Glycols in Polyurethane Foam Formulations with a Starch–Oil Composite

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ABSTRACT: A dry starch–oil composite was blended with each of three glycols; ethylene, polyethylene, and propylene, and then reacted with isocyanate to produce polyurethane foams. The liquid glycols permitted the dry composite to blend well with the other ingredients in the foam formulations. Infrared spectra confirmed the presence of urethane structures in the composite–glycol foams. Polyethylene glycol provided a slightly less dense foam than the other glycols in the composite–glycol products. Microscopy showed a greater number of larger cells in the composite–polyurethane glycol foams. Infrared spectra indicated essentially no qualitative differences in the composite–glycol foams with the three glycols. By prestaining starch with toluidene blue and oil with sudan red, the location of the starch and oil components of the milled composite were observed in the composite–propylene glycol foam. Intact flakes of the composite were observed in the foam. An apparent loss of mobility of oil in the composite–polyurethane foam, as evidenced by NMR analysis, is probably due to crosslinking by isocyanate diffusing into the flakes. Both the cell structure and uniformity of blending were improved by using these glycols rather than the polyester polyol described previously.
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Key words: Fourier transform infrared spectroscopy; ethylene glycol; light microscopy; polyethylene glycol; propylene glycol; scanning electron microscopy

INTRODUCTION

The use of polymeric foam continues to grow rapidly throughout the world.[1] Some of the reasons for this growth are the light weight, excellent strength/weight ratio, superior insulating abilities, energy absorbing performance, and comfort features of the foams. The development of new foams continues. Most polymers can be used in foam making with a gas being introduced into the polymer matrix. It is imperative that the ingredients of the foam formulations be mixed adequately. With the use of dry materials, a compatible ingredient needs to be incorporated into the formulation to permit adequate mixing. An example of the use of dry materials in foam formulations is the drum-dried starch-oil composite,[2–5] which incorporates oil-soluble components and imparts biodegradability to foam products.[6] Drum drying is essential after jet cooking of this starch–oil composite, as excess water is not conducive to the preparation of urethane foams.

We previously described the properties of foams using polyester polyol and including the starch–oil composite. Uniform mixing of ingredi-

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Table I Ingredients in Foam Formulations[a]

Glycol			
Ethylene	Polyethylene	Propylene	Isocyanate[b]
15	0	0	78
0	15	0	44
0	0	15	66

[a] Ingredients are given in parts by weight. All formulations contained 20 parts Fantesk™ (m-f), 1.5 parts water, 2 parts surfactant, and 0.05 parts dibutyltin dilaurate catalyst.
[b] Quantity necessary to give an isocyanate index of 105.

ents was difficult, and cell structure deteriorated with increasing composite content. Therefore, we examined other materials with a lower viscosity as potential polyol reagents. Glycols were found to be excellent compounds in which to blend ingredients for mixing well with isocyanate in polyurethane formulations. Ethylene, polyethylene, and propylene glycols were used in this series of experiments. Glycols are compounds with two hydroxyl groups attached to separate carbon atoms in an aliphatic carbon chain.[7] These compounds are used in automotive, aviation, cosmetic, explosives, food, petroleum, pharmaceutical, surface coatings, textile, and other industries. These glycols with their diverse hydroxyl values were examined for their effect on cell structure by light and scanning electron microscopy. The density values of the foams were determined. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize these new foam formulations.

EXPERIMENTAL

Materials

The materials used in the foam formulations were dibutyltin dilaurate and ethylene glycol (Aldrich Chemical Company, Inc., Milwaukee, WI), polyethylene glycol, average mol wt. 200 and propylene glycol (Sigma Chemical Co., St. Louis, MO), DABCO DC 193 surfactant (Air Products and Chemicals, Inc., Allentown, PA), and polymeric isocyanate (PAPI 27, Dow Chemical Co., Laporte, TX). Fantesk™, a stable emulsion of epoxidized soy oil, water, and cornstarch, was produced at the National Center for Agricultural Utilization Research in Peoria, IL.

Preparation of Foams

Dry solids of the composite were determined by drying at 105°C for 2 h in a mechanical convection oven (model STM 135, Precision Scientific, Chicago, IL).

