Synthesis and *In situ* Foaming of Biodegradable Malonic Acid ESO Polymers

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ABSTRACT: In this study, biodegradable rigid cellular materials were synthesized from the reaction of malonic acid with epoxidized soybean oil. Malonic acid reacts with two epoxy groups to give a network polymer. In the course of this reaction, initially formed malonic acid monoester (MAME) can decarboxylate and produce CO_2, which acts as the blowing agent leading to *in situ* foaming of the polymer. Epoxide addition and decarboxylation reactions of MAME occur competitively and simultaneously and by controlling their relative rates, foams of controlled density were produced. ^{1}H NMR spectrum of the synthesized foams showed that increasing the temperature increases the rate of decarboxylation reaction of MAME and decreases crosslink density leading to softer and lower density foams. Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst also increases the rate of decarboxylation. Load deflection curves of the cellular materials showed that decreasing the temperature and addition of DABCO increase compressive modulus of samples. Cell morphology was studied by microscopic images of foam samples that showed that foam samples have a closed cell structure and a wide distribution of cell volume. Soil burial test was done to determine rate of biodegradation of foam samples. A half-life of 815 days showed that foam samples are highly biodegradable. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1129–1135, 2008

Key words: biodegradable; renewable resources; cellular material; epoxidized soybean oil; malonic acid

INTRODUCTION

For the last 50 years, petroleum has been used for raw material for the synthesis of most of the commercially important polymers. Synthesis of new polymers from plant and animal products reduces the dependence on petroleum and provides cheap and highly biodegradable plastics. Social acceptance of polymers based on plant and animal products is also high since they represent a high technology use for traditional agricultural products. One of the important current incentives for the study of biodegradable polymers is their easier disposal. Industrially, fats and oils containing mainly triglyceride esters of fatty acids are excellent examples of plant- and animal-based products. We report here our efforts to synthesize a biodegradable polymeric foam from epoxidized soybean oil (ESO).

Epoxidized triglycerides are synthesized from unsaturated oils such as linseed, sunflower, and soybean oils by epoxidation reactions. Also some naturally occurring oils, such as vernonia oil, contain epoxidized triglycerides. Epoxidation of unsaturated oils or fatty derivatives can be performed using hydrogen peroxide with formic acid or acetic acid.[1] Recently, soybean oil has been epoxidized by enzymatic reactions with above 90% conversion.[2]

We have examined soybean oil and ESO chemistry in some depth and reported our results in earlier publications.[3–5] We have also reported on the reactions of ESO with various carboxylic acids.[6] Malonic acid, the acid used in this work, has two carboxylic acid groups, each of which can nucleophilicly open an epoxy ring and therefore polymerize ESO. The difference between malonic acid and most of the other dicarboxylic acids is its ease of decarboxylation. Numerous studies have been reported in the literature on the decarboxylation of malonic acid alone and in solution.[7–9] Pedersen et al. reported that some derivatives of malonic acid can decarboxylate even at room temperature.[10] Amines can catalyze the decarboxylation reaction, and the rate of this reaction is proportional to the concentration of the amine.[11] Thus, malonic acid should polymerize ESO, acting as a dinucleophile, and the monoester initially formed should also decarboxylate to provide CO_2 for the foaming of the product polymer. With this goal in mind, we set out to synthesize foamed polymers from ESO and malonic acid.

Materials

Malonic acid, dioxane, diethyl ether, barium hydroxide, 1,4-diazabicyclo[2.2.2]octane (DABCO) and chloroform were obtained from Aldrich. ESO with a brand name of Paraplex G-62 was obtained from C.P. Hall Company (Bedford Park, IL). ESO has 4.2 epoxy groups per triglyceride molecule as declared by the manufacturer, which corresponds to an average molecular weight of 950.

