Gelation of Soybean Oil With Polybutadiene

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ABSTRACT: In this study self-supporting, resilient, load bearing polybutadiene - soybean oil gels were obtained. The gels were made by dissolving polybutadiene (PBD) in soybean oil (SO) and selectively crosslinking PBD with a free radical source. PBD concentration, free radical source concentration, and the temperature and time of the crosslinking reaction were varied, and the effects of these changes on the mechanical properties of the gels were examined. Our experiments show that successful gelation is possible within PBD concentration limits of 7.5 to 12%, peroxide concentration between 25 to 100% (based on PBD), temperature between 110°C and 130°C and reaction times of 3 hours with tert.butyl-peroxybenzoate as the free radical source. The crosslinking reaction was followed by IR and H-NMR spectra, and the crosslinking density was followed by compression testing and swelling behavior. Higher radical source concentration and higher PBD concentration gave gels with better mechanical properties. The spectra and the viscosity increase of SO extracted from the gels indicate that there is dimer and trimer formation of SO during the reaction. The spectra of the PBD extracted from gels indicate that SO was added to PBD in a small but measurable amount. Integration of peak intensities in the NMR spectrum of methylene groups of PBD and methylene groups of triglyceride indicated one triglyceride molecule for approximately 45 repeating units in PBD. The modulus of the best gel sample (PBD 10%. peroxide 50%) was 1.96×10^{-2} MPa. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2240–2246, 2005

Key words: crosslinking; free radical; gels; plant oil; polybutadiene

INTRODUCTION

A gel is a crosslinked polymer swollen in a liquid medium. When a soluble polymer is crosslinked, large infinite network structures are built up. When this network is swollen in a compatible liquid, a gel is produced. Gel properties depend strongly on the interaction of the crosslinked polymer and the liquid used for swelling. The liquid prevents the polymer network from collapsing into a compact mass, and the network, in turn, retains the liquid.[1]

A familiar gel is the dessert Jello, where the network polymer is highly hydrogen bonded animal protein gelatin. The cornea, and the interior of the eye, is a gel. Blood vessel walls and connective tissues contain gels. The epithelial cells in the stomach are protected from the extremely acidic gastric juice by a gel. The lung surface is covered by a similar gel. Some plants' roots are covered by gels produced by bacteria, which affect the plants' metabolic functions. Gels are also used as prosthetics in humans for corrective and esthetic surgery.[2]

In our general aim of using plant oils as renewable resources for the preparation of advanced products such as polymers, composites, and surface coatings, we undertook a study of gelation of soybean oil (SO).[3–6] Our aim was to obtain a gel that is self-supporting and is capable of bearing a load without leaching the oil. The gels were made by dissolving polybutadiene (PBD) in SO and selectively crosslinking the PBD by a free radical source. We examined the chemical reactions that led to gelling by NMR and IR spectroscopy and measured the mechanical properties of the gels by compression and swelling tests. The effect of changing PBD concentration, free radical source concentration, crosslinking reaction temperature, and reaction time on the mechanical properties of the resulting gels were also studied.

EXPERIMENTAL

Apparatus

The IR analysis was performed on a Perkin–Elmer 1600FT-IR spectrometer using KBr discs or NaCl windows. H-NMR spectra were obtained on a Varian 400 Mhz NMR spectrometer. A Gaertner Scientific Corporation traveling microscope was used to measure the swelling behavior of the samples. Compression tests were done with a Devotrans A-200 universal tester at a strain rate of 0.15 mm/sec. Viscosity measurements were done on a Viscotester VT-02 rotating cup viscometer.