The hydroxyl values of the Fantesk™ were determined by Association of Official Analytical Chemists (AOAC) Methods 28.016-28.017 (American Oil Chemists' Society Method).[8]

Foams were prepared by adding polymeric isocyanate to a mixture of Fantesk,™ water, surfactant, glycol, and dibutyltin dilaurate. Formulations and descriptions of raw materials are given in Tables I and II. The quantity of isocyanate added in each formulation was dependent on available hydroxyl content. Four replicate foams of each formulation were prepared. The ingredients (without the isocyanate) were added in se-

Table II Description of Materials

Name	Description
Fantesk™	Jet-cooked composite of an emulsion of epoxidized soy oil, water and cornstarch
Ethylene glycol	1,2-Ethanediol $HOCH_2CH_2OH$ OH value, 1801
Polyethylene glycol	Av. mol. wt.: 200 $H(OCH_2CH_2)_nOH$, where n is greater than or equal to 4 OH value, 874
Propylene glycol	1,2-Propanodiol $CH_3CHOHCH_2OH$ OH value, 1474
DABCO DC 193 surfactant	Nonhydrolyzable silicone glycol copolymer
PAPI 27 Polymeric MDI	Diphenylmethane diisocyanate (containing methylene bisphenyl isocyanate) and polymethylene polyphenyl isocyanate
Dibutyltin dilaurate	Organotin compound

Table III Reaction Times and Densities of Foams

Glycol in Foam	Ethylene	Polyethylene	Propylene
Reaction profiles (s)			
Gel time	120	70	155
Rise time	255	160	355
Tack-free time	255	160	355
Apparent core density (kg/m^3)	62.1 ± 2.4	49.7 ± 8.5	64.4 ± 2.7

quence as listed above and mixed for 1 min at 11 Hz in a blender (model 5203 P1 with a 8051 Waring Blender adapter, Eberbach Corp., Ann Arbor, MI) equipped with a Fincor 5200 adjustable frequency ACD motor control (Eberbach Corp., Ann Arbor, MI). After addition of the isocyanate, the ingredients were mixed for 30 s at 11 Hz and then mixed with a spatula for 15 s. The contents were poured into wooden boxes (178 × 178 × 76 mm) and allowed to rise at ambient conditions. Foams were removed from the boxes after 2–3 h and allowed to cure at room temperature for 1 week before cutting into test specimens. Foams were cut into 1-inch cubes with a hand saw after all forming skins had been removed.

Apparent Core Density

Densities were determined by American Society for Testing and Materials (ASTM) D 1622-93, Standard Test Method for Apparent Density of Rigid Cellular Plastics. A manually operated dial-type gage having a foot with an area of 1.2 cm^2 was used for the measurements.

Nuclear Magnetic Resonance (NMR)

Polyurethane foams containing Fantesk™ were chopped into 0.5 mm-sized pieces using a razor blade. Spectra were recorded on a Bruker MSL-300 NMR instrument. The spectra were obtained employing all of the following techniques: Magic Angle Sample Spinning (MAS), cross polarization (CP), and high-power proton decoupling. The spinning speed was 3 kHz.

Fourier Transform Infrared Spectroscopy (FTIR)

Prior to FTIR analysis, all foam samples were dried under vacuum at 30°C for 24 h. Test specimens were ground, mixed with KBr, and pressed into transparent KBr disks. This was accomplished by pulverizing 5.0 mg of specimen for 3 min at liquid nitrogen temperature in a stainless-steel vial containing two stainless-steel ball-bearings on a mixer mill (Brinkmann Instruments

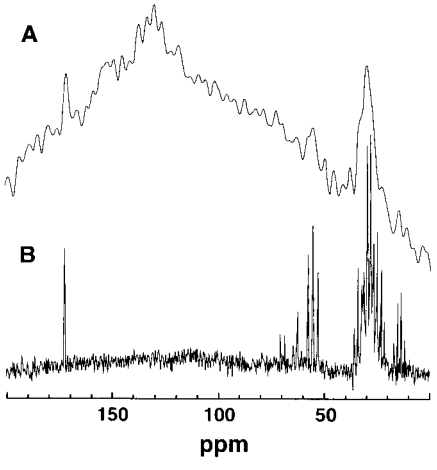

Figure 1 Nuclear Magnetic Resonance (NMR) Block decay (BD) without proton decoupling C-13 spectra (A) for polyurethane foam containing glycol and Fantesk™ and (B) for Fantesk™ alone.