Apparatus

The IR analysis was performed on a Perkin–Elmer 1600FTIR spectrometer using KBr discs or NaCl windows.[1]H spectra were recorded on Varian 400 MHz NMR (*Varian*, Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz. Spectra were reported as ppm (δ) with tetramethylsilane as internal standard. Compression tests were done with a Devotrans A-200 universal tester at a strain rate of 0.15 mm/s. Photomicrographs of foam samples were obtained with Carl Zeiss Jeamed 2 Optical Microscope.

## Synthesis of samples for chemical analysis

Three grams of ESO (3.1 mmoles), 1.024 g of malonic acid (9.8 mmoles), 0.06 g DABCO (0.53 mmoles), and 3 mL of dioxane were mixed in a round bottom flask, and the mixture was stirred for 10 h at 100°C. The product was solution cast in an open mold, and the solvent was evaporated at 50°C under vacuum to give ESO-malonic acid polymers (ESOMA) as a thin film.

Synthesis of samples for mechanical test

In a typical synthesis, 10 g of ESO (10.5 mmoles), 3.03 g of malonic acid (29.1 mmoles), 0.10 g DABCO (0.88 mmoles), and 30 mL of diethyl ether were placed in a 250-mL round bottom flask. This mixture was stirred for 24 h at 40°C. Then, diethyl ether was evaporated under vacuum at room temperature. Prepolymer was obtained as a viscous liquid and was placed in a Teflon® mold of cylindrical shape having the dimensions of 4 cm diameter and 10 cm height. The sample was heated to 65°C for 5 h and then removed from the mold to ESOMA polymer as a white foam in the shape of the mold.

Soil burial test

ASTM D 5988 was used to determine the biodegradability of samples; Figure 1 shows the schematic view of the biodegradation test apparatus. To get
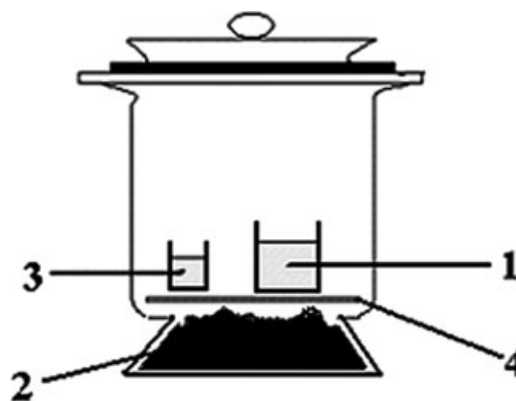
1) Barium hydroxide solution
2) Soil and sample
3) Water
4) Perforated plate

Figure 1   Soil-contact incubation apparatus.

more accurate results, tests were done in duplicate. Ordinary soil was sieved to less than 0.8-mm particle size, and obvious plant material and stones were removed. First, 500 g of soil was placed in the bottom of each desiccator, and then 2 g of crumbled foam (or 2 g of soybean oil, which was used for positive control) was added to the soil and thoroughly mixed. Two other dessicators were left with blank soil, to determine the amount of CO_2 evolution due to the small amount of organic material present in the soil. Seventy-five milliliters of $0.027M$ barium hydroxide solution in a 100-mL beaker and 25 mL water in a 50-mL beaker were placed on the perforated plate inside the dessicator, and then each desiccator was placed in a dark cabinet at room temperature. The barium hydroxide solution absorbed the evolved CO_2 quantitatively, and water provided the correct humidity. The amount of CO_2 was determined by titrating the remaining barium hydroxide with $0.017M$ hydrochloric acid to a phenolphthalein end point. Since barium carbonate builds up on the surface of the liquid, dessicators were occasionally shaken gently to ensure continued absorption of the evolved CO_2. The barium hydroxide traps were removed and titrated before their capacity was exceeded. Frequency of titration was every 3 days in the first 3 weeks and every 5 days after 3 weeks. The test was continued for 12 weeks.