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TABLE I
Gel Samples

Sample no	Sample code	PBD % (% of solution)	Trigonox % (% of PBD)	Comments
1	G - 7.5/25	7.5	25	Very soft gel
2	G - 7.5/50	7.5	50	Very soft gel
3	G - 7.5/75	7.5	75	Soft gel with small bubbles
4	G - 7.5/100	7.5	100	Soft gel with small bubbles
5	G - 10/25	10	25	Soft gel
6	G - 10/50	10	50	Soft gel with small bubbles
7	G - 10/75	10	75	Gel with large bubbles
8	G - 10/100	10	100	Gel with large bubbles
9	G - 12/25	12	25	Gel with large bubbles
10	G - 12/50	12	50	Gel with large bubbles

Chemicals

Acetone and chloroform were obtained from Merck. PBD was obtained from Bayer. Its reported *Mn* was 40,000 and is predominantly in the cis configuration. Deutrochloroform was obtained from Aldrich. tert.Butyl-peroxybenzoate was obtained from Akzo Nobel. SO was obtained from MarSA. In this study the molecular weight of SO was taken as 878 g. (This is a number used in the oil industry obtained from the weighted average of the most common fatty acids in this oil.) The oil had an iodine number of 135.

Procedures

Preparation and gelation of soybean oil–polybutadiene mixture

SO–PBD solutions containing 7.5%, 10%, and 12% of PBD were made by dissolving finely chopped PBD with mechanical stirring at room temperature for 5–7 days. The resulting product was a clear and tacky viscous liquid. Gelations were carried out in 3 cm diameter glass vials. In a typical procedure, the desired percentage of tert.Butyl- peroxybenzoate was dissolved in PBD–SO solution and the mixture was purged with N_2 for 3 minutes and sealed. The mixture was heated in an oil bath at 120°C for 3 hours without stirring. The products were clear gels and could be removed by breaking the glass vial. The compositions of the samples are shown in Table I.

Extraction of soybean oil from gel

In a typical procedure, 3.29 g of a sample of G - 10/25 (see Table 1) was extracted with 100 ml of chloroform until the color of the gel became colorless. Then the same extraction process was repeated with 50 ml of pentane. Chloroform and pentane extracts were combined and evaporated, and 2.92 g SO was obtained. The IR and NMR spectra of both SO and crosslinked PBD were taken.

Sweating experiments

In a typical procedure, 5.23 g of a sample of G - 10/25 in the form of a cylinder of 1 cm radius and 2 cm height was pressed with a 110 g weight for 4 days on a filter paper. No SO release was observed on the filter paper.

Swelling test

Rectangular shaped pieces of gel samples approximately 9 × 3 × 2 mm were placed in chloroform, and the initial length (I_o) was measured with the traveling microscope. The swollen length (I_t) was measured at definite time intervals. The linear swelling ratio was calculated according to the following formula:

$$\text{Linear Swelling Ratio} = ((I_t - I_o)/I_o)$$

RESULTS AND DISCUSSION

Characterization of PBD

PBD used in our work contains both 1,4 and 1,2 polymerized butadiene repeating units. The H-NMR spectrum shown in Figure 1 shows the presence of pendant vinyl groups that result from 1,2 polymerization. The integration ratio of the NMR signals at 5.0 ppm due to the pendant vinyl groups and at 5.4 ppm due to the internal double bonds indicates that 4% of the PBD unsaturation is on pendant vinyl groups. These are known to be much more reactive towards free radicals than the backbone unsaturation.[6] The IR spectrum of the sample indicated a 737 cm^{-1} peak, which showed the predominantly cis geometry of the backbone double bonds.

Characterization of soybean oil

SO is glycerol esters of fatty acids. Fatty acids have four characteristic functional groups in their structure. These are: the carbonyl group, unsaturated centers, allylic positions, and hydrogen alpha to the carbonyl

