Chemical modification of bacterial elastomers: 1. Peroxide crosslinking

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(Received 10 December 1993)

An enhancement in the elastic response of two bacterial thermoplastic elastomers, poly(β-hydroxyoctanoate), a saturated copolymer, and poly(β-hydroxyoctanoic-*co*-undecylenic acid), an unsaturated copolymer, was attempted using peroxide crosslinking both with and without multifunctional co-agents. Sol–gel analysis verified that crosslinking had occurred and that crosslinking varied with peroxide type and concentration. A peroxide efficiency model suggested that the olefin group improved the peroxide efficiency and reduced the probability of chain scission. Differential scanning calorimetry showed that crosslinking could eliminate all crystallinity. The elastic response was improved as indicated by a reduced tensile set. In general, the crosslinked materials exhibited a decrease in tensile modulus, and a very low tensile strength and tear resistance.

(Keywords: peroxide crosslinking; *Pseudomonas oleovorans*; microbial polyester)

INTRODUCTION

Polyesters produced by bacteria (PHAs) are under intensive investigation because they are considered to be truly biodegradable polymers[1]. PHB/HV is a thermoplastic copolymer which has properties similar to polypropylene and is commercially available from ICI under the tradename BIOPOL. The polymer is produced by *Alcaligenes eutrophus* using a mixture of glucose and propionic acid feed stocks[2].

In contrast, the PHAs produced by *Pseudomonas oleovorans* are considered to be thermoplastic elastomers (TPEs)[3]. One such elastomeric copolymer, poly(β-hydroxyoctanoate) (PHO), has been studied extensively in our laboratory and has been shown to have properties similar to a commercially available elastomeric alloy type of TPE composed of polypropylene (PP) and ethylene/polypropylene/diene monomer (EPDM)[4]. The chemical structure of PHO is shown in *Figure 1*.

The elastomeric material properties of PHAs produced by *P. oleovorans* come from the long pendent groups in these copolymers. The long pendent groups influence the glass transition temperature (T_g) and degree of crystallinity. These medium length alkyl pendent groups result from the long chain carbon sources required by the bacteria to produce polymer[5–9]. The long pendent groups decrease the T_g to well below room temperature[3], thereby broadening the temperature range over which these materials are in the rubbery regime.

The degree of crystallinity is significantly reduced in PHAs produced by *P. oleovorans* because the intrusion of different repeat units in PHO disrupts the crystallinity, whereas the PHB/HV copolymers exhibit isodimorphism[3]. Random[10] copolymers are produced by *P. oleovorans* even when grown on a single carbon source, such as sodium octanoate[5–9]. Even though the copolymers are 100% isotactic, the overall degree of crystallinity is reduced to approximately 25%[3] because of the copolymer effect.

The combination of a low T_g and degree of crystallinity results in these materials exhibiting rubber-like elasticity where the crystalline regions act as the physical crosslinks for the otherwise amorphous polymer[3]. However, the crystalline regions undergo various changes upon deformation which result in substantial tensile set[4], a drawback for a material considered to be rubber-like.

The motivation behind conducting chemical crosslinking experiments on PHO and the olefin-containing copolymer poly(β-hydroxyoctanoic-*co*-undecylenic acid) (PHOU) was to improve the elastic response of these materials. The goal of chemical crosslinking was to eliminate all crystallinity and rely solely upon the chemical crosslinks for the polymer chain junction points. The chemical crosslinks would not be expected to be as susceptible to changes upon deformation.

Peroxides are commonly used to crosslink rubbers and have the advantage of being able to crosslink both saturated and unsaturated polymers[11,12]. Unsaturation is believed to increase the efficiency of the peroxide.

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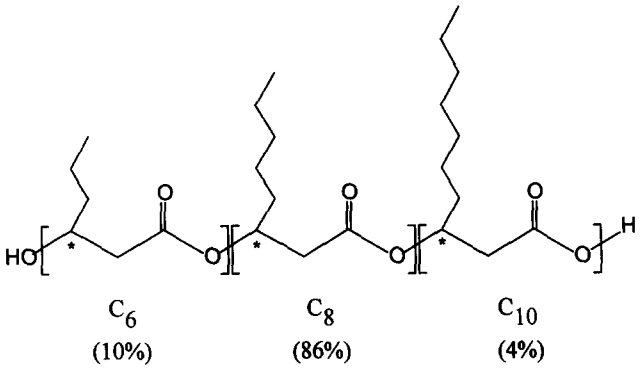

Figure 1 Chemical structure of PHO with the percentage composition of repeat units indicated: C_6, β-hydroxyhexanoate; C_8, β-hydroxyoctanoate; C_{10}, β-hydroxydecanoate

Multifunctional co-agents were also used with the peroxides in order to promote crosslinking *versus* chain scission reactions[12,13]. Vinyl specific peroxides[14] were included in an attempt to restrict the location of the crosslink to the pendent group, keeping the chiral backbone intact.

This paper discusses the use of several peroxides to produce chemical crosslinks and how the crosslinks affect the thermal properties, tensile set and mechanical properties of the polymer. The network structure of the chemical crosslinks was elucidated through the determination of the molecular weight between crosslinks. Chemical modification of several olefin-containing PHOUs using sulfur vulcanization was also attempted and is the subject of the accompanying paper (Part 2: sulfur vulcanization).

EXPERIMENTAL

Polymer biosynthesis

A fed batch biosynthesis technique was used to produce polymer from *P. oleovorans* as described in previous publications[4,15]. A New Brunswick microfermenter using a 12 l glass fermentation tank was used for all biosyntheses. A stir rate of 200 rev min^{-1}, a 5 l min^{-1} air flow rate and a temperature of 31°C were the standard growing conditions. Multiple or continuous feeding was achieved by either manually pouring in a concentrated feed solution or using a peristaltic pump and programmable timer. The optical density of the culture was determined using a Bausch and Lomb Spectronic 20 instrument.

PHO was produced when *P. oleovarans* was grown on sodium octanoate. The biosynthesis of PHOU with a controlled olefin content was accomplished by proportional mixing of two carbon sources, namely octanoic acid and 10-undecylenic acid. *Figure 2* shows the general chemical structure of PHOU. Five different compositions of PHOU were biosynthesized: 95/5, 93/7, 91/9, 80/20 and 74/26, where the first number indicates the molar percentage of saturated repeat units and the second number the molar percentage of unsaturated repeat units. The olefin contents in the copolymers were verified using either a Bruker 200 MHz or Varian 300 MHz ^1H n.m.r. spectrometer with 10 mg samples of polymer in 1 ml of deuterated chloroform.

Peroxides and multifunctional co-agents

Four different peroxides were included in the experiments: two low temperature peroxides[16], lauroyl and benzoyl, and two vinyl specific peroxides[14], dicumyl peroxide and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DBPH). Two different multifunctional crosslinking co-agents[11] were employed: a difunctional agent, ethylene glycol dimethacrylate, and a trifunctional agent, triallyl cyanurate. The chemical structures and cure temperatures and times of the peroxides and multifunctional co-agents used[13,14,16,17] are shown in *Figure 3*.

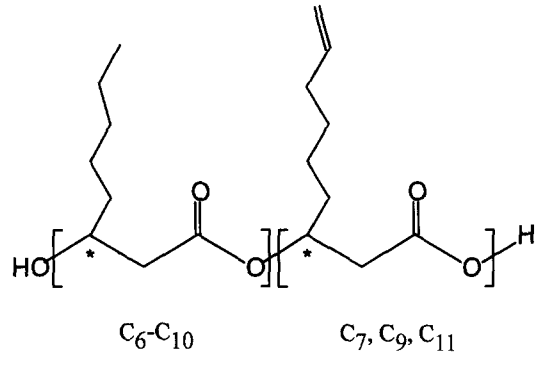

Figure 2 Chemical structure of PHOU. C_6–C_{10} and C_7, C_9, C_{11} indicate the numbers of carbon atoms in the repeat units

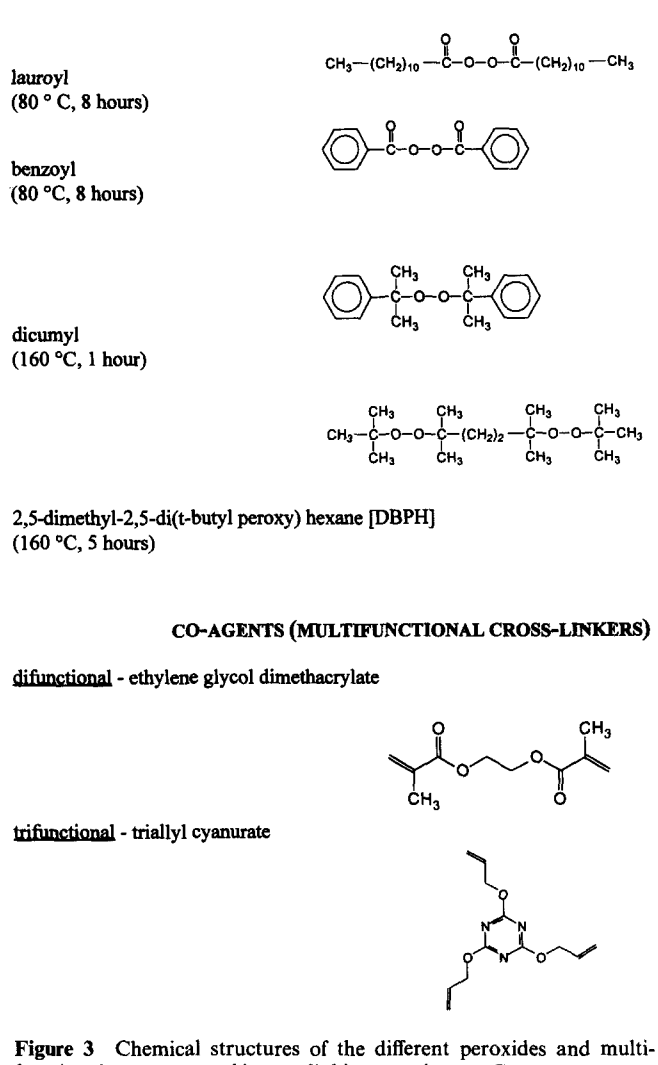

Figure 3 Chemical structures of the different peroxides and multifunctional co-agents used in crosslinking experiments. Cure temperatures and times used for each peroxide are also included

Table 1 Summary of peroxide-crosslinked samples tested (weight percentage peroxide and weight percentage co-agent/peroxide ratio listed)

		Sample							
Peroxide	Polymer	1	2	3	4	5	6	7	8
Lauroyl	PHO	0.05	0.1	0.5	1.0	1.5	2.0	3.0	4.0
1.5 wt%[a] and di[b]	PHO	15	25	50					
1.5 wt% and tri[c]	PHO	15	25	50					
	PHOU(95/5)	0.05	0.1	0.5	1.0	1.5	2.0	3.0	4.0
	PHOU(93/7)	0.5							
0.5 wt% and di	PHOU(93/7)	15	25	50					
0.5 wt% and tri	PHOU(93/7)	15	25	50					
Benzoyl	PHO	0.05	0.1	0.5	1.0	1.5	2.0	3.0	4.0
1.0 wt% and di	PHO	25							
1.0 wt% and tri	PDO	25							
	PHOU(95/5)	0.05	0.1	0.5	1.0	1.5	2.0	3.0	4.0
	PHOU(93/7)	0.1	1.0	3.0					
Dicumyl	PHOU(93/7)	0.05	0.1	0.25	0.5	1.0	1.5		
0.5 wt% and di	PHOU(93/7)	25							
0.5 wt% and tri	PHOU(93/7)	25							
	PHOU(80/20)	0.05	0.1	0.25	0.4				
	PHOU(74/26)	0.05	0.1	0.25	0.4				
DBPH	PHOU(93/7)	0.05	0.1	0.5	1.0	2.0	3.0		
0.5 wt% and di	PHOU(93/7)	25							
0.5 wt% and tri	PHOU(93/7)	25							

[a] Refers to peroxide level
[b] Ethylene glycol dimethacrylate
[c] Triallyl cyanurate

Sample preparation

PHO or PHOU, the peroxide and a multifunctional co-agent (if used) were all dissolved in chloroform and then pipetted into a glass casting dish. The solvent was allowed to evaporate over approximately one week to ensure that network formation occurred in the absence of solvent. The polymer films, typically 0.5 mm thick, were heated in a vacuum oven under either a vacuum or a nitrogen atmosphere. The cure temperature and time depended on the peroxide (see *Figure 3*). Typically, a series of four to eight different peroxide concentrations were used for each polymer. Several co-agent to peroxide concentration ratios were tested, usually at one peroxide concentration where gel formation was previously confirmed. *Table 1* summarizes the various samples tested.

Sol–gel analysis

Sol–gel analysis[18] was conducted on all films and was the primary means of determining if crosslinking had occurred. A sample of the cured film (typically 0.1–0.5 g) was weighed and placed in a round-bottomed flask containing approximately 3–10 ml of chloroform. The film was allowed to sit in the solvent for 2 h at room temperature and was agitated periodically. If a gel was present after 2 h, it was retrieved by filtering off the sol and catching it on a filter paper using a Büchner filter flask under vacuum. The gel was placed in a glass dish and dried overnight in a vacuum oven at room temperature. The gel was reweighed and the percentage of sol calculated from

$$\% \text{ sol} = \frac{\text{sol}}{\text{sol} + \text{gel}} \times 100 \qquad (1)$$

A comparative evaluation of the different peroxides and the effects of olefin groups was accomplished by using a peroxide efficiency model first developed for radiation-crosslinked polymers but extended successfully to chemical crosslinking[19]. Equation (2) was used for this purpose

$$S + S^{0.5} = p_0/q_0 + (2EM_n[\text{i}])^{-1} \qquad (2)$$

where S is the soluble fraction of partially crosslinked polymer, p_0/q_0 is the ratio of the probabilities of degradation and crosslink formation per monomer per unit initiator, E is the number of crosslinks per decomposed peroxide molecule, M_n is the number average molecular weight of the polymer prior to crosslinking and [i] is the peroxide concentration in moles per gram of polymer.

When $S + S^{0.5}$ is plotted against $(2M_n[\text{i}])^{-1}$, the inverse of the slope provides the efficiency and the y intercept yields the p_0/q_0 ratio. A y value of 2 indicates that no gel formation has occurred and the minimum peroxide concentration needed to instigate gel formation can be determined.

Gel permeation chromatography (g.p.c.)

All molecular weight data were obtained using a Rabbit model solvent delivery system with a Waters R401 differential refractometer detector and three Polymer Labs PL 5 μm gel columns with mean pore diameters of 10^5 Å, 10^4 Å and 10^3 Å (1 Å = 0.1 nm). A 2 ml min^{-1} tetrahydrofuran flow rate was used with a toluene flow marker. The molecular weight was based on polystyrene standards.

Thermal analysis

Differential scanning calorimetry (d.s.c.) was conducted using a TA Instruments 2910. Samples were tested from −85 to 100°C at a 20°C min^{-1} heating rate. The glass transition temperature reported was at the inflection point. The melting temperature reported was the peak temperature.

Thermogravimetric analysis (t.g.a.) was conducted using a TA Instruments 2950. T.g.a. was conducted in both air and nitrogen atmospheres from 30 to 500°C at a 20°C min^{-1} heating rate. Degradation temperatures are reported as the onset temperature of weight loss.

Tensile set/tensile modulus

All testing was conducted using an Instron TTBM. Strip samples approximately 2–5 mm wide by 20–40 mm long were used. Tensile set testing was based on the procedures described in ASTM D412-87[20]. The samples were extended at a 1 or 2 min^{-1} strain rate and held for 10 min at the intended elongation, then released at the same strain rate. The samples were then allowed to recover for 10 min prior to final measurement of the recovery. The tensile modulus was determined from the initial slope of the stress–strain curve obtained during the tensile set testing.

Impulse viscoelasticity

Impulse viscoelasticity, a dynamic mechanical technique, affords direct measurement of the equilibrium shear modulus[21] G_{eq}. A double-lap shear sample geometry was used. After a baseline was established, a small, known step strain was placed on the sample for a duration of 10 s and then released. The material was allowed to relax for 60–120 s before another pulse was applied. The relaxation times were chosen to ensure that the material had ample time to relax back to the established baseline. The stress and strain were integrated over the entire pulse and relaxation time and the equilibrium modulus G_{eq} was calculated from

$$G_{eq} = \int_0^\infty \sigma \, dt \Big/ \int_0^\infty \gamma \, dt \qquad (3)$$

where σ is the engineering shear stress and γ is the angle of strain (deformation/thickness). From G_{eq}, the molecular weight between crosslinks M_c can be calculated using

$$M_c = \frac{\rho RT}{G_{eq}} \qquad (4)$$

where ρ is the polymer density[3] (1.019 g ml^{-1}), $R = 8.21 \times 10^6$ ml Pa mol^{-1} K^{-1} and $T = 298$ K.

Several samples while still mounted in the apparatus were heated above the melting temperature, allowed to cool and were then retested. A significantly reduced equilibrium shear modulus after the heat treatment would indicate that crystallites had been present.

RESULTS AND DISCUSSION

PHO

The biosynthesis and characterization of the PHO used in this study have been described in previous publications[4,15].

PHOU

Previous studies have indicated that pure undecylenic acid produces polymers with 100% unsaturation[22]. A mixture of octanoic and undecylenic acids was used to produce a PHA with a controlled olefin content. The olefin content was established by ^{1}H n.m.r. analysis and the results indicate that the amount of olefin in the mixed carbon source feed directly correlates with the amount of olefin in the polymer, as shown in *Figure 4*.

Table 2 summarizes the characterization results for the different olefin-containing polymers compared to PHO. The glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) all tend to decrease as the amount of olefin in the copolymer increases. These results are as expected because of the change in structure caused by the incorporation of many more repeat units and repeat units with long pendent groups. These changes in structure will disrupt the ability of the copolymer to crystallize and thus lower the heat of fusion. A lower melting temperature would occur if the crystallites that did form were smaller. Some scatter was observed because the T_m and ΔH_m are dependent on the crystallization history[23], and not all samples were crystallized for the same length of time. As was shown by Marchessault *et al.*[3], long pendent groups tend to decrease the T_g.

The other characterization results show that the thermal decomposition temperature as measured by thermogravimetric analysis did not change significantly for the olefin-containing polymer. The molecular weight distribution of the PHOUs was broadened slightly.

Sol–gel analysis

The sol–gel analysis results are shown for several peroxide cures. *Figure 5* depicts the results for PHO crosslinked with lauroyl peroxide and benzoyl peroxide both with and without co-agents. *Figure 6* shows the results for PHOU(93/7) crosslinked with lauroyl peroxide benzoyl peroxide, DBPH and dicumyl peroxide, including the effect of co-agents.

A crosslinked material did result in all cases as long as enough peroxide was used. The sol content at first decreased as the amount of peroxide increased. This trend was followed by a levelling off of sol content even though the peroxide concentration was increased further. The final sol content was non-zero, indicating that there was always some polymer not incorporated into the gel no

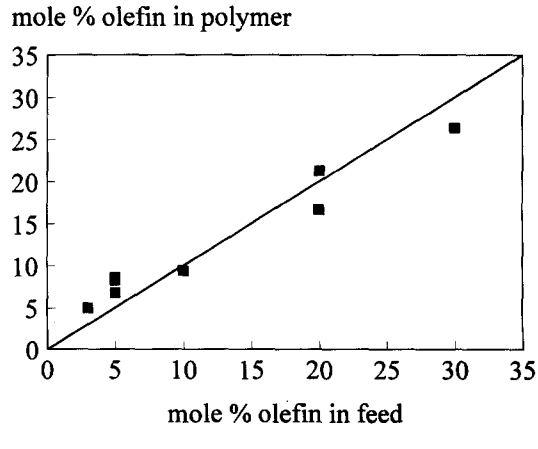

Figure 4 PHOU olefin content as a function of feed composition for *P. oleovorans* grown on a mixture of octanoic and 10-undecylenic acids

Table 2 Characterization results for several PHOUs (PHO included for comparison)

Technique	PHO	PHOU 93/7	PHOU 91/9	PHOU 80/20	PHOU 74/26
D.s.c.					
T_g (°C)	−35	−34	−33	−38	−40
T_m (°C)	61	59	58	53	49
ΔH_m (J g^{-1})	15	22	20	14	13
T.g.a.					
T_{onset} air (°C)	297		285		
T_{onset} N_2 (°C)	290		280		
G.p.c.					
M_w (g mol^{-1})	161 000	165 000	148 000	168 000	172 000
N_n (g mol^{-1})	86 000	62 000	64 000	80 000	68 000
Polydispersity index (PDI)	1.9	2.7	2.3	2.1	2.5

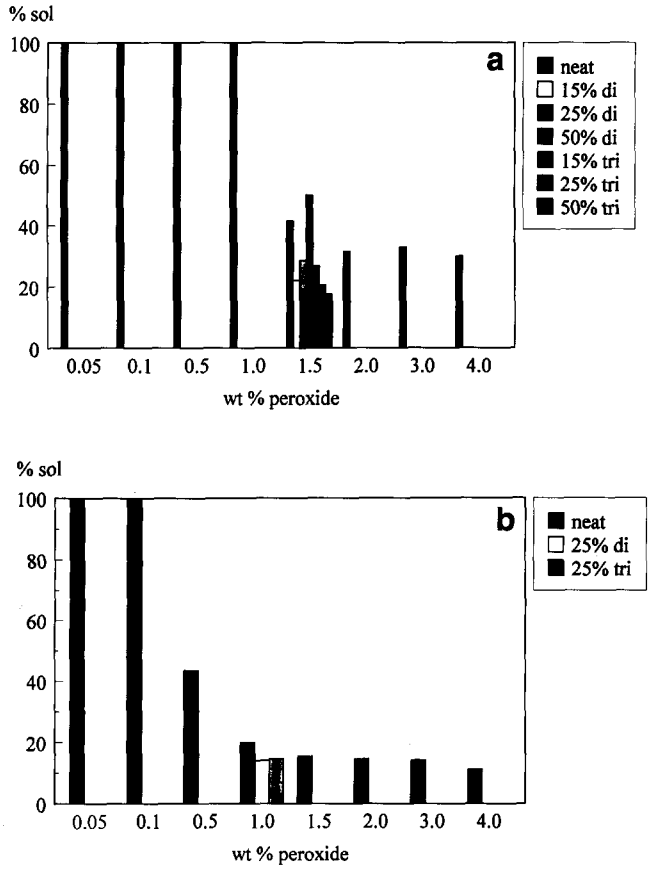

Figure 5 Sol–gel analysis results for PHO crosslinked with (a) lauroyl peroxide and (b) benzoyl peroxide both with and without co-agents (di = difunctional co-agent, tri = trifunctional co-agent). Percentages indicate the co-agent to peroxide weight ratios

matter how much peroxide was used. Perhaps a loss of chain mobility prevented total gel formation or perhaps this sol was the result of chain scission reactions. A molecular weight analysis using gel permeation chromatography was conducted on the sol fraction to try and address this issue and will be discussed later.

The effect of the co-agent on the extent of gel formation was complex and depended on the amount and type of co-agent and which peroxides were used. For the non-vinyl specific peroxides, lauroyl peroxide and benzoyl peroxide, the addition of co-agents generally improved the crosslinking reaction in that lower amounts of extractables were recovered. This was true independent of whether saturated or unsaturated polymers were used. In contrast, the vinyl specific peroxides with co-agents resulted in a higher amount of sol, sometimes a dramatic increase as was the case for DBPH (see *Figure 6b*). Perhaps the vinyl specific peroxides were capable of homopolymerizing the co-agents. This undesired side reaction would consume the co-agents, thus increasing the sol content by both precluding the desired gel formation and creating an extractable homopolymer.

Several PHOUs with a broad range of olefin contents were crosslinked with dicumyl peroxide to study the effect of olefin content on gel formation. The results are shown in *Figure 7*. Higher olefin content copolymers generally resulted in lower amounts of extractables; however, very brittle gels were formed which were difficult to retrieve for final weighing. This problem would account for the higher than expected sol content and data scatter.

Efficiency determination

The peroxide efficiency model allows comparison of peroxides using two criteria. The first criterion is the amount of peroxide required to crosslink the polymer, which implies the efficiency of the thermal degradation of the peroxide to produce viable free radicals that are not susceptible to non-productive side reactions. The second criterion is whether the free radicals cause more chain scission than crosslinking.

Figure 8 shows the typical plots obtained when using the peroxide efficiency model for PHO, PHOU(95/5) and PHOU(93/7) crosslinked with benzoyl peroxide. As the amount of olefin was increased, the efficiency of peroxide crosslinking improved (smaller slope) and the tendency for degradation to occur decreased (smaller y intercept).

The results for PHOU(93/7) crosslinked with lauroyl, benzoyl and dicumyl peroxides and DBPH are shown in *Figure 9*. This comparison shows that dicumyl peroxide was the most efficient peroxide, while DBPH showed the least tendency towards degradation. A compilation of the model results is given in *Table 3*.

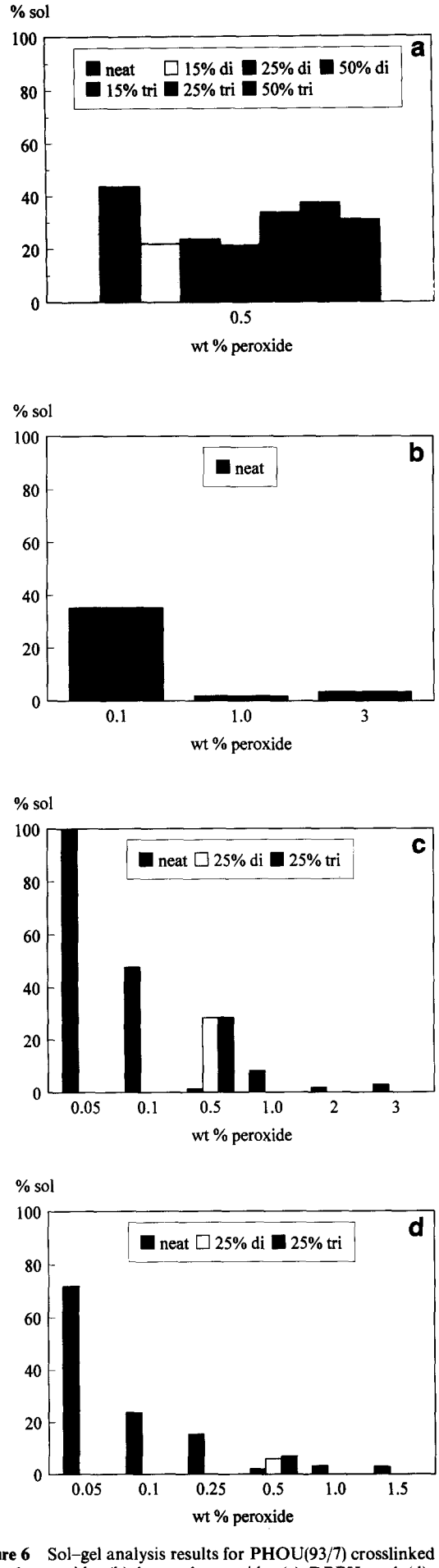

Figure 6 Sol–gel analysis results for PHOU(93/7) crosslinked with (a) lauroyl peroxide, (b) benzoyl peroxide, (c) DBPH and (d) dicumyl peroxide both with and without co-agents

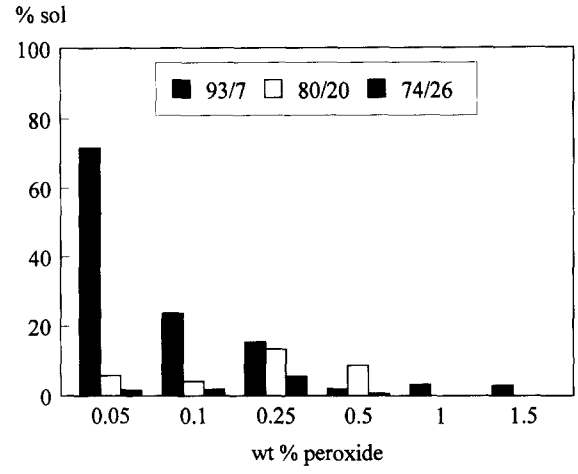

Figure 7 Sol–gel analysis results for several PHOUs with varying olefin content crosslinked with dicumyl peroxide

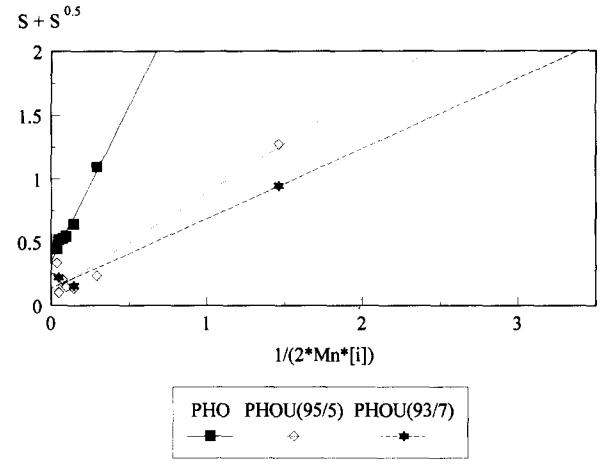

Figure 8 Comparison using the peroxide efficiency model between PHO, PHOU(95/5) and PHOU(93/7) crosslinked with benzoyl peroxide

Gel permeation chromatography

To determine if heating the neat copolymers would alter the molecular weight distribution, g.p.c. analysis was done both before and after heating the neat copolymers at temperatures and for times used during peroxide crosslinking. The results are tabulated in *Table 4* and they indicate that simply heating the neat copolymers decreased the molecular weight and altered the molecular weight distribution. Interestingly, neat PHOU(80/20) formed a crosslinked gel solely from heating, and therefore g.p.c. analysis could not be conducted. Therefore, the neat polymers under thermal conditions which mimic the peroxide crosslinking conditions are not thermally stable and degradation would be occurring concurrently with the crosslinking reactions.

Several sol fractions extracted from the crosslinked polymers were evaluated for molecular weight distribution. The samples chosen represented levels of peroxide where low levels of extractables were found; in the case of lauroyl peroxide, the sample represented the highest level of peroxide. Molecular weight analysis of these sols would help determine if chain scission had occurred. If chain scission had occurred, a very low molecular weight fraction, lower than observed for the non-crosslinked polymer, would be expected.

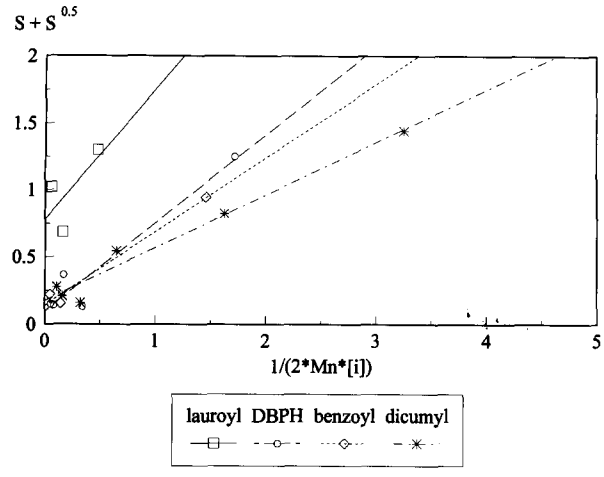

Figure 9 Comparison using the peroxide efficiency model between samples of PHOU(93/7) crosslinked with lauroyl peroxide, benzoyl peroxide, dicumyl peroxide and DBPH

Table 3 Summary of peroxide efficiency model results for peroxide-crosslinked PHO, PHOU(95/5) and PHOU(93/7)

Polymer	Peroxide	Peroxide efficiency E	Ratio of probabilities of degradation to crosslink formation p_o/q_o
PHO	Lauroyl	0.55	0.73
	Benzoyl	0.41	0.35
PHOU(95/5)	Lauroyl	1.04	0.21
	Benzoyl	1.28	0.11
PHOU(93/7)	Lauroyl	1.03	0.78
	Benzoyl	1.82	0.14
	DBPH	1.52	0.10
	Dicumyl	2.54	0.17

Table 4 Summary of g.p.c. results for neat PHO and PHOU(93/7) both before and after heating

Polymer	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI
PHO	110 000	44 000	2.5
PHO 80°C, overnight	89 000	34 000	2.6
PHOU(93/7)	165 000	62 000	2.6
PHOU(93/7) 80°C, overnight	80 000	29 000	2.8
PHOU(93/7) 160°C, 1 h	72 000	36 000	2.0

Figure 10 and *Table 5* summarize the g.p.c. results for the sol fractions extracted after peroxide crosslinking PHOU(93/7) with several different peroxide and co-agent combinations. The sol fraction molecular weight distribution for lauroyl peroxide crosslinked PHOU(93/7) revealed M_w and M_n values that were higher and broader than the original polymer with a definite high molecular weight shoulder observed. These results imply that chain extension had occurred, but from the high sol content the extent of reaction was not sufficient to produce a continuous gel even with the high concentration of peroxide used. Or perhaps as a gel was forming, chain scission reactions split off pieces of the gel which would appear as higher molecular weight fractions.

The peroxide efficiency model indicated that lauroyl peroxide has a very high probability (0.78) of producing chain scission reactions (see *Table 3*). Such a high probability of chain scission reactions would most likely produce a sol with a low molecular weight fraction. From this argument, it appears that the g.p.c. data do not corroborate the model predictions for this combination of reactants.

When the difunctional co-agent was used in conjunction with PHOU(93/7) and lauroyl peroxide, the g.p.c. analysis of the extracted sol revealed a main peak with a molecular weight distribution similar to the neat polymer and an additional small, very low molecular weight peak (see *Table 5*). The low molecular weight peak may be a sign that chain scission had occurred, or possibly that partial homopolymerization of the co-agent had taken place.

The use of benzoyl peroxide at a 1.0 wt% level resulted in a very small sol fraction (2%). The g.p.c. analysis of the sol fraction shown in *Table 5* reveals a very low molecular weight peak, lower than any fraction found in the original polymer. These results suggest that some chain degradation had occurred during the crosslinking reaction.

The g.p.c. chromatogram of the sol obtained from the dicumyl peroxide crosslinked polymer is shown in *Figure 10*. Again, a molecular weight peak lower than the original polymer suggests that some chain degradation had occurred even with the relatively low peroxide concentration.

The use of the difunctional co-agent with DBPH and PHOU(93/7) produced a very large sol content, higher

Table 5 G.p.c. results of neat PHOU(93/7) and various sol fractions extracted after peroxide crosslinking with the indicated peroxides and co-agents

PHOU(93/7) with	M_w (g mol^{-})	M_n (g mol^{-1})	PDI
No additives	165 000	62 000	2.6
4.0 wt% lauroyl peroxide (sol 39%)	327 000	88 000	3.7
0.5 wt% lauroyl peroxide and difunctional co-agent (sol 24%)	146 000 875	51 000 740	2.9 1.2
1.0 wt% benzoyl peroxide (sol 2%)	855	720	1.2
0.5 wt% dicumyl peroxide (sol 2%)	650	490	1.3
0.5 wt% DBPH and difunctional co-agent (sol 28%)	133 000 860	32 000 720	4.2 1.2

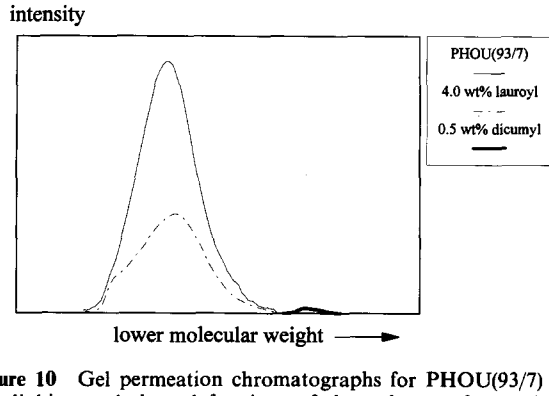

Figure 10 Gel permeation chromatographs for PHOU(93/7) before crosslinking and the sol fractions of the polymer after undergoing peroxide crosslinking with different peroxide and co-agent combinations

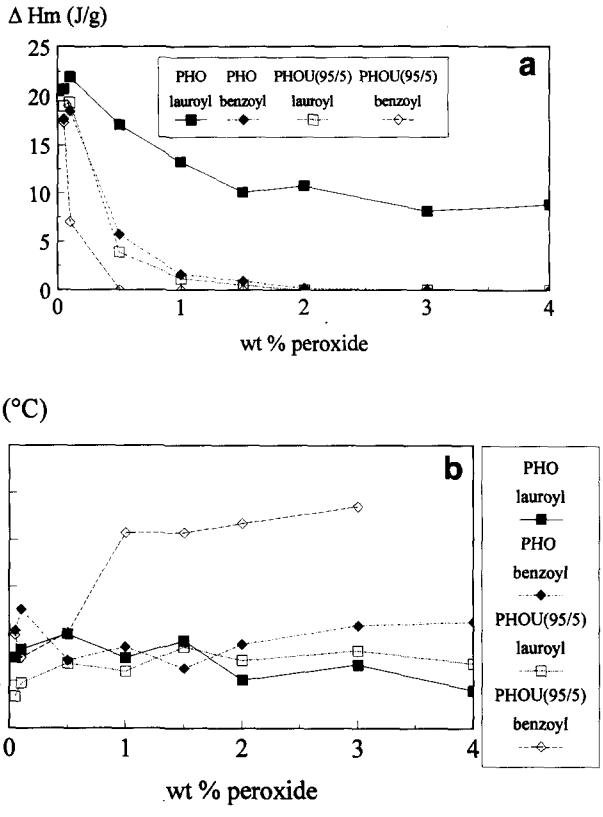

Figure 11 D.s.c. results for (a) heat of fusion and (b) glass transition temperature for PHO and PHOU(95/5) crosslinked with lauroyl peroxide and benzoyl peroxide

than that found without the co-agent (refer to *Figure 6c*). Analysis of the sol fraction did not reveal the cause of the high sol content. The g.p.c. results on the sol fraction were similar to those obtained for PHOU(93/7) crosslinked with lauroyl peroxide and the difunctional co-agent, where both a main peak with similar molecular weight to the neat polymer and a very low molecular weight peak were observed.

Thermal analysis

One goal of chemical crosslinking was to eliminate crystallinity totally and rely solely on a chemically crosslinked network for the elastic response. Thermal analysis was conducted on many of the cured films to determine if peroxide crosslinking was successful in eliminating crystallinity. If enough chemical crosslinking is present, crystallinity should be eliminated because of a reduction in chain entropy. An increase in the glass transition temperature could also result from chemical crosslinking.

Figure 11 shows the d.s.c. results for both PHO and PHOU(95/5) crosslinked with lauroyl and benzoyl peroxides. *Figure 11a* shows that as the weight percentage of peroxide is increased, the crystallinity, which is proportional to the heat of fusion, is reduced or eliminated. The amount of peroxide needed to eliminate all crystallinity varied with the peroxide and polymer olefin content. For either polymer, benzoyl peroxide was required in smaller amounts to eliminate crystallinity compared to lauroyl peroxide. Unsaturation drastically decreased the amount of peroxide required to eliminate crystallinity. In contrast, not even the highest lauroyl peroxide concentration tested was sufficient to eliminate all crystallinity in PHO.

It is interesting that the addition of 5% olefin groups should so dramatically improve the efficiency of the crosslinking reaction and allow elimination of crystallinity at a much lower peroxide concentration. The disappearance of crystallinity at lower peroxide levels agrees with the efficiency model results, which indicated that less peroxide was needed to crosslink olefin-containing polymers.

Several samples of PHOU(93/7) crosslinked with DBPH were tested for the presence of crystallinity while mounted in the impulse viscoelasticity test apparatus, as described earlier. The results indicated that all crystallinity was eliminated at and above a 0.5 wt% peroxide concentration.

The glass transition temperature can increase as crosslinking occurs, owing to the added constrains crosslinks impose on the polymer chains. *Figure 11b* shows the effect on the T_g of several crosslinked systems. Only PHOU(95/5) crosslinked with benzoyl peroxide showed a significant increase in the glass transition temperature after crosslinking.

Thermogravimetric analysis of both non-crosslinked and peroxide-crosslinked polymers revealed that no significant change in the decomposition temperature associated with weight loss had occurred as a result of the peroxide crosslinking. The onset of weight loss occurred at approximately 290°C for all samples tested, which included PHO and PHOU(95/5) both non-crosslinked and crosslinked with lauroyl and benzoyl peroxides and PHOU(93/7) non-crosslinked. The shapes of all the decomposition curves were also similar. A typical thermal decomposition curve has been published previously[4]. These results show that thermal decomposition can appear to occur at dramatically different temperatures depending on whether weight loss or changes in the molecular weight distribution are considered.

Tensile set

Another goal of chemical crosslinking was to improve the elastic response of the material. Peroxide crosslinking did dramatically improve the elastic response of the polymers, as shown in *Figures 12a* and *12b*. The results show that as the amount of peroxide was increased, the tensile set was reduced significantly. For example, PHOU(95/5) cured with 0.5 wt% lauroyl peroxide showed more than an 80% decrease in tensile set (from 57 to 9.8%) after being elongated 100% (see *Figure 12b*).

However, as the peroxide levels were increased, the tensile strength, tear resistance and elongation to break decreased drastically for most films, as shown by the lack of data at high elongations or high peroxide levels in *Figure 12b*. The material integrity had been compromised by the crosslinking which resulted in materials with little or no tensile strength and poor tear resistance, best described as 'cheesy'.

The choice of peroxide influenced this phenomenon. Whereas most films with lauroyl peroxide could be tested, the number of testable films was reduced when benzoyl peroxide was used. Sample films cured with DBPH or dicumyl peroxide could not be removed from the glass casting dishes intact, so tensile set evaluations were impossible.

The effect of the olefin group was even more dramatic in decreasing the testable peroxide levels and ultimate

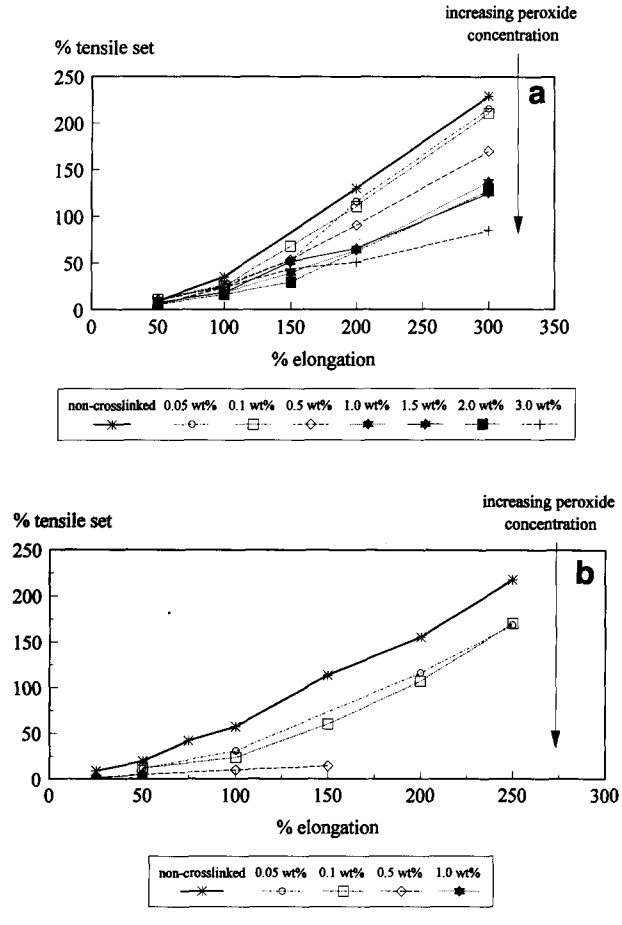

Figure 12 Typical tensile set results for (a) PHO and (b) PHOU(95/5), both crosslinked with lauroyl peroxide. Non-crosslinked polymer results are also included for comparison

elongations achievable in the cured films, as shown in *Figure 12b*. PHO films cured with lauroyl peroxide could be evaluated up to 3.0 wt% peroxide, but PHOU(95/5) could be tested only up to 1.0 wt% peroxide. PHO crosslinked with 0.1 wt% benzoyl peroxide could be tested up to 300% elongation, but PHOU(95/5) could be tested only up to 150% elongation. Why the addition of 5% olefin groups to the polymer should so drastically change the crosslinking reaction and produce such a 'cheesy' material is not understood. The peroxide efficiency model had indicated that the addition of olefin groups would reduce the probability of degradation.

One explanation for the general loss of material integrity upon crosslinking could be that the gain of chemical crosslinks did not offset the loss of crystallinity. To explore this idea, higher olefin content polymers, PHOU(80/20) and PHOU(74/26), were biosynthesized. If more olefin groups provided more crosslinks, perhaps the loss of material integrity associated with the loss of crystallinity would be surmounted. These polymers were crosslinked with several different concentrations of dicumyl peroxide. However, these materials still displayed very poor mechanical integrity.

Tensile properties

Only the modulus could be determined from the strip samples cut from the films. Ultimate properties could not be determined since the strip samples broke at the grips. *Figure 13* shows the modulus as a function of weight percentage peroxide for PHO, PHOU(95/5) and PHOU(93/7) crosslinked with various peroxides. Again, results could only be obtained on a limited number of samples because of the lack of material integrity. The results show a large decrease in the modulus as the amount of peroxide is increased.

Only PHO crosslinked with lauroyl peroxide could be tested at most peroxide levels. As mentioned earlier, this combination of polymer and peroxide never totally eliminated all crystallinity even at the highest peroxide concentrations. Since crystallites impart a filler effect as well as physical crosslinks, a decrease in modulus would be expected as the amount of crystallinity decreased. However, an increase in modulus would be expected as the crosslink density increased. These observations support the argument that the gain of chemical crosslinks did not offset the loss of crystallinity, resulting in a material with lower modulus and compromised integrity.

Network structure

The network structure, as revealed by the molecular weight between crosslinks M_c, was determined for PHOU(93/7) crosslinked with DBPH using the impulse viscoelasticity technique and equation (4). M_c was estimated at 2400–3000 g mol^{-1} for the polymers crosslinked with 0.5–2.0 wt% peroxide.

CONCLUSIONS

Peroxide crosslinking was successful in producing a gel. The crystallinity was reduced or eliminated and the tensile set was reduced in the samples tested. However, the loss of tensile strength and tear resistance was a general feature of peroxide-crosslinked PHO, and especially PHOU, both with and without multifunctional co-agents.

It is believed that the gain of chemical crosslinks was not substantial enough to overcome the loss of crystallinity in providing mechanical integrity to the material even when high olefin content PHOUs were used. It is possible that chain scission was a factor in reducing material integrity through the β scission mechanism. Many potential tertiary radical sites could form if a hydrogen atom was abstracted from the backbone of PHO at the pendent group location, similar to the

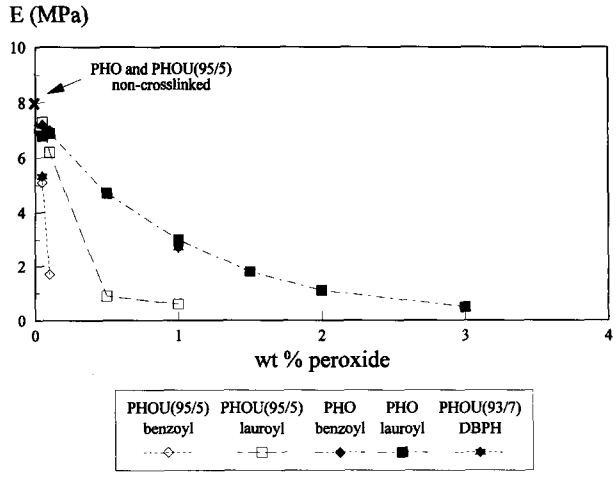

Figure 13 Tensile modulus as a function of peroxide concentration. Samples in the form of strips were tested at a strain rate of 2 min^{-1}

potential tertiary sites in polypropylene as compared to polyethylene[13]. This suspicion appears plausible, although the peroxide efficiency model did not indicate that chain scission was a large factor.

Perhaps the 'vinyl specific' peroxides which had been identified as vinyl specific for silicones are not vinyl specific for polyesters and random crosslinking (and chain scission) had occurred. This is supported by the g.p.c. analysis conducted on the sol, which showed that a very low molecular weight fraction was present after the crosslinking reaction.

Another explanation may be the detrimental effect of chain ends, which would be more pronounced in a random crosslinking reaction. Generally, synthetic rubbers which are to be peroxide crosslinked must have a high molecular weight of the order of 200 000–500 000 g mol^{-1}. The high molecular weight is required to overcome the network defects introduced by chain ends[12]. The bacterial polyesters used have substantially lower molecular weights, approximately 80 000 g mol^{-1}.

Improvement of the material properties may be possible by using fillers such as fumed silica or carbon black. The use of fillers for mechanical property improvement is common from many crosslinked synthetic rubbers[24].

Biodegradation studies are underway on the chemically modified materials. Alteration of the material properties should not preclude biodegradation.

ACKNOWLEDGEMENTS

We thank the Office of Naval Research (grant N00014-86K-0369), Procter and Gamble (Cincinnati), the National Science Foundation and the Focused Giving Program from Johnson & Johnson (R.W.L., R.C.F.) for their financial support. Special thanks to Ed Knee and Erik Bouquet for help in polymer production and Dr Charlie Dickinson and Joanne Curley for ^{1}H n.m.r. analyses.

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