Chemical modification of bacterial elastomers: 2. Sulfur vulcanization

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Enhancement in the elastic response of a bacterial thermoplastic elastomer, poly(β-hydroxyoctanoic-*co*-undecylenic acid), containing varying amounts of unsaturation was attempted through sulfur vulcanization. Sol–gel analysis verified that crosslinking had occurred and that crosslinking varied with vulcanizing agent type and concentration. Differential scanning calorimetry showed that crosslinking could eliminate all crystallinity. The elastic response was near ideal with less than a 5% tensile set after 200% elongation. In general, sulfur-vulcanized materials exhibited a decrease in tensile modulus, tensile strength and tear resistance which did not appear to vary with crosslink density. Unlike the case of peroxide crosslinking, material integrity was left intact and mechanical property results are reported. The network structure was elucidated through the determination of the molecular weight between crosslinks.

(Keywords: sulfur vulcanization; crosslinking; microbial polyester)

INTRODUCTION

Many of the microbial polyesters produced by *Pseudomonas oleovorans* have the properties of thermoplastic elastomers (TPEs).[1] One such elastomeric copolymer, poly(β-hydroxyoctanoate) (PHO), has been studied extensively in our laboratory. This material has been shown to have properties similar to those of the commercially available elastomeric alloy TPEs consisting of polypropylene (PP) and ethylene/propylene/diene monomer (EPDM), except that the elastic response of the as-extracted microbial TPEs is only fair[2]. The crystalline regions, which act as the physical crosslinks in PHO, change upon deformation, as does the overall extent of crystallinity, and these changes result in substantial tensile set, namely 35% after 100% elongation.

The motivation behind conducting chemical crosslinking experiments on microbial TPEs 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 as susceptible to physical changes upon deformation. As described in the previous paper, peroxides are successful crosslinking agents, but the materials show little or no tensile strength or tear resistance after cure. The substantial decrease in material integrity may have been caused in part by chain scission, a common problem with free radical chemistry.

The use of sulfur crosslinking or vulcanization was then attempted and is the topic of this report. An olefin-containing polymer is essential for sulfur crosslinking. Fortunately, *Pseudomonas oleovorans* can produce an olefin-containing polymer when fed an appropriate carbon source. For this study, a mixture of carbon sources was used to control the amount of olefin in the polymer poly(β-hydroxyoctanoic-*co*-undecylenic acid) (PHOU). *Figure 1* shows the chemical structure of PHOU.

A comparison between peroxide crosslinking and sulfur vulcanization is made in *Table 1*. Sulfur vulcanization would not be expected to degrade the material as much during the vulcanization reaction, and the location of the crosslink should be limited to the olefin group. These are definite advantages over peroxide crosslinking. One major disadvantage of sulfur vulcanization is the need for many additives in the vulcanization process.

Although elemental sulfur alone was first used to vulcanize natural rubber, accelerated sulfur cures are predominately used today[3–5]. Elemental sulfur, which has a tendency to form non-productive, cyclic sulfur linkages, has been replaced by sulfur-donating vulcanizing agents which require accelerators and accelerator activators to optimize the cure cycle and properties. An empirical approach appears to be the most widely used method of optimizing the amount and combination of these crosslinking agents to produce the required properties.

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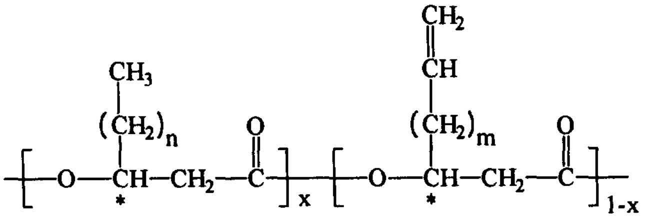

Figure 1 Structure of poly(β-hydroxyoctanoic-*co*-undecylenic acid) ($n=3$–7, $m=2,4,6$)

Table 1 Comparison between peroxide and sulfur processes used to crosslink PHOU

Peroxide	Sulfur
Crosslinks both saturated and unsaturated polymers	Crosslinks only unsaturated polymers
Reaction site less predictable except with 'vinyl specific' peroxides	Reacts only with unsaturated moiety
Controlled cure temperature through choice of peroxide	Generally higher cure temperatures required
Expensive chemicals	Less expensive chemicals
Free radical chemistry can cause chain scission reactions	Chain scission reduced
Transparent films	Opaque tan films

This report describes the results of sulfur vulcanization of several PHOUs with varying levels of unsaturation. Different vulcanizing agents, accelerators and accelerator activators were examined. Cure curves were obtained with a rheometer and crosslinking was verified from a sol–gel analysis. Thermal properties were evaluated after cure using differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). Mechanical property and elastic response evaluations were conducted on several vulcanizates. The network structure of the cured rubbers was elucidated through the determination of the molecular weight between crosslinks. Ageing effects of the rubber were also evaluated.