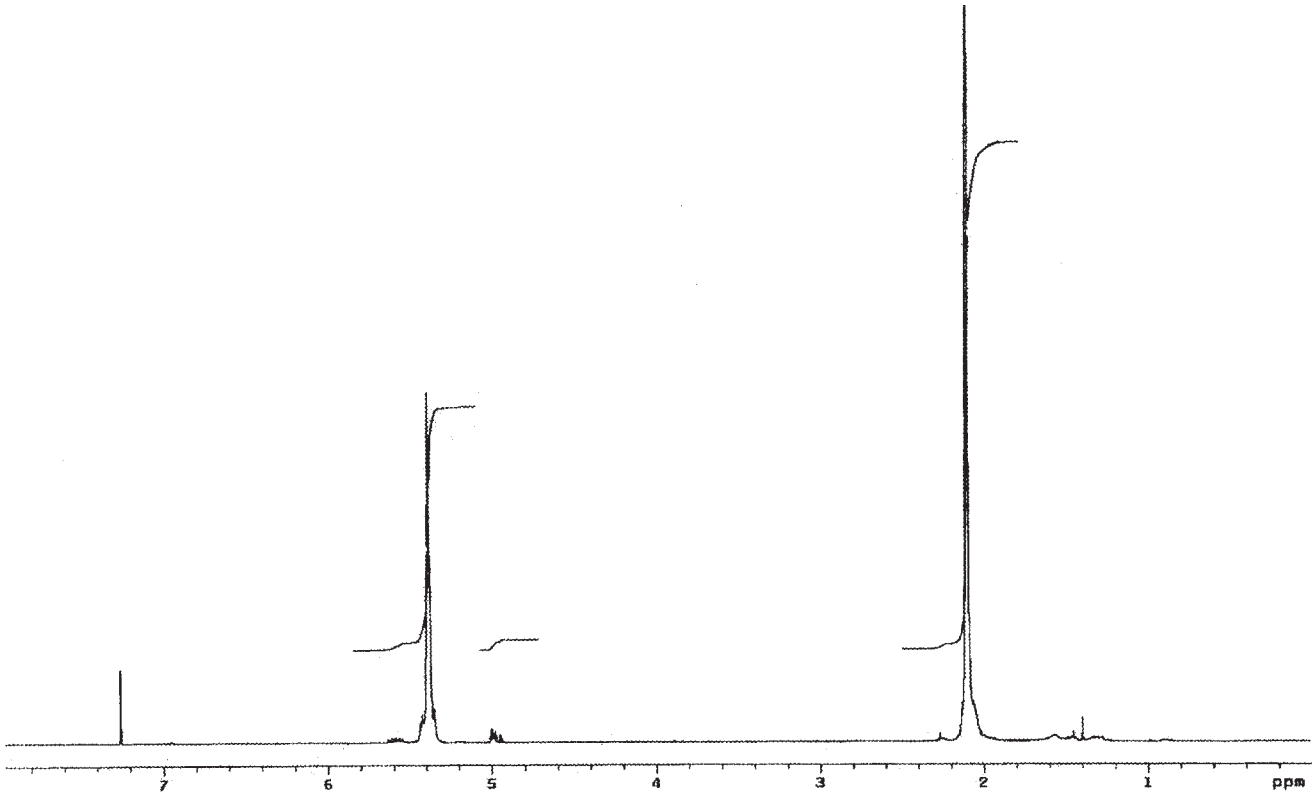

Figure 1 Proton NMR spectrum of PBD.

group. The SO sample used in this work has the following fatty acid composition, shown in Table 2, as determined by gas chromatography.[7] This ratio of fatty acids corresponds to 4.2 double bonds per triglyceride on the average.

Peroxide crosslinking of polybutadiene

In order to crosslink PBD but not polymerize SO, we tried different free radical sources during our experiments. t-Butyl-peroxybenzoate, a liquid free radical source with a high decomposition temperature range and good solubility in SO, gave the best result.

Samples were made with different PBD and peroxide concentrations. As expected, gels with high PBD and high peroxide concentrations were the most resilient. The required peroxide concentrations indicate that the peroxide is consumed during crosslinking. Samples with less than 10% peroxide based on PBD failed to give a gel. The reasons for this may be the presence of natural free radical inhibitors, such as tocopherols, in SO that have to be consumed first to allow the crosslinking reaction to proceed and the facile chain transfer to the allylic positions present both in SO and PBD.[8]

To be able to do physical property measurements, it is necessary to prepare gel samples that have no voids or gas bubbles. This proved to be difficult. t-Butyl-perbenzoate dissociation produces CO_2, which is insoluble in SO. The gelation reaction must proceed slowly to allow CO_2 to escape; otherwise, gel samples have gas bubbles in them. At high peroxide concentrations, it is impossible to make samples suitable for mechanical testing.