RESULTS AND DISCUSSION

Synthesis and foaming

To convert epoxy resins into useful products, they must be polymerized and crosslinked by chemical
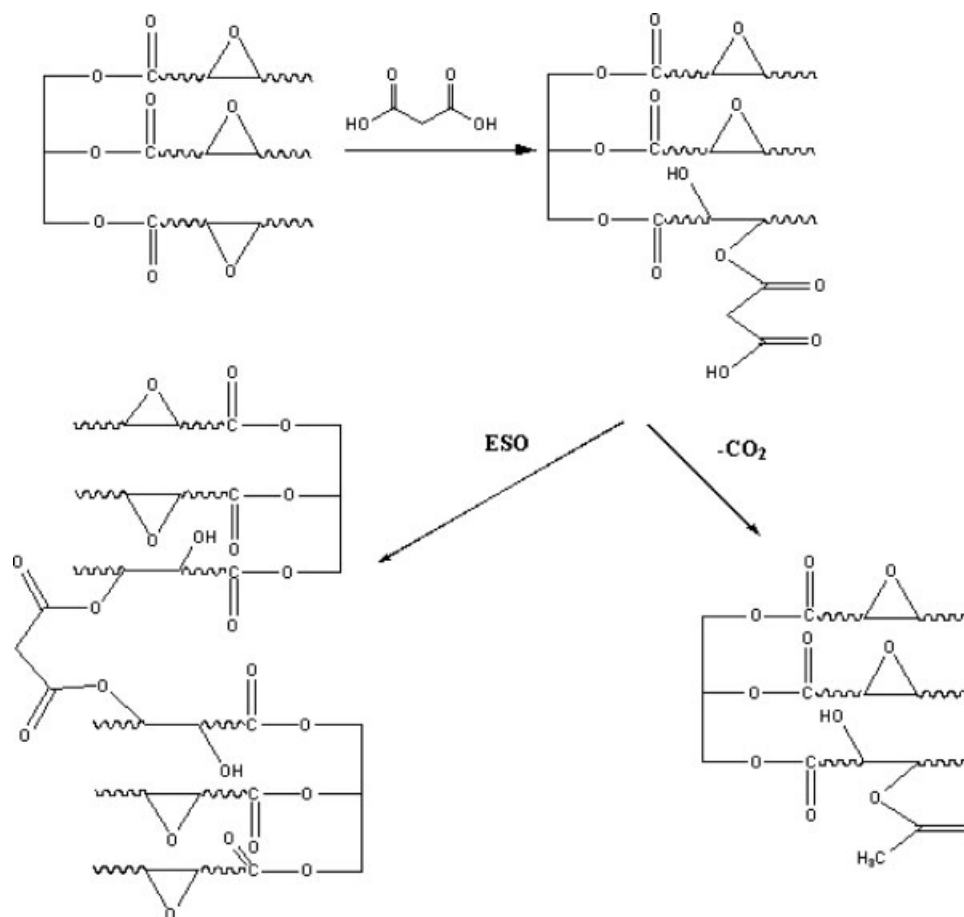
Figure 2 Reactions of malonic acid with ESO.

reactions into three-dimensional infusible networks by reacting with at least a difunctional reagent. Crosslinking reactions proceed by two possible routes, first by the reaction of epoxide functionality with a difunctional nucleophile such as a diamine, dicarboxylic acid, or acid anhydride and second by homopolymerization by ring opening polymerizations through the intermediate alkoxide formed in basic conditions or hydroxide formed in acidic conditions. Malonic acid is a difunctional carboxylic acid; therefore, it can be used for the polymerization of ESO. Unlike other dicarboxylic acids, malonic acid and its monoester can also decarboxylate upon heating. Since solid malonic acid melts and decarboxylates around 135°C and the rate of decarboxylation of malonic acid in dioxane around 100°C is very low,[12] the decomposition of malonic acid may be neglected at temperatures less than 100°C. Once the malonic acid monoester (MAME) is formed by the reaction of one end of malonic acid, there are two possible reactions that are shown in Figure 2. First is the nucleophilic addition of the remaining carboxylate to another epoxide, leading to polymerization. Second is the decarboxylation of the remaining carboxylate to give CO_2, leading to foaming.