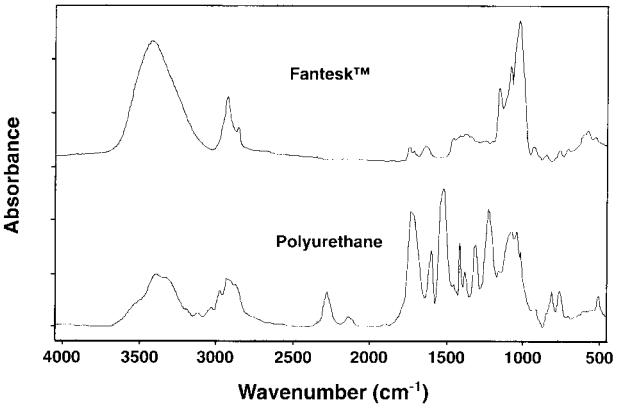

Figure 2 Fourier Transform Infrared Spectrometric Analysis (FTIR) spectra of Fantesk,™ starch–oil composite, and a polyurethane control foam.

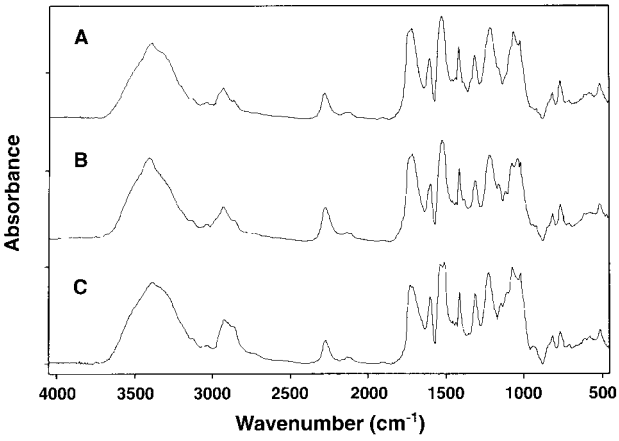

Figure 3 Fourier Transform Infrared Spectrometric Analysis (FTIR) spectra of foams prepared from Fantesk™ and glycols (A) ethylene, (B) polyethylene, and (C) propylene.

Inc., Subsidiary of Sybron Corp., Westbury, NY). After warming to ambient temperature, 95.0 mg of spectral grade KBr (Spectra-Tech Inc., Samford, CT) was added to the vial. All weighings and transfers of specimens were done in a dry box to prevent moisture absorption by the hygroscopic KBr. The specimen in KBr was then pulverized on the amalgamator (Wig-L-Bug, Crescent Dental Mfg. Co., Lyons, IL) for 60 s at liquid nitrogen temperature in the same vial. At ambient temperature, 25 mg of the pulverized KBr mixture was diluted to 750 mg in KBr and mixed without the stainless-steel balls on the amalgamator. Finally, 300 mg of the pulverized KBr mixture was transferred in the dry box to a 13-mm KBr die (Perkin-Elmer Corp., Analytical Instruments, Norwalk, CT), and the die was evacuated for 5 min before pressing *in vacuo* at 110 MPa on a laboratory press (Fred S. Carver, Menomonee Falls, WI). Infrared spectra were measured on an FTIR spectrometer (Model RFX-75, KVB- Analect, Irvine, CA) equipped with a TGS detector. Interferograms were processed on an APT-824 array processor using triangular apodization for linear response. Spectra were acquired at 4 cm^{-1}, resolution and signal averaged over 32 scans with no zero filling. The interferometer and specimen chambers were purged with dry nitrogen to remove spectral interference from water vapor and carbon dioxide.

Light Microscopy

Thin sections of foam were cut by hand with a No. 11 stainless-steel scalpel blade. Sections from 0.3 to 0.5 mm in thickness were selected because they contained enough material to prevent disintegration while allowing visualization of the cell struc-