After mechanical property measurements, gel samples were extracted with chloroform, which separated SO from the crosslinked PBD.

TABLE II
Fatty Acid Composition of Soybean Oil

Name	Mol %
Palmitic acid	10.7
Stearic acid	4.0
Oleic acid	30.0
Linoleic acid	50.5
Linolenic acid	4.0

Gelling of soybean oil

It was found that in order to obtain a network that will hold the SO without leaching out, there is a critical PBD concentration. This concentration was found by trial and error. Below 7% PBD, gelation does take place but the resulting gel is not self-supporting. At the other extreme of concentration, gels with more than 12% PBD cannot be made because the solubility of PBD in SO is exceeded.

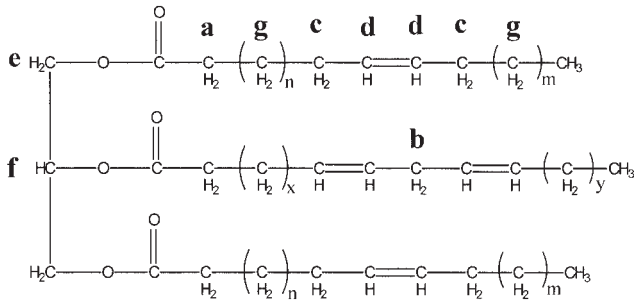

Figure 2 A typical soybean oil triglyceride.

So in our experiments, we were limited to PBD concentrations between 7 and 12%.

The temperature and the duration of the reaction also affect the product. At temperatures below 110°C, the peroxide does not dissociate and no gelation is observed. At temperatures higher than 130°C, gels with big gas bubbles that were useless for compression tests are obtained. Between these temperatures, the half-life of the peroxide is about one hour.[9] To make sure that most of the peroxide is consumed, the reactions were run for at least 3 half lives of the peroxide, which is 3 hours.

Investigation of soybean oil and crosslinked polybutadiene extracted from gels

Repeated chloroform and pentane extractions of the gels were made until the residue reached a constant weight. Both the extracted SO and the residual crosslinked PBD were spectroscopically examined. In the NMR spectrum of the extracted SO, peaks due to the protons of the carbon α to the carbonyl group (a in Fig. 2) appearing at 2.4 ppm were used to compare relative intensities of the other peaks.

In the NMR spectrum of the original SO, the ratio of the integration of the alpha -CH_2- 'protons (a in Fig. 2) to doubly allylic protons (b in Fig. 2) is found to be 1.58. On the other hand, this ratio was found to be 4.5 in the H-NMR of the extracted SO. The ratio of allylic protons (c in Fig. 2) to alpha protons (a in Fig. 2) was found to be 1.62 in the original SO 0.93 in the extracted SO H-NMR spectrum. These differences are significant evidence that doubly allylic protons of linoleic fatty acid and the allylic positions of unsaturated fatty acids in SO were consumed during the reaction. Meanwhile, there was no measureable decrease in vinyl protons (d in Fig. 2) of SO.

