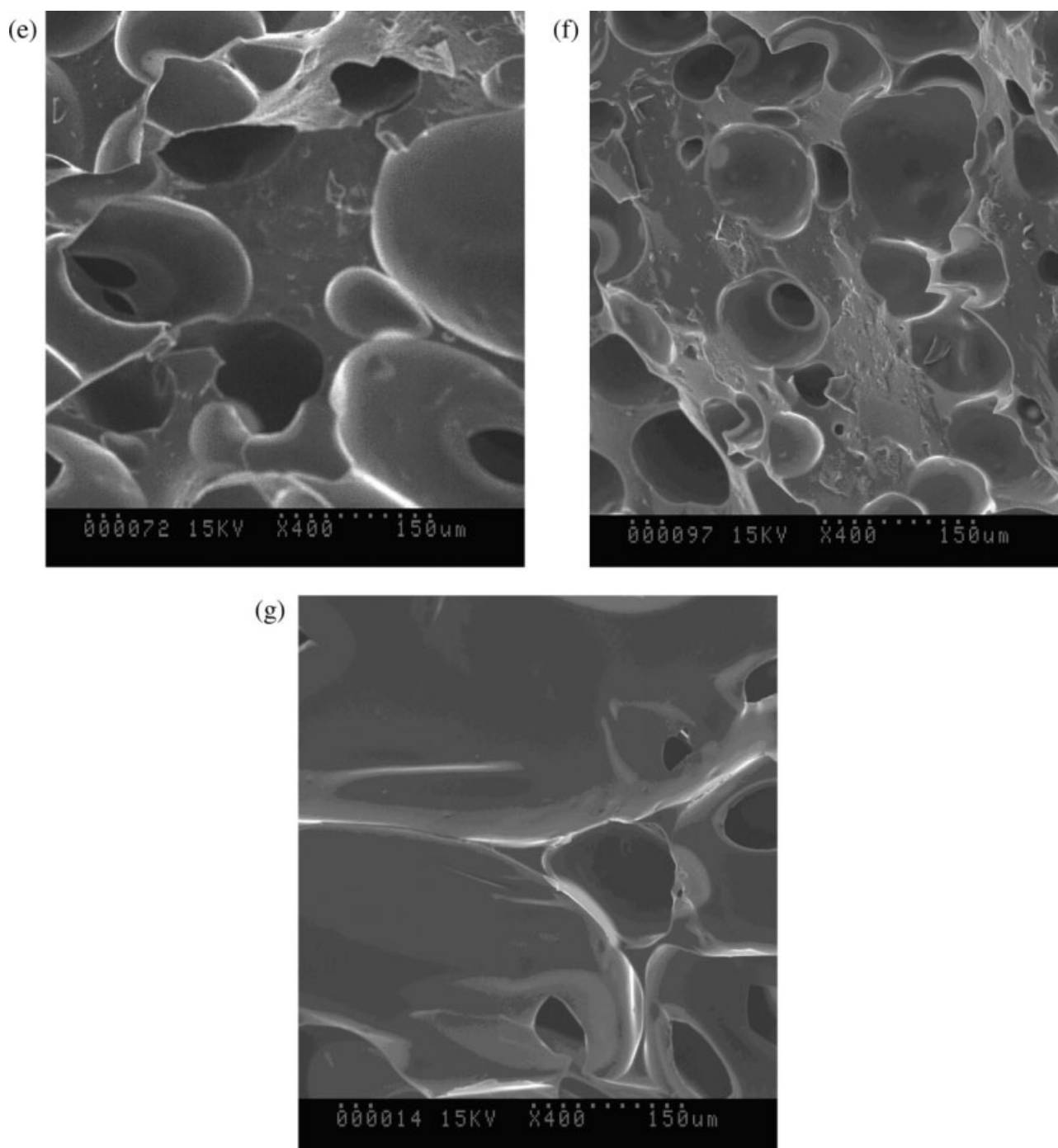
Figure 3 *(Continued from the previous page)*

foaming tendency in the presence of RF, more so at higher levels and after drying. It appears that the hydroxyl groups in RF acted to modify and enhance the curing reaction. As indicated by the results of the gel fraction measurements, probably the urea reaction, competing with the curing, led to relatively smaller changes in the density at intermediate levels of RF. However, at relatively higher levels of RF (50 php), a higher concentration of OH groups appeared to promote the curing reaction. The observed

increase in the curing and the resultant foam density after drying could be assigned to an enhanced urethane reaction. The increased curing tendency was also supported by a reduced RH in the foam system modified with RF at a level of 50 php. The moisture in RF was expected to increase the tendency toward the blowing reaction through its reaction with water. Hence, the drying of RF eliminated the bound moisture and reduced the blowing tendency further. The reduced tendency toward blowing was also

evidenced by an increase in the CS to 18.8 kPa from 6.5 kPa for the foam sample modified without RF. As mentioned earlier, a reduction of the void structure for the dried RF modified sample led to an increase in the CS of the product.