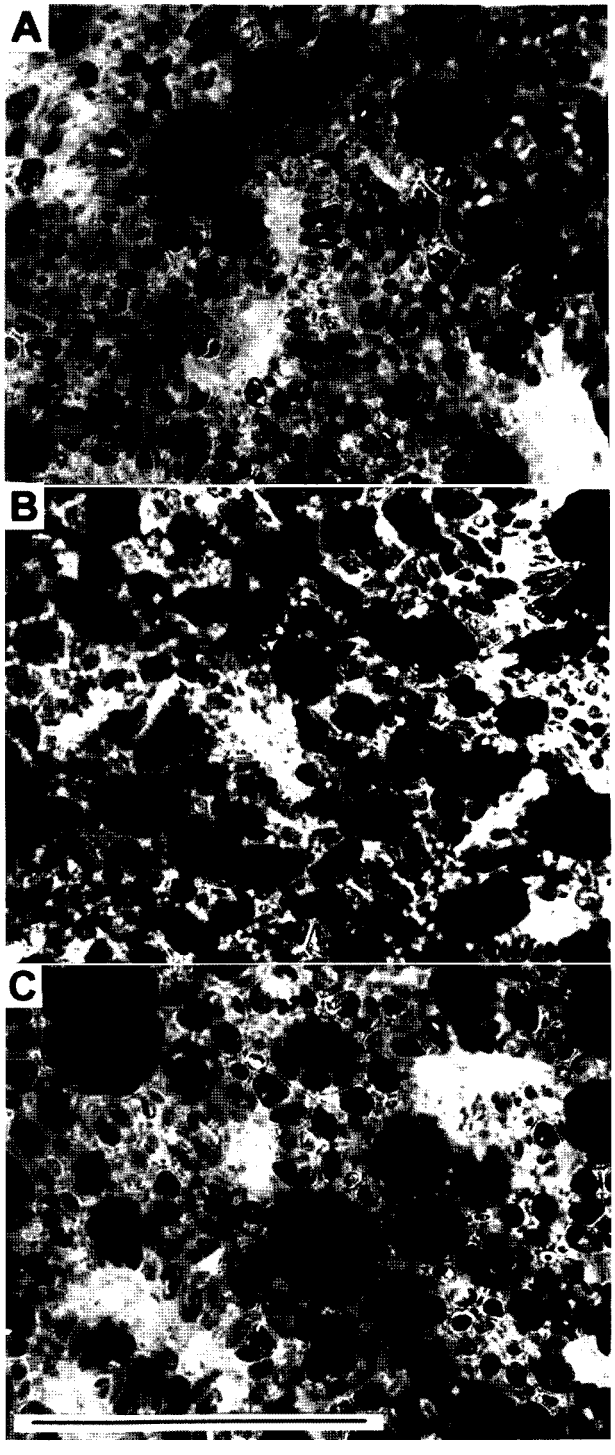

Figure 4 Light micrographs of thin sections of foams prepared with (A) ethylene, (B) polyethylene, and (C) propylene glycols. Bar represents 1 mm.