Significantly, the extracted SO spectra show no peaks due to PBD. The viscosity of SO extracted from

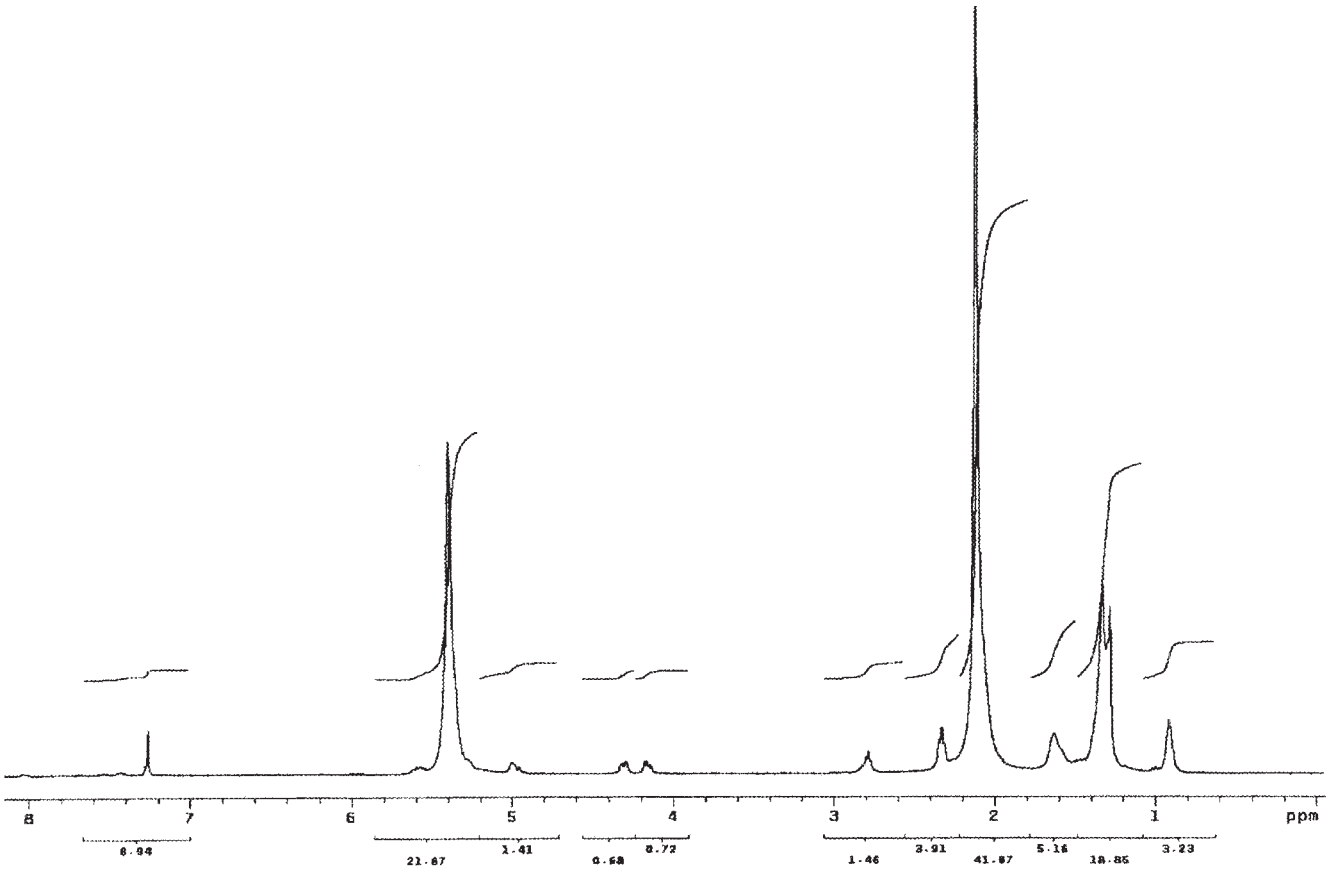

Figure 3 The H-NMR of the extracted PBD.