To complement the foaming behavior in the presence of RF, TGA observations were made on the BiSPU systems with and without RF. Table IV lists the degradation characteristics of RF-modified foam samples. Both T_5 and T_{50} were reduced with increasing level of RF. The decrease was sharper for the sample mixed with dried RF at a dosage of 50 php. The results point to the formation of a relatively rigid foam system generated through enhanced curing in the presence of RF. The formation of thermally unstable urethane groups reduced the thermal stability of the SPU foams in the presence of RF.

To verify the foaming behavior in the presence of RF, SEM observations were made at two selected samples in the absence and presence of RF, the latter at a level of 50 php. For the 50-php RF-filled system, dried RF was highlighted, as only at this level were large changes in the foam properties been observed. However, to check the cellular features at an intermediate level, a foam system mixed with 30 php RF was also considered. Figure 3(d–f) shows the SEM pictures of foam modified in the presence and absence of RF. The cellular characteristics of the foams are shown in Table VI. For the foam without any RF, cells were generated at random throughout the bulk of the foam matrix, which indicated a relatively enhanced expansion of the polymer. However, in the presence of RF, blowing was hindered, and the cell walls of the pore seemed to be relatively thicker than those of the foam without RF. In addition, at a very high level (50 php) of dried RF, the cells appeared to be shallow in nature and the void formation seemed to be restricted mainly to the surface of the foamed polymer. Again, cells size was decreased with the rise in level of RF, and the drop was sharp for the foam modified in the presence of dried RF at a dosage of 50 php. Cell density, on the other hand, decreased with a rise in RF dosage. The observed cellular features and the decrease in the cell size and the density appeared to result from the barrier to matrix expansion (blowing) in the presence of the filler as mentioned earlier. RF, particularly the dried material, made the foam system more rigid. On the basis of the results obtained and the reported features, it may be said that an enhanced curing tendency in the presence of RF led to the formation of a relatively rigid foam with a decreased tendency toward blowing. Cell walls of a rigid foam have been observed to be thicker.[10]

To further justify the foaming aspect, DSC analysis was performed on two foam samples in the absence and presence of RF, the latter with 50 php RF dried

TABLE VII
Density and RH of the TriSPU Foams With and Without RF

CM	Density (kg/m³)	RH (m)
TriSPU, without RF	151	0.095
TriSPU, 50 php RF, 5 h dried	284	0.040

for 5 h. The transition points are listed in Table V. The T_g of the fiber modified sample was slightly higher, and there was a notable increase in the β-transition temperature of the foam modified with dried RF. It appeared that, for BiSPUs, the RF modified the secondary (β) transition more than the primary glass-transition point. The observed increase in the transition temperatures seemed to be in line with the enhanced curing tendency of the foam in the presence of RF, which was expected to provide a barrier to the rotation of side chains/groups on the backbone of the polymer.

For comparison purposes, experiments were also conducted with RF on the foaming of PU derived from a trifunctional polyol. Foaming was performed in the presence of RF at a level of 50 php and dried for 5 h, as RF at this level has been observed to cause considerable changes in the density in case of BiSPUs. In both the cases, the time of mixing was fixed at 5 min. Table VII presents the density and RH of the two chosen systems. The density of the RF-filled system was enhanced compared to that of the foam sample in the absence of RF with a concomitant decrease in RH. As mentioned earlier, these features pointed to a reduced tendency toward foaming in the presence of RF at the expense of curing.

To verify the curing tendency in the presence of RF, TGA measurements were made on two systems. Table IV shows the thermal decomposition temperatures of the two systems. Both T_5 and T_{50} were reduced considerably in the presence of RF, which indicated the formation of a relatively rigid foam system. The formation of thermally unstable urethanes could account for such a rigid system generated in the presence of RF. To corroborate the TGA observation, DSC analysis was carried out on two systems, and the features are reported in Table V. There was a significant increase in both the primary and the secondary transition temperatures of the system modified with RF. The observed increase in the β- and α-transition points appeared to be in line with an increased extent of networking arising from the urethane reaction. To verify the morphology of the RF-filled system, microscopic measurement was carried out. Figure 3(g) shows the SEM morphology of a dried 50-php-filled TriSPU system. The cellular parameters are shown in Table VI. Compared to those of the system without any fiber, the cell size and density were decreased significantly. Reduced

void formations thus pointed to a possible decrease in the blowing tendency in the presence of RF.

CONCLUSIONS

The effects of different cellulosic fibrous materials on the foaming of PUs derived from soy bean oil based polyol were determined. In general, fiber was observed to have a considerable effect on the foaming behavior of SPU. The relative effect on curing and foaming was found to depend on the concentration and nature of the fiber material used. The properties of the foam were affected considerably in the presence of fiber. The presence of a relatively lower concentration of fiber led to an increased density and CS of the foam. However, for RF, such changes in the properties were noted at much higher levels of the fiber. Dried RF generated a relatively more rigid foam. A reduced tendency toward blowing was observed in the presence of fiber. On the basis of IR observations and thermal analysis, the noted change in the density of the foam was understood to arise from the modification of the foaming behavior through intermolecular interactions of the fiber. SEM observations were in line with the observations from IR and thermal analysis and agreed with the reduced expansion of the foam matrix in the presence of the fibrous materials used.

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