EXPERIMENTAL

Many of the experimental techniques used for this study are described in the previous paper on peroxide crosslinking and will not be repeated here. Included in this section is a description of the polymers studied, reagents used and the additional experimental techniques applied to the sulfur-vulcanized samples.

Polymer biosynthesis

Four different compositions of PHOU were biosynthesized for sulfur vulcanization: 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. More details on the biosynthesis and characterization are given in the previous paper.

Sulfur vulcanization compounds

Two different vulcanizing agents, elemental sulfur and dipentamethylenethiuram tetra/hexasulfide (DPTT), were used. Four different accelerators – zinc dibutyldithiocarbamate/di-n-butylamine combination (ZBUDX), zinc dibutyldithiocarbamate (BZ), 2-benzothiazolesulfenamide (BBTS) and 2,2′-dibenzothiazyl disulfide (MBTS) – were employed. Finally, two compounds to act as accelerator activators, zinc oxide and stearic acid, were included in this study*. Therefore, to cure a sample, four different compounds were required: a vulcanizing agent, an accelerator and the two accelerator activators. *Figure 2* shows the chemical structures and required cure temperatures for the different compounds.

Sample preparation

Approximately 0.5 g (or 4 g for samples which underwent full mechanical property evaluation) of PHOU(91/9), PHOU(93/7), PHOU(80/20) or PHOU(74/26) was softened by heating the polymer in a watchglass, then the polymer was allowed to cool. All the sulfur vulcanization ingredients were kneaded into the softened polymer which was then formed into a ball in preparation for curing.

For the 0.5 g samples, the vulcanization curing process was monitored with a Rheometrics RMS or RDS II rheometer using a parallel plate geometry and a frequency of 2–5 rad s^{-1} at a cure temperature appropriate for the specific chemistry (see *Figure 2*). The sample was loaded onto the preheated bottom plate. The plates were closed

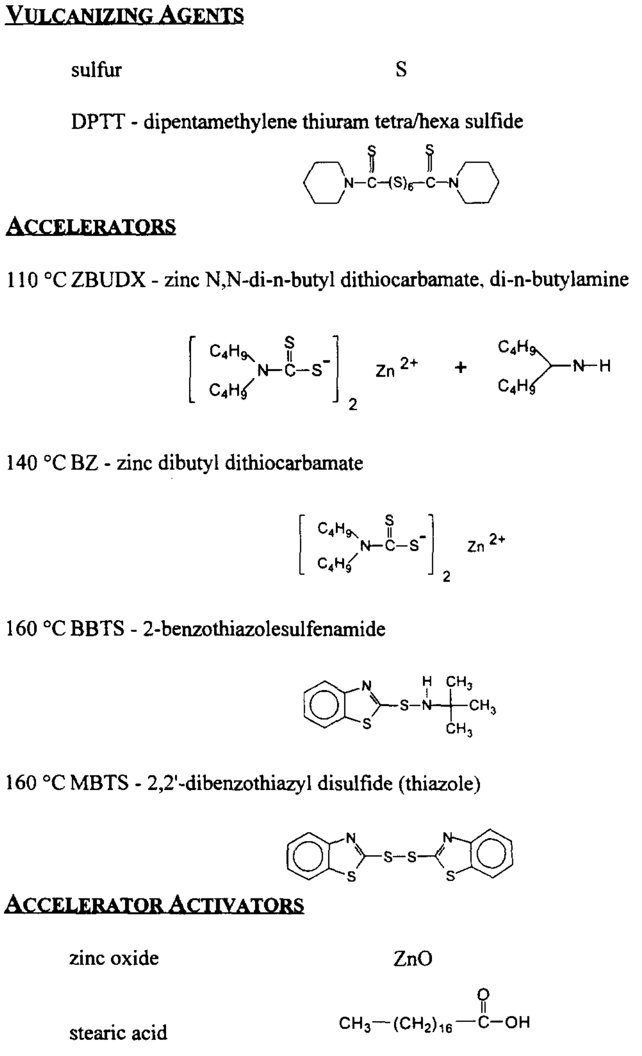

Figure 2 Structures of the various sulfur vulcanization chemicals grouped as vulcanizing agents, accelerators and accelerator activators. The required cure temperatures are indicated for the different accelerators