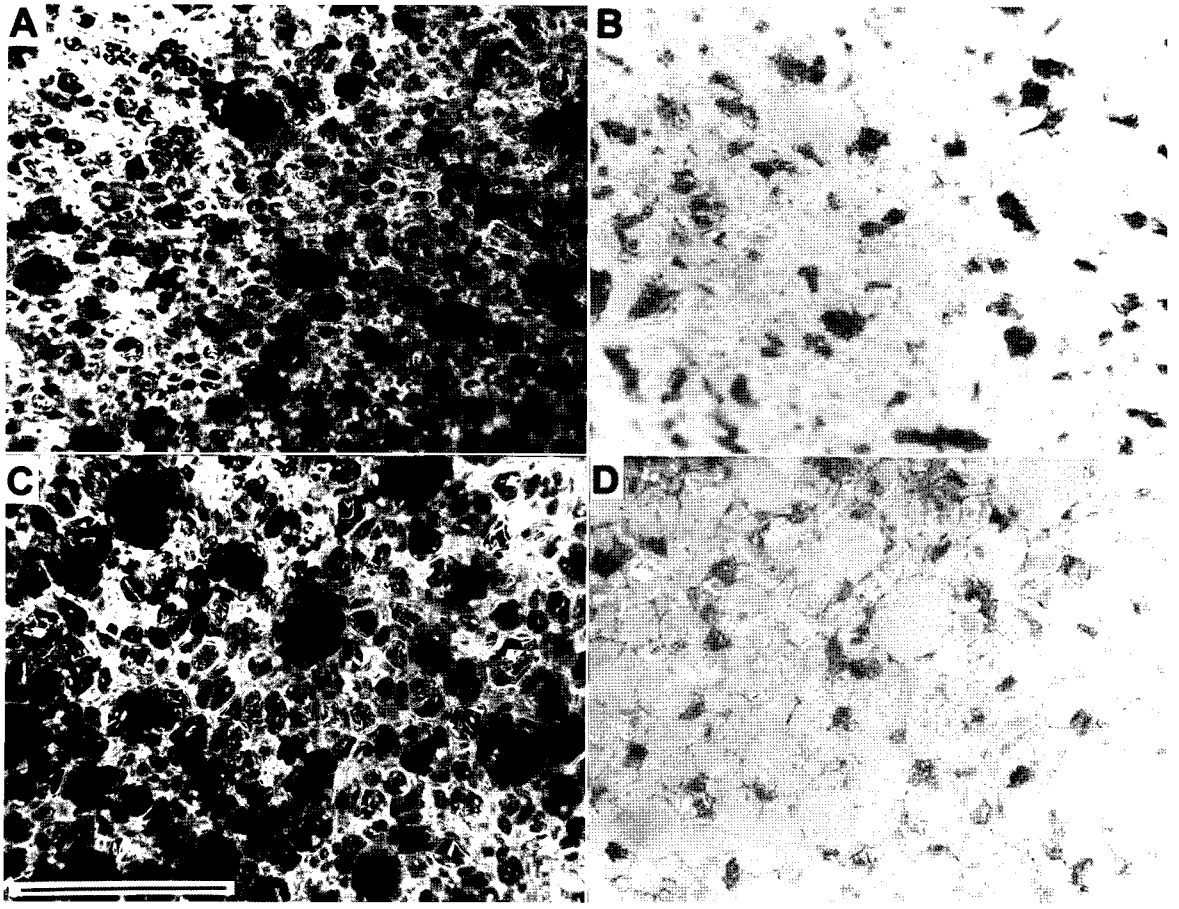

Figure 5 Light micrographs of foams containing Fantesk™ stained with (A,B) toluidene blue and (C,D) sudan red. B and D show the same foam sections as A and C, but photographed against a white background to selectively view the stained material. Bar represents 1 mm.

ture. Sections were positioned on a pair of hairs stretched across the opening of a dark chamber and illuminated from above with a Schott fiber optic ring illuminator. Photographs were made through a Zeiss stereo microscope.

To visualize the location of starch and oil components from the milled Fantesk,™ two types of stained foams were prepared using propylene glycol. One was made with Fantesk™ stained with toluidene blue by making the initial starch slurry in aqueous 1% toluidene blue, then adding epoxidized soy oil, jet cooking, drum drying, and milling. This dye stained only the starch component of the dry Fantesk™ flakes. Another foam was made with Fantesk™ in which the oil was stained to saturation with sudan red (a water-insoluble, oil-soluble dye) prior to jet cooking. Foam sections were photographed both with a dark background to visualize the foam cell structure and against a white background to allow selective visualization of the stained material.

Light micrographs of Fantesk™ flakes in the thinnest foam sections obtainable were taken with a Zeiss Axioskop transmitted light microscope using dry sections and bright field.

Scanning Electron Microscopy (SEM)

Specimens were mounted on aluminum stubs using double-sided carbon tape and were coated with gold–palladium (60 : 40) to a thickness of about 0.015 micron in a sputter coater. The coated specimens were observed in a SEM (model JSM-6400, JEOL Inc., Peabody, MA) at a specimen angle of 0°. Accelerating voltage was 10 kV, and final aperture was 200 microns.

Figure 6 Bright-field light micrograph of a Fantesk flake in a propylene glycol foam. Bar represents 0.1 mm.

RESULTS AND DISCUSSION

General

Compared with previous work with polyester polyol, Fantesk™ flakes could be very easily and quickly blended into the glycols, presumably due to the lower viscosity and hydrophilic nature of the glycols. The starch–oil composites had hydroxyl values of 99 and 116. The reaction of isocyanates with hydroxyl containing compounds to form urethanes is the most important reaction commercially.

Reaction Times and Densities of Foams

Foams containing polyethylene glycol were faster in their reaction times than those foams containing either ethylene or propylene glycol (Table III). Gel times and rise times occurred two times faster for these foams. Tack-free times were the same as the rise times for all of these foams. The apparent core densities of the foams containing polyethylene glycol were lower (50 kg/m^3) but with more variability than those containing the same quantities of either ethylene or propylene glycol (62–64 kg/m^3).