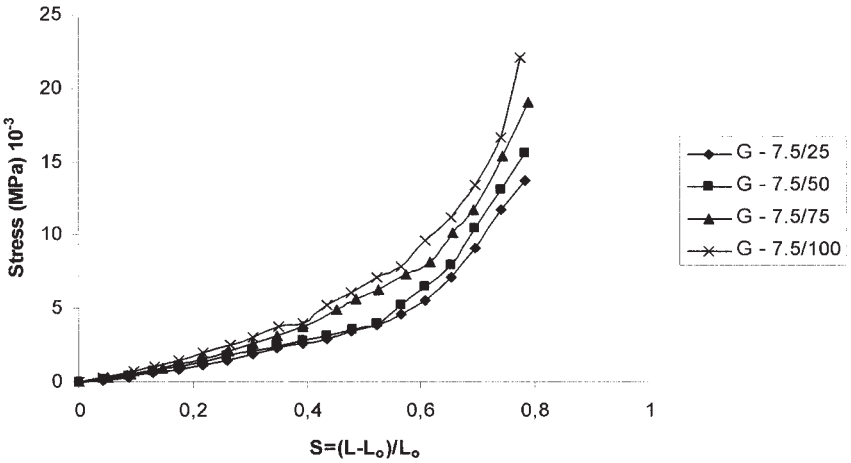

Figure 4 Stress–Strain curve for G-7.5 series.

the gels was 125 cps, while the original SO has a viscosity of 50 cps. We conclude that dimers and trimers of SO are formed to some extent by allylic coupling reactions.

The H-NMR spectrum of the extracted PBD is given in Figure 3. The peak clusters around 4.2 ppm, corresponding to the glyceride protons (e and f in Fig. 2), indicate that SO is actually bonded to PBD. Other SO peaks coincide with PBD and are not suitable for identification. Integration of peak intensities of methylene groups of PBD and methylene groups of triglyceride (g in Fig. 2) indicated one triglyceride molecule for approximately 45 repeating units in PBD. (An idealized glycerol trioleate was used for calculation.) A quantitative extraction shows that with a typical 10% PBD gel sample, 0.15% of the oil is coupled with PBD and the remainder could be solvent extracted. PBD vinyl protons of both internal and pendant unsaturated groups remained essentially unchanged during crosslinking.

In summary, we found that during the peroxide mediated gelation reaction, the following processes occurred simultaneously:

i) Cosslinking of PBD primarily by allylic coupling.
ii) Dimerization and trimerization of SO primarily by coupling at the allylic and doubly allylic positions.
iii) Measurable but small coupling between PBD and SO, resulting in the appearance of SO molecules in the PBD network, but leading to no PBD molecules in the extractable oil.

Compression testing of gel samples

The mechanical properties of the gels were measured by compressive testing. Three sets of gel samples with different PBD concentration were made, and each set was then gelled with four different peroxide concentrations under identical reaction conditions.

The strain rate for the experiments was found by trial, and the best data were obtained at 0.15 mm/sec strain rate. The precision of the experiments is $\pm 20\mu$m in strain and ± 0.01 gforce in stress. As all samples were made in the same cylindrical mold, all have the same initial crosssectional area of 1.57 cm^2. As the

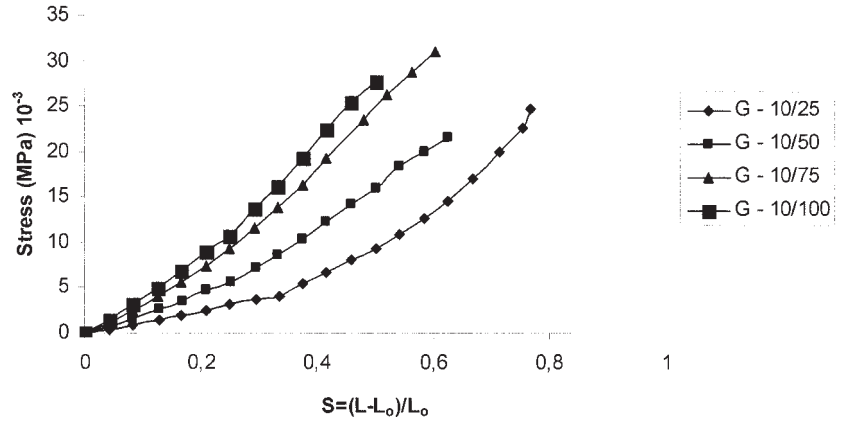

Figure 5 Stress–Strain curve for G - 10 series.

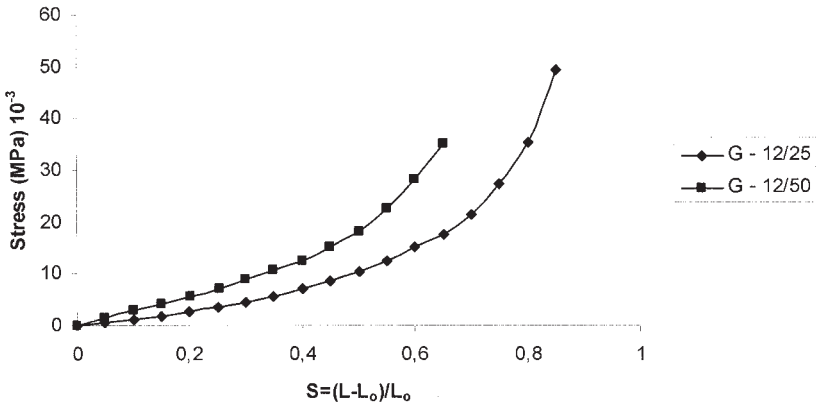

Figure 6 Stress–Strain curve for G - 12 series.

gelled sample does not fail but just continues to deform under load, the experiments were arbitrarily stopped when the height of the sample was reduced by half. The stress–strain curves are given in Figures 4, 5, and 6. Moduli calculated from the stress–strain curve at 5% of total strain are shown in Table III. As expected, samples with high PBD and high peroxide contents have the highest moduli.

Swelling test

Generally, if a linear polymer dissolves in a solvent, the same polymer will swell in the same solvent, when crosslinked. Three-dimensional polymer networks are capable of absorbing a large quantity of a suitable solvent. As the network is swollen by absorption of the solvent, the chains between network junctions are required to assume elongated conformations.

If a sample has a high crosslink density, it will absorb less solvent. By following the change in length during swelling, it is possible to compare the relative crosslink density of different samples. Generally, the smaller the equilibrium swelling ratio, the higher is the crosslink density. The useful parameter that may be obtained from a swelling test is the linear equilibrium swelling ratio, reported as $((I_t - I_o)/I_o)$ where I_t and I_o are the swollen and initial lengths of the samples. This ratio depends on the molar volume of the solvent and the crosslink density and crosslink segment length of the polymer. If two samples are swollen in the same solvent, the parameter that determines the swelling ratio is the crosslink density and crosslink segment length.

$((I_t - I_o)/I_o)$ versus a time graph for the gels in chloroform is plotted in Figure 7. As shown in Figure 7, the polymer that has higher peroxide content (G-10/100) swelled less. As the peroxide concentration increases, the crosslink density increases.

TABLE III
Modulus of the Samples

Sample	Modulus (10^{-3} MPa)
G - 7.5[a]/25[b]	4.9
G - 7.5/50	5.7
G - 7.5/75	6.9
G - 7.5/100	8.3
G - 10/25	10.5
G - 10/50	19.6
G - 10/75	31.9
G - 10/100	38.6
G - 12/25	12.5
G - 12/50	27.1

[a] Percentage of PBD based on SO.
[b] Percentage of peroxide based on PBD.

Sweating and other miscellaneous tests

We performed some extreme tests on the gel samples of the G-10 series. First, the behavior of the gel under a load was examined to see if it would release the oil. A rectangular prism shaped sample of G − 10/25 weighing 5 g was pressed with a 110 g weight for 4 days on a filter paper. No SO release was observed on the filter paper. This shows that the crosslink density is high enough that the SO molecules are entangled and are unable to pass through this network structure at room temperature. But when the gel samples were heated to 80°C, they started to release the oil. This is probably because at high temperature, the kinetic energy of the SO molecules in the network increases and the chains of the network undergo motion at a larger scale. This also shows that the SO is physically trapped by the network structure. After the SO was sweated out, the remaining PBD network was placed in excess SO and heated again. It was observed that the network structure absorbed SO again and swelled but retained its original shape. Therefore, sweating out and swelling are reversible processes. Moreover, sweating and swelling experiments can be carried out simultaneously whereby a plug of the gel can be placed halfway up in a test tube, the test tube can be filled with SO to the top and then warmed to 60–65°C.

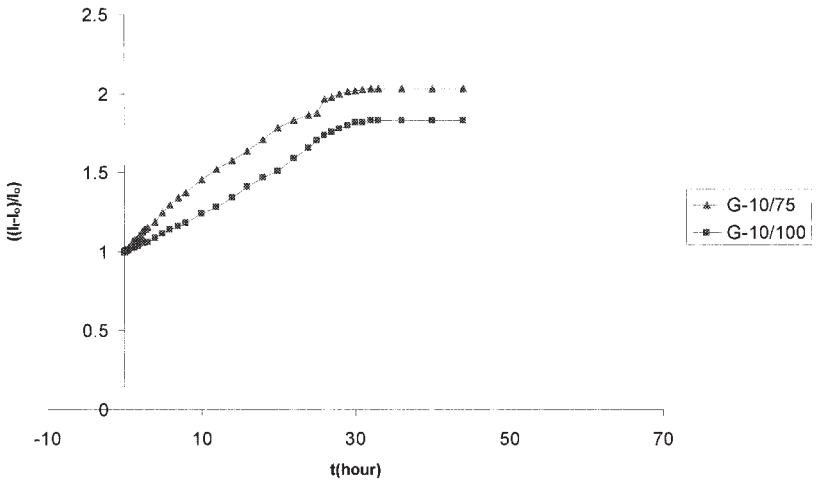

Figure 7 Swelling data of G-10 sample.

As the sample sweats oil downward, it is also swollen by fresh SO from the top, as shown in Figure 8. The situation is very much like size exclusion chromatography. Analytical work to determine the resolution capabilities of such gels and further experiments to see if these gels may be used as molecular sieves to separate free acids from triglycerides is now being carried out. If successful, this separation could have considerable industrial applications.

CONCLUSION

In this study we successfully obtained self-supporting, load bearing PBD–SO gels. The mechanical properties of the gels improve with higher PBD and higher peroxide concentrations, as expected.

We found that successful gelation is possible within PBD concentration limits of 7.5 to 12 per cent, peroxide concentration between 25 to 100 per cent (based on PBD), and temperature between 110°C and 130°C.

Characterization of the products and reactants was made by H-NMR and IR spectrometry. The spectra and viscosity increase of carefully extracted SO indicate that there is dimer and trimer formation of SO during the reaction. No crossover products of PBD and SO were observed in the extract.

The crosslinking of PBD proceeded through the allylic positions, and there was no measurable decrease in the double bond content. Samples from which SO was carefully extracted still showed NMR peaks due to SO. This leads us to conclude that a small but measurable amount of cross reaction between PBD and SO is taking place. After extraction, the cross-reacted SO remains in the PBD network. Integration of NMR peak intensities of PBD methylene groups and SO methylene groups indicate one triglyceride molecule for approximately 45 repeating units in PBD.

It is hoped that the gelled products obtained in this work can be used as candles, shock absorbers, prosthetics in plastic surgery, non flowing fuels, and molecular sieves.

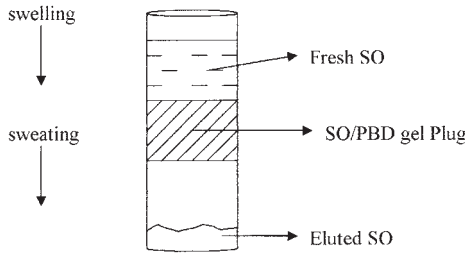

Figure 8 The use of SO/PBD gels as a molecular filtration medium for SO.

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