Figure 3 shows decarboxylation mechanism of MAME. Decarboxylation of MAME involves a pericyclic six electron process in the cyclic six-membered transition state. The formed unstable enol rapidly tautomerizes to acetate ester. It should be noted that, if MAME decarboxylates, the polymer is terminated at that epoxide site. Other epoxide sites of ESO, of
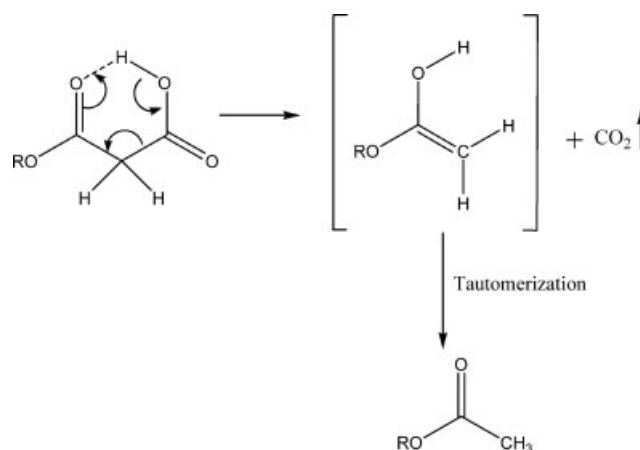

Figure 3 Decarboxylation mechanism of MAME.

which there are 4.2 on each triglyceride on the average, can of course continue to grow. Therefore, increased decarboxylation produces both a low density foam and a low crosslink density polymer.

The epoxide content of epoxy is another critical factor in the synthesis of polymeric foams. Since decarboxylation reaction terminates polymerization, the average molecular functionality of the epoxy component must be higher than 2. If an epoxy component that has two epoxide groups is used, only low molecular weight polymer would be obtained which is not sufficient to stabilize the cells. But if ESO that has an average of 4.2 epoxide groups per molecule is used, chain growth and CO_2 formation will be sufficient to synthesize a cellular material with stable cells.

Reaction of epoxide groups with malonic acid can be deduced from infrared spectroscopy. Epoxide groups have C—O bending absorption around 822 cm^{-1}. Disappearance of this peak shows the epoxide ring opening reaction. Figure 4 shows consumption of epoxide groups with reaction time.

The rate of decarboxylation reaction of MAME depends on MAME concentration, temperature, tertiary amine catalyst, and rate constant, but rate of nucleophilic addition reaction of MAME to another epoxide group depends also on concentration of epoxide groups. This difference provides a very good advantage for the foaming. At the beginning of the reaction, probability of nucleophilic addition reaction of MAME will be higher due to the higher epoxide group concentration, and probability of decarboxylation will be lower because of fast consumption of MAME by nucleophilic addition reaction. Decarboxylation and CO_2 evolution rate increases toward the end of the reaction when the epoxide group concentration decreases. This provides higher CO_2 captivity in the polymer matrix, because the gas is produced later in the reaction when the viscosity of the polymer is now higher.

Relative rates of reactions of MAME

Since decarboxylation of malonic acid itself in dioxane below 100°C can be neglected, chemical and physical properties of the foam depend on the relative rates of the two reactions of MAME, which are shown in Figure 2. The extent of both decarboxylation reaction and nucleophilic addition reaction of MAME depend on the temperature and the tertiary amine catalyst used.