NMR Analysis

The NMR spectra show the Fantesk™ alone and incorporated into polyurethane foam (Fig. 1). The spectrum of Fantesk™ (B) is typical of the high mobility of unrestricted aliphatic chains such as could be present in oil droplets. The broadening of the peaks (A) shows the loss of mobility of the oil after incorporation into the polyurethane foam. This strongly suggests that the isocyanate diffused into the Fantesk™ flakes and crosslinked some of the epoxidized oil.

FTIR Analysis

Formation of polyurethane in the foams was established by FTIR spectroscopy. FTIR analysis also provided estimates of carbodiimide and unreacted isocyanate in the Fantesk™–polyurethane foams and provided a better understanding of the influence of the glycols and process variables. The FTIR spectrum of the starch–oil composite, Fantesk™, is compared with the spectrum of a polyurethane control sample made with a commercial polyol in Figure 2. Major differences appear, as expected, in the hydroxyl (3350 cm^{-1}), carbonyl (1730 cm^{-1}), and phenyl (1600 cm^{-1}) absorbance regions. Differences due to unreacted isocyanate (2270 cm^{-1}) and carbodiimide (2135 cm^{-1}) byproduct appear in the polyurethane spectrum. A large excess of isocyanate was used in the polyurethane preparation. It can be seen in Figure 2 that the urethane band at 1730 cm^{-1} is much stronger than the relatively weak ester band at the same frequency from the oil in Fantesk.™ In contrast, the hydroxyl band at 3350 cm^{-1} due to starch is relatively stronger in Fantesk™ than in polyurethane. FTIR spectra of foams prepared from Fantesk™ and the glycols are shown in Figure 3. The three spectra are of foams prepared from (A) ethylene glycol, (B) polyethylene glycol, and (C) propylene glycol. Little, if any, qualitative difference exist between the three foams by this analysis. All of the Fantesk™ and polyurethane spectral features are clearly evident in each foam. Also, the relative amounts of unreacted isocyanate and carbodiimide byproduct appear similar in each foam. Not surprisingly, there appears to be a significant quantitative difference between the foams only in the relative amounts of methylene absorbance at 2930 cm^{-1}. The spectra of the Fantesk™–polyurethane foams in Figure 3 all show relatively more hydroxyl (3350 cm^{-1}) and C—O (1020 cm^{-1}) absorbance than the polyurethane control in Figure 2, due to the starch content in Fantesk.™