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* Recommended and supplied by Chuck Lamb of Akrochem

Table 2 Sulfur vulcanization samples tested[a]

		Sample				
Reagents	Ingredients	1	2	3–6	7–9	10–12
DPTT and BZ	PHOU	(91/9)	(95/5)	(91/9)	(80/20)	(74/26)
	DPTT	1	2	2.5, 3.5, 4.5, 5.5	3.5, 4.5, 5.5	3.5, 4.5, 5.5
	BZ	0.5	0.5	0.5	0.5	0.5
	Zinc oxide	3	3	5	5	5
	Stearic acid	1	1	3	3	3
S and ZBUDX	PHOU	(91/9)	(93/7)	(93/7)		
	S	2	3	3		
	ZBUDX	1.5	1.5	3		
	Zinc oxide	5	5	5		
	Stearic acid	2	2	2		
DPTT and ZBUDX	PHOU	(93/7)	(93/7)	(93/7)		
	DPTT	3	3	2.5		
	ZBUDX	2	1	1		
	Zinc oxide	3	3	3		
	Stearic acid	1	1	1		
DPTT and BBTS	PHOU	(93/7)	(93/7)	(93/7)		
	DPTT	3	2.5	3		
	BBTS	1.5	1.5	1.5		
	Zinc oxide	5	5	5		
	Stearic acid	2	2	2		
S and BBTS	PHOU	(93/7)				
	S	2				
	BBTS	1.5				
	Zinc oxide	5				
	Stearic acid	2				
DPTT and MBTS	PHOU	(93/7)	(93/7)			
	DPTT	3	3			
	MBTS	1.5	1.5			
	Zinc oxide	5	5			
	Stearic acid	2	2			
S and MBTS	PHOU	(93/7)				
	S	2				
	MBTS	1.5				
	Zinc oxide	5				
	Stearic acid	2				

[a] Values given are phr, parts per hundred rubber, where polymer used is 100 phr

to give typically a 0.5–1 mm gap. The storage modulus was monitored as a function of time. *Table 2* summarizes the various samples tested.

For tensile property and tensile set testing, 4 g samples of PHOU(93/7), PHOU(80/20) and PHOU(74/26) were placed in a 140 mm diameter mould, 0.25 mm thick, and compression moulded and cured using a preheated Carver press set at 140°C. The vulcanization time was determined from the rheometry experiments. The cured films were dusted with talc for easier handling.

Tensile testing

All tensile testing was conducted using an Instron TTBM with an Interface SM-10 load cell. Ring samples as per ASTM D412-87[6] (type 2) were punched from the films using a steel rule die and Carver hot press Model C at room temperature. Special grips were made to hold the ring specimens. The ring was supported at each end by a pin, approximately 5 mm in diameter. Each pin was engaged at both ends in the inner track of a ball bearing to ensure that the stress and strain remained equal on both sides of the ring during testing. The pins were removable for loading the sample. The initial gauge length was based on half the average circumference of the ring die. A strain rate of 1 min^{-1} was used for all tensile tests.

RESULTS AND DISCUSSION

Polymer biosynthesis and characterization

The characterization results for the olefin-containing PHOUs are reported in the previous paper on peroxide crosslinking.

Vulcanization

The vulcanization process was typically monitored using a modified rheometer termed a 'cure meter' (ASTM D2084-88), which measures the torque as a function of

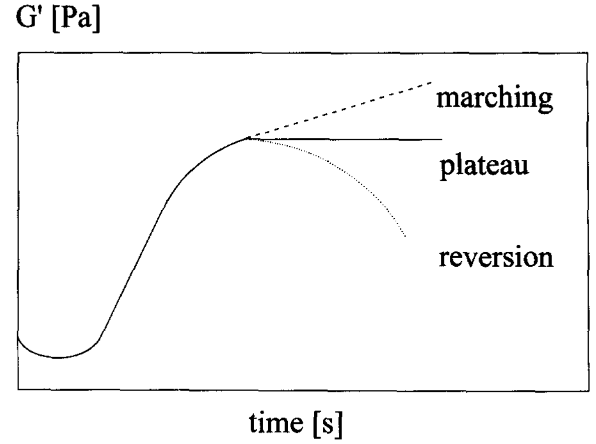

Figure 3 Examples of different cure curves encountered with sulfur vulcanization

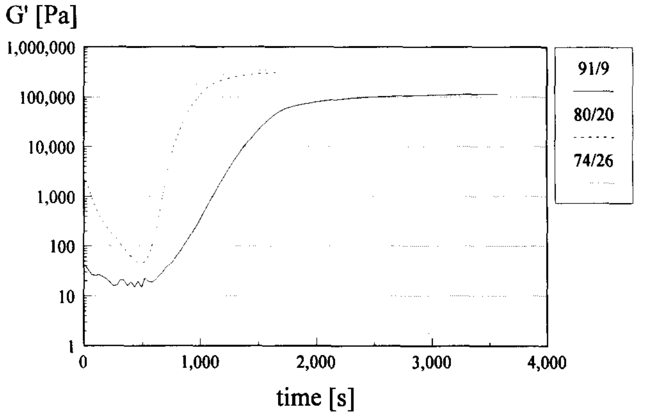

Figure 4 Effect of olefin content on cure for several PHOUs using 4.5 phr DPTT and 0.5 phr BZ (cure temperature 140°C)

time during isothermal curing[7]. For this study, the storage modulus, which is proportional to the torque, was monitored over time using a rheometer.

Cure curves can take on three different shapes – plateau, reversion and marching – depending on how the torque (or storage modulus in this study) varies with time[7]. *Figure 3* shows examples of these different types of cure curves. It is important to know which type of cure a specific chemistry will produce to ensure that the cure is optimized. Most reactions exhibited plateau modulus behaviour. The combinations DPTT/MBTS and DPTT/BBTS exhibited reversion. The test samples with these reagents were prepared again and cured below the reversion time. The DPTT/ZBUDX reagent combination exhibited a marching modulus at low DPTT concentrations and low cure temperatures (70–100°C). A higher cure temperature of 110°C was used and the cure then displayed plateau behaviour.

All samples were an opaque cream colour after compounding. After cure, most samples had darkened to a tan or dark tan colour and remained opaque. This tan colour was similar to the colour of a sulfur-vulcanized rubber band. One sample cured with sulfur and BBTS turned into a dark brown liquid shortly after heating began and this combination was abandoned.

Figure 4 shows a series of cure curves typically observed for the thiuram (DPTT) and dithiocarbamate (BZ) sulfur reagents. As the olefin content was increased, the final dynamic modulus attained at the plateau also increased. The higher modulus reflects the higher crosslink density achieved with more reactive groups available for crosslinking.

Cure curves for PHOU(80/20) cured at several vulcanizing agent concentrations are shown in *Figure 5*. A trend of an increasing plateau dynamic modulus with increasing vulcanizing agent concentration is observed. The increase was substantial from 3.5 to 4.5 phr vulcanizing agent, but insignificant when the concentration was raised to 5.5 phr. These results imply that the vulcanizing agent did not limit the curing process above 4.5 phr. Similar results were obtained for PHOU(74/26).

The feel of the material after cure also changed with olefin content. The copolymers with low olefin content, PHOU(93/7), remained sticky and were soft after curing, whereas PHOU(80/20) and PHOU(74/26) were harder and dry to the touch.

Sol–gel analysis

The neat copolymers should produce 100% sol, i.e. no crosslinking should be detectable. A sol–gel analysis was conducted on many of the vulcanized samples. *Figure 6* compares the results for samples cured with several different reagent combinations and shows the effect of

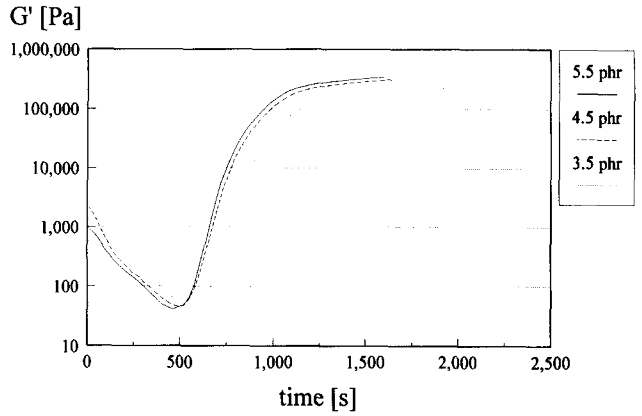

Figure 5 Effect of vulcanizing agent concentration on cure for PHOU(80/20) using DPTT and 0.5 phr BZ (cure temperature 140°C)

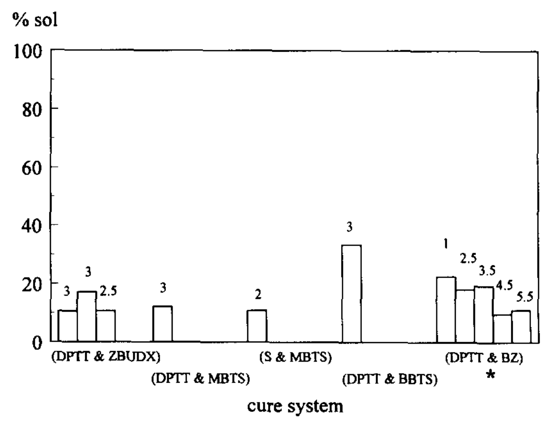

Figure 6 Sol–gel analysis results for PHOU(93/7) sulfur vulcanized with several different sulfur reagent combinations. The numbers above the bars indicate the amount of vulcanizing agent in phr. The * indicates that PHOU(91/9) was used for these samples

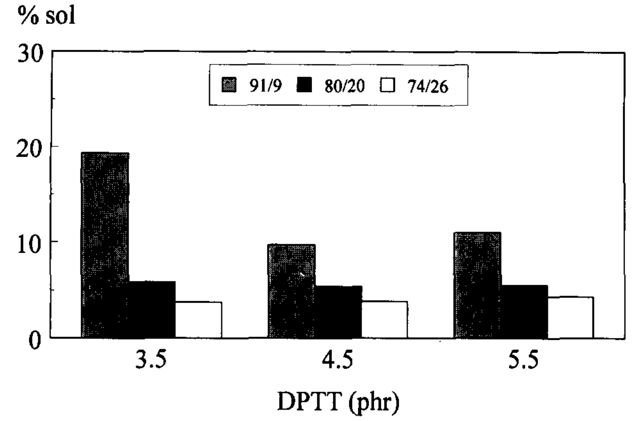

Figure 7 Sol–gel analysis showing the effects of polymer olefin content and concentration of DPTT vulcanizing agent on sol content

Table 3 G.p.c. results for neat PHOU(93/7) before and after heating at vulcanization conditions

Polymer	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity index (PDI)
PHOU(93/7)	165000	62000	2.6
PHOU(93/7) 140°C, 1 h	110000	47000	2.4
PHOU(93/7) 160°C, 1 h	72000	36000	2.0

varying the level of the vulcanizing agent within some of the reagent mixtures. Generally, a trend of decreasing sol content with increasing amount of vulcanizing agent is observed. The sulfur/BBTS and sulfur/ZBUDX reagent combinations did not crosslink the copolymers and both combinations were found to give a 100% sol content.

The DPTT/BZ combination was evaluated further with polymers containing different amounts of olefins. The sol–gel results of these samples are given in *Figure 7*. The trends observed in the amount of sol results reflect the results obtained from the cure curves. Increasing the olefin content produces a material which is more thoroughly crosslinked, as indicated by a decreasing percentage sol in each group of three bars. The use of more vulcanizing agent also decreased the amount of extractables but with less dramatic an influence than the olefin content.

Gel permeation chromatography

To determine if heating the neat copolymers would alter the molecular weight distribution, gel permeation chromatography (g.p.c.) was performed both before and after heating for 1 h the neat copolymers at the temperatures used during sulfur vulcanization. The results for PHOU(93/7) are tabulated in *Table 3*, and they indicate that simply heating the neat copolymer decreased the molecular weight and altered the molecular weight distribution. Interestingly, neat PHOU(80/20) samples formed crosslinked gels solely from heating at either 140 or 160°C for 1 h, and g.p.c. analysis could not be conducted on these samples.

The neat polymers under thermal conditions similar to the sulfur vulcanization conditions were not thermally stable, and degradation occurred concurrently with the crosslinking reactions at the lower olefin contents. In PHOUs with higher olefin contents, the crosslinks formed were caused by a combination of vulcanization and heat.

The sol fractions extracted from several sulfur-vulcanized samples were evaluated for molecular weight distribution. *Figure 8* and *Table 4* show the results for the sol fractions of PHOU(91/9) after undergoing sulfur vulcanization with three different DPTT vulcanizing agent concentrations with a constant BZ accelerator concentration. The samples were vulcanized in the rheometer for 25–60 min.

The molecular weight distribution had changed from that of the original polymer for all sols analysed. In addition, a shift to a lower molecular weight fraction was seen as the level of vulcanizing agent was increased. At least part of the sol molecular weight distribution fell outside the range defined by the original polymer. This result indicates that some chain scission reactions had occurred during cure.

It is interesting that the samples cured with 4.5 and 5.5 phr DPTT gave lower amounts of extractables, but the sols had higher and broader molecular weights than the sol cured with 3.5 phr DPTT. Perhaps the presence of abundant DPTT was capable of linking together some of the polymer chains that had been scissioned from either the thermal or chemical process.

Thermal analysis

D.s.c. analysis was conducted approximately one week after vulcanization to give time for the polymer to crystallize. The goal of eliminating all crystallinity was achieved with several reagent combinations. Generally, a trend of decreasing crystallinity and increasing glass transition temperature was observed as the amount of

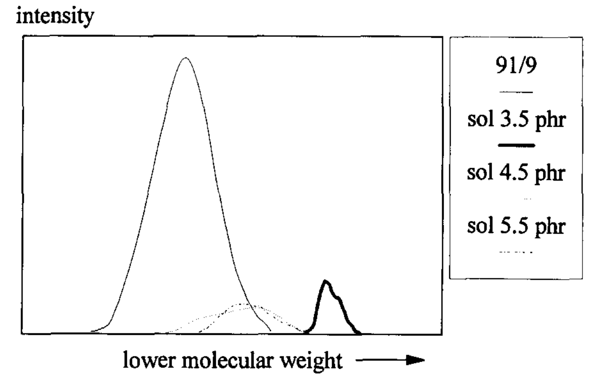

Figure 8 Gel permeation chromatographs for PHOU(91/9) before vulcanization and the sol fractions of the polymer after undergoing sulfur vulcanization with various levels of DPTT and 0.5 phr BZ

Table 4 G.p.c. results for neat PHOU(91/9) and various sol fractions extracted after sulfur vulcanization with DPTT at the concentrations indicated

Sample	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI
PHOU(91/9)	148000	64000	2.3
3.5 phr sol (19.3%)	600	490	1.2
4.5 phr sol (9.7%)	27000	12000	2.3
5.5 phr sol (11.0%)	18000	12000	1.6

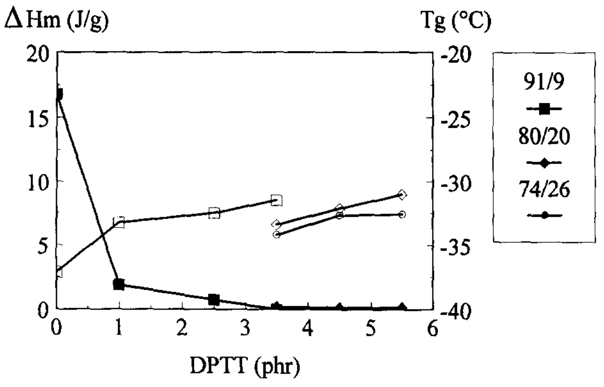

Figure 9 D.s.c. results for several PHOUs vulcanized with DPTT and BZ: open symbols indicate T_g; closed symbols indicate ΔH_m

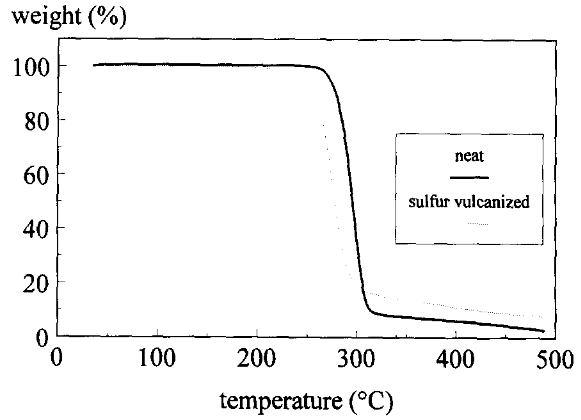

Figure 10 T.g.a. results for PHOU(93/7) neat and after sulfur vulcanization with 1.0–3.5 phr DPTT and 0.5 phr BZ

vulcanizing agent was increased, as shown in *Figure 9*. Simply through crosslinking the polymer, the molecules were constrained in such a way that crystallization was prevented or disrupted, and the glass transition temperature was increased because of the presence of covalent junction points. These results indicate that other reagent combinations which did not eliminate all crystallinity may still be viable candidates if higher vulcanizing agent concentrations are employed.

Interestingly, for 3.5 phr DPTT, the glass transition temperature for a 7% olefin containing vulcanized polymer appeared higher than for 20% and 26% olefin containing polymers, although the difference was only approximately 2°C.

The results of thermogravimetric analysis are shown in *Figure 10*. Thermal decomposition of sulfur-vulcanized PHOU as measured by weight loss occurred approximately 20°C below the decomposition temperature for neat PHOU, yet the two samples retained a similar decomposition curve shape. The onset of thermal decomposition as measured by weight loss was independent of the amount and type of vulcanizing agent used. Perhaps the added compounds promoted the mechanism of decomposition in the bacterial polyesters. 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

Tensile set was virtually eliminated in the sulfur-vulcanized PHOUs, as shown in *Figure 11*. Even after 200% elongation, PHOU(93/7) showed less than 5% tensile set. Non-crosslinked PHOU(93/7) would typically exhibit a tensile set of approximately 150% after 200% elongation (not shown). Unfortunately, the tensile strength was so compromised in the higher olefin content PHOUs that less than 100% elongation was achievable; but even at these low strains, the tensile set was reduced five-fold. A typical value for non-modified PHOU was a tensile set of approximately 20% after 50% elongation (not shown).

Tensile properties

The mechanical properties of several vulcanized polymers are summarized in *Table 5* and compared to a non-crosslinked PHOU. The modulus, tensile strength and elongation are all substantially below the values for the non-modified polymer. The PHOU with only a 7% olefin content still retains a relatively high elongation. The stress–strain curves are illustrated in *Figure 12*.

The tensile modulus as a function of olefin content is shown in *Figure 13*. The modulus increases slightly when the olefin content is increased from 7 to 20%. The modulus does not increase substantially even when the olefin content is increased to 26%. The effect of strain rate was negligible even when varied between 1 and 25 min^{-1} (not shown). In addition, the modulus did not change after repeated stretching of the same sample at any of the strain rates.

Network structure

Impulse viscoelasticity experiments were conducted on several sulfur-vulcanized samples. *Figure 14* shows the

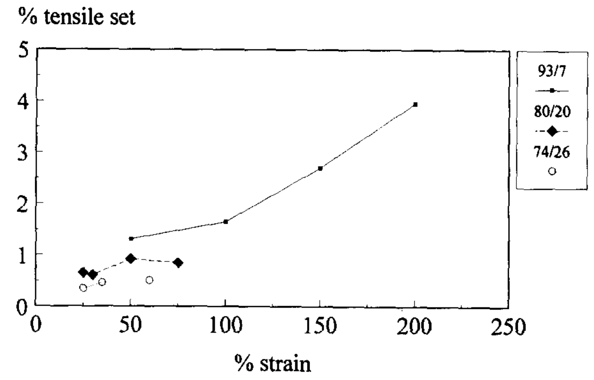

Figure 11 Tensile set for several PHOUs sulfur vulcanized with 4.5 phr DPTT

Table 5 Tensile properties of PHOU(91/9) non-crosslinked and several PHOUs sulfur vulcanized with 4.5 phr DPTT (strain rate 1 min^{-1}, standard deviation approximately 20%)

Polymer	*E* (MPa)	Tensile strength (MPa)	Ultimate elongation (%)
PHOU(91/9) non-crosslinked[a]	8	10	370
PHOU(93/7)	1.2	0.8	250
PHOU(80/20)	1.8	0.8	90
PHOU(74/26)	1.2	0.8	80

[a] Samples tested at a 2 min^{-1} strain rate