The product polymer was analyzed by ^{1}H NMR. The pertinent peaks in the ^{1}H NMR spectra of the product, shown in Figure 5, are the 2.1 ppm peak belonging to the acetate methyl produced by decarboxylation, 3.0 ppm peak belonging to the unreacted epoxy ring protons, and the 3.45 ppm peak belong-
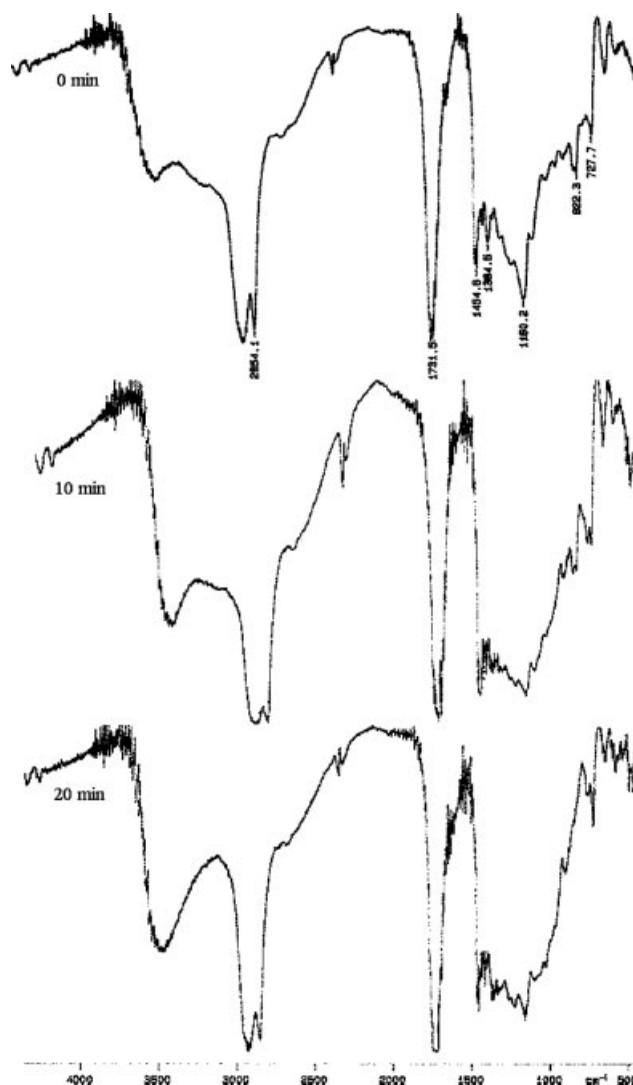

Figure 4 IR spectra of ESOMA polymer at different stages of its synthesis.

ing to the methylene protons of malonic acid diester. By comparing the intensities of these peaks to other triglyceride peaks that are unchanged during the reaction, the course of the reaction carried out at different temperatures can be followed conveniently.