Evidence of urethane crosslinks from reaction

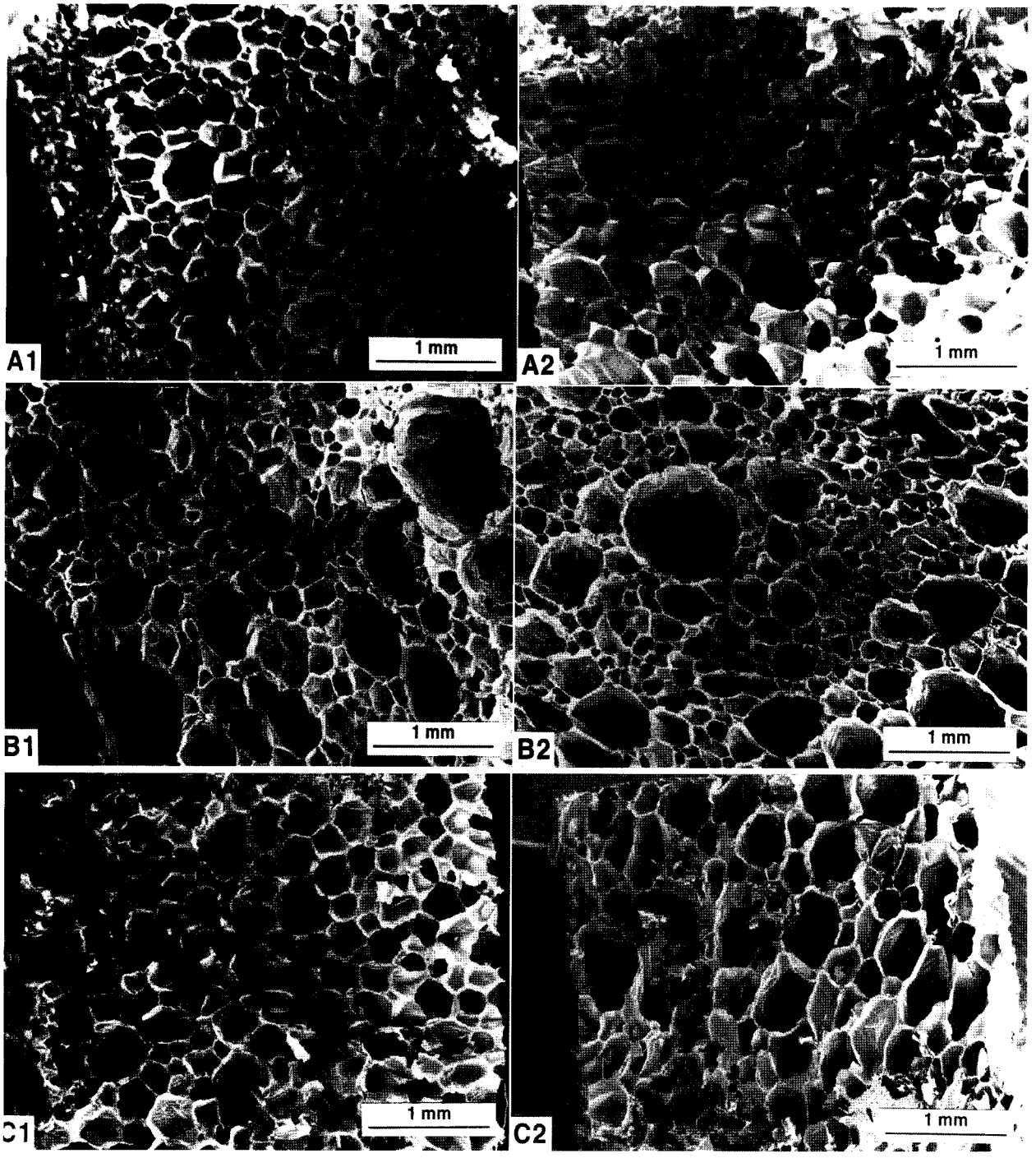

Figure 7 Scanning electron micrographs of foams containing Fantesk™ with glycols (A) ethylene (B) polyethylene and (C) propylene: (1) transverse or cross and (2) longitudinal sections.

of isocyanate with starch hydroxyls in Fantesk™ was obtained in an earlier study.[6] Crosslinking produces a highly branched and interconnected molecular structure that would tightly encapsulate the oil droplets in Fantesk.™ For this reason, the apparent loss of mobility of the oil in the rigid Fantesk™–polyurethane foam suggested by the NMR analysis is presumed to result from isocya-

nate reacting with epoxidized oil in the flakes, rather than oil migrating out of the flakes into the glycol phase.

Light Microscopy

The greater number of larger cells in Figure 4(B) compared to A and C explain the lower density exhibited by foams containing polyethylene glycol vs. foams containing either ethylene or propylene glycols. All three glycols resulted in foams with uniform, continuous cell networks with essentially transparent walls and connections. Areas of reduced transparency in each foam type reflect the presence of Fantesk™ flakes in the foam network. Figure 5 shows the location of the starch and oil components of the milled Fantesk™ in a propylene glycol foam. Toluidene blue stained only the starch component (A,B) and sudan red stained the oil (C,D) of the dry Fantesk™ flakes. The flakes were independently and randomly dispersed in the foam with no evidence of clumping. Although the red sudan stain was clearly evident in the flakes, the possibility of some oil separating from the flake surfaces and entering the continuous phase cannot be excluded. Figure 6 shows an apparently intact flake, with distinct edges and characteristic oil droplet inclusions, within a propylene glycol foam.

SEM

Photomicrographs of foams containing Fantesk™ and glycol [Fig. 7(A)–(C)] show their cell sizes and shapes. Foams containing polyethylene glycol (B) show a greater number of larger cells and, hence, have lower densities than foams containing either ethylene or propylene glycol. The longitudinal section of the foam containing propylene glycol (C2) shows the elongated (elliptically) cells in the direction of rise.

CONCLUSIONS

Ethylene, polyethylene, and propylene glycols were easily blended with Fantesk™ flakes and produced foams with desirable cell structures. NMR, FTIR, and microscopy were used to characterize the new foam formulations. Little qualitative differences existed between the Fantesk™–polyurethane foams provided by the three glycols. NMR spectra suggested that oil droplets in the Fantesk™ were crosslinked by isocyanate. Microscopic examination revealed the presence of intact Fantesk™ flakes in the foams, and their presence would make the foams more susceptible to biodegradation.

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