For example at 60°C, 0.6 mol of acetate, and therefore the same amount of CO_2, is formed; 1.45 mol of malonic acid diester is formed, and 0.35 mol (8%) of the epoxy groups are unreacted per mole of ESO. At 100°C 1.1 mol of CO_2 is formed; 1.15 mol of malonic acid diester is formed per mole of ESO, and no measurable unreacted epoxide is left. If we compare the results of these two examples synthesized at different temperatures, we observe that an increase of temperature increases the amount of CO_2 gas released, decreases polymer connectivity, and lowers the unreacted epoxide percentage. We therefore have an excellent and simple method for controlling foam properties. At low temperature, higher
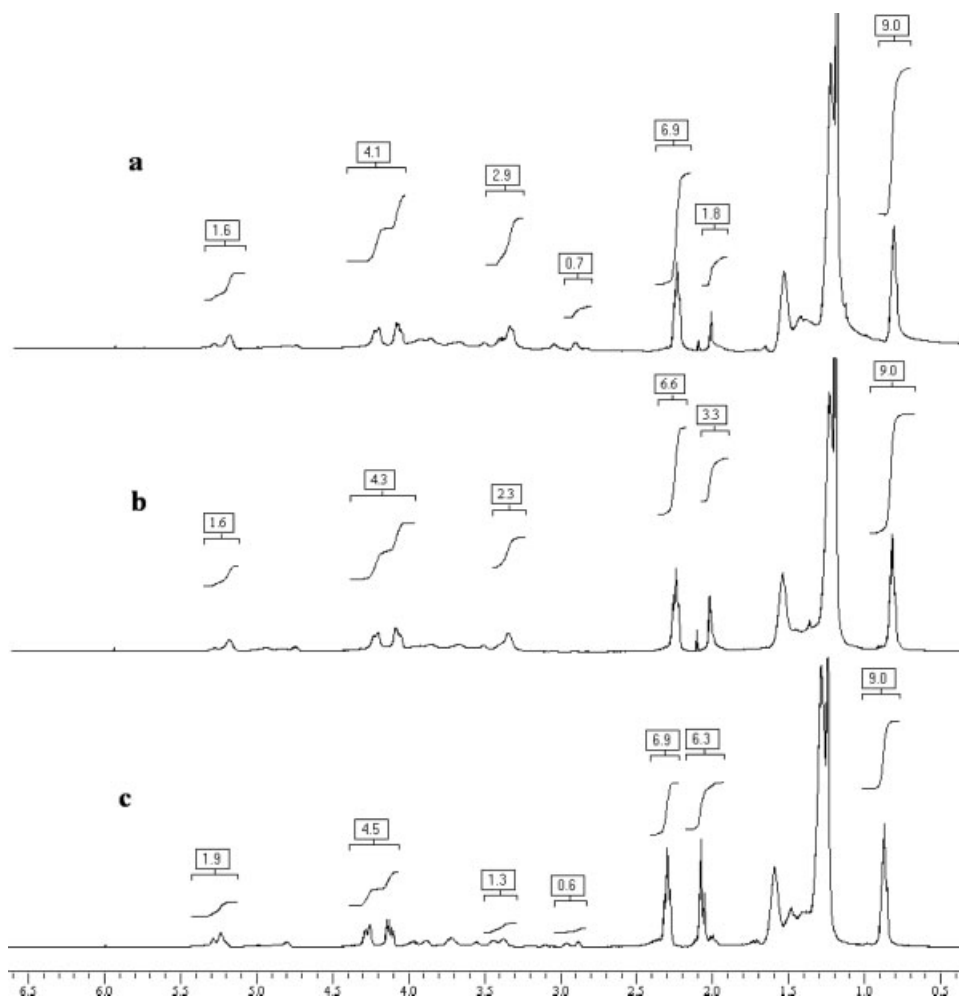
Figure 5 ^{1}H NMR spectrum of ESOMA polymer synthesized at (a) 60°C without catalyst; (b) 100°C without catalyst; (c) 100°C with DABCO catalyst.

connectivity of the polymer and reduced foaming is observed. This gives a more rigid and higher density foam. At higher temperature, lower connectivity and higher foaming leads to softer and lower density foam.

If we compare DABCO catalyzed ESOMA synthesis reaction with the noncatalyzed reaction, ^{1}H NMR data, which is shown in Figure 5, shows that rate of decarboxylation reaction of MAME increases with the DABCO usage, and rate of nucleophilic attack of MAME on the epoxide group decreases with increasing DABCO concentration.

Compressive behavior of ESOMA foams

Compressive modulus of the cellular materials made by foaming a given polymer is related to the density of the foam. With decreasing density, the number of cells and the average volume of cells increase, and the cell walls become thinner, therefore compressive modulus decreases.[13] Table I shows the densities and compressive moduli of 10 different ESO based

foams. When we compare these foam samples with commercial polystyrene foams and polyurethane foams, ESOMA foams show lower compressive moduli. The reason may be that ESO has a short chain length between epoxide groups and the nine carbon chains beyond the epoxide groups remain as dangling chains on the polymer segment. These behave as internal lubricating agents and decrease the mechanical properties of the polymer matrix.

Since the compressive modulus of the foamed article depends on the mechanical properties of the polymer matrix, polymeric foam synthesized at high temperature has a low compressive modulus because of lower crosslinking density of the matrix. Table I also shows that increasing temperature and increasing of malonic acid percentage in the mixture lowers the density and the compressive modulus of foam samples. This is because higher malonic acid concentration rapidly reduces the amount of epoxide, and MAME cannot find any more epoxies to react with and has no other reaction possibility other than to decarboxylate.

TABLE I
Densities and Compressive Modulus of Foam Samples

Sample number	Temperature (°C)	[Malonic acid]/ [ESO]	Catalyst	Density (g/cm^3)	Compressive modulus (KPa)
1	65	2.8	DABCO	0.494	238
2	75	2.8	DABCO	0.458	158
3	85	2.8	DABCO	0.309	140
4	95	2.8	DABCO	0.238	39
5	65	2.8	–	0.329	82
6	75	2.8	–	0.304	60
7	85	2.8	–	0.246	38
8	95	0.28	–	0.228	22
9	65	0.25	–	0.382	63
10	75	0.25	–	0.358	40

The compressive modulus of the cellular material depends not only on the polymer matrix and density but also on the cell structure.[13] In the synthesis described here, the CO_2 formation and polymerization start at the same time and continue till the end of the reaction. At the beginning of the reaction, when few molecules of polymer exist, the viscosity is low and most of the CO_2 is allowed to escape. During the initial stage of gas release and before the viscosity of the polymer increases to a level required for cell stabilization, bigger closed cells as well as open cells are produced. After a sufficient degree of polymerization is reached, the viscosity increases, gas escape is minimized, and small closed cells are produced. At this higher degree of polymerization, cell movement and cell collapse is prevented by the high viscosity. Therefore, bigger cells are produced early and smaller cells are produced later in the reaction, and a wide distribution of cell diameters is finally obtained. Figure 6 shows photomicrographs of these closed cells.

Rebounding

Most applications of cellular materials especially comfort cushioning and packaging require that cellular material should return to its original shape after removal of load. This property is called "rebound." Foams with less than 100% rebound are essentially useless as a small number of load and release cycles change the shape of the foam irreversibly. It is well known that some low-quality upholstery cushions get flat after a short use. In our work samples 1, 2, and 3, shown in Table I, which possessed useful compressive modulei showed 100% rebounding after a 50% compression. Since ESO has 4.2 average epoxide groups per molecule, samples have enough crosslink density to behave as an almost ideal rubber, which gives the desired property of 100% rebound.

Aerobic biodegradation in soil

The test for aerobic biodegradation of plastic materials in soil gives information about the degree and the rate of aerobic biodegradability of synthetic polymers. Since the foam samples described in this work are plant oil based materials, their biodegradation should be easier. ASTM 5988 describes a convenient method for determining the rate of biodegradation of rigid plastics in soil. Triglycerides are easily hydrolyzed by lipase enzyme that every living creature secretes. Soil is used as the biodegradation medium because it is extremely rich in species. When maintained appropriately with regard to moisture content, oxygen availability and temperature, biological activity is quite considerable, although lower than other biologically active media such as sewage-sludge or compost.

The source of the carbon atoms of CO_2 that is evolved by aerobic species, is the carbon atoms of the samples. To find the percent biodegradation versus time, first we have to find the carbon content of the sample. The starting materials for the polymer are ESO and malonic acid, and the final products are foamed polymer and CO_2. Since we know the exact structure of the reactants, and we know the approximate number of decarboxylation per ESO, we can easily calculate carbon content of the foam sample that is used in the biodegradation test. The blank soil samples also evolve some CO_2 due to the small amount of organic materials already present in it. Net CO_2 evolution from the aerobic biodegradation of foam sample is calculated by subtracting the CO_2 evolution of blank soil from the CO_2 evolution of mixture of soil and foam sample.

Figure 7 shows the rate of aerobic biodegradation of a 2-g test sample containing 1.29 g of carbon atoms. About 7% of the foam sample was biodegraded after 85 days. A simple calculation gives a biodegradation half-life of 815 days for the sample in soil. Different microbial populations and different environmental conditions can change this result but
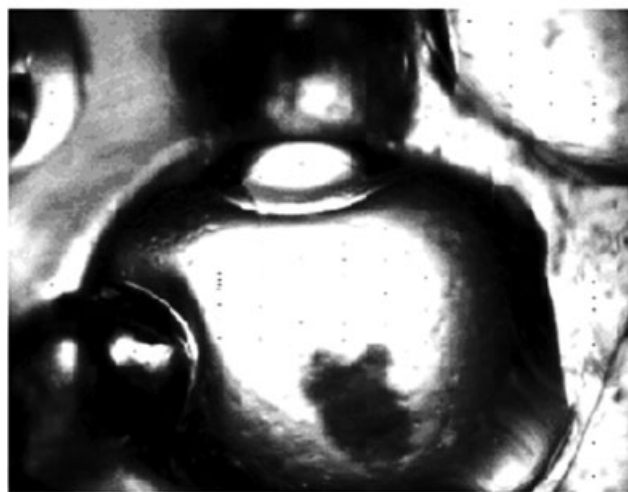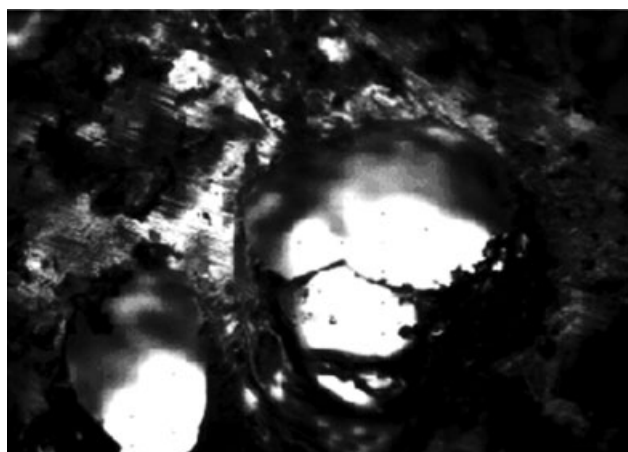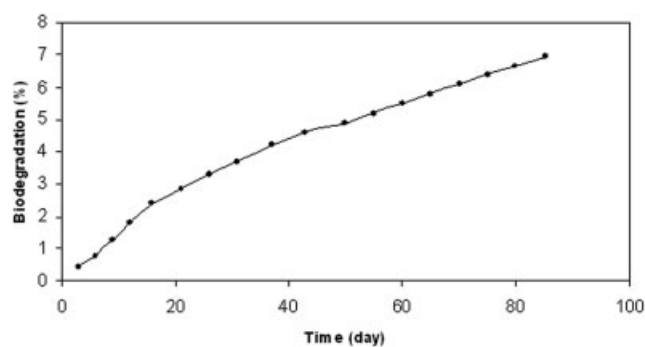
Figure 7 Biodegradation curve of sample 1 in soil.

CONCLUSIONS

In this study, biodegradable cellular materials were synthesized from the reaction of malonic acid with epoxidized soybean oil. This reaction provides not only polymerization but also blowing of synthesized polymer due to the decarboxylation capability of malonic acid monoester. Therefore, the proposed synthesis has the elegance of using the same chemical, malonic acid, as chain extender, crosslinking agent, and the blowing agent. We can control the relative rates of the decarboxylation reaction and the nucleophilic addition reaction of MAME by varying the temperature and by the use of catalyst, which gives an excellent and simple method for controlling foam properties.

Figure 6 Photomicrograph of sample 1.

we can easily argue that the test sample is highly biodegradable when compared to commercial polystyrene, which shows essentially no biodegradation in soil after more than 30 years.[14] Optimization of the molding properties of the synthesized polymeric foams is in progress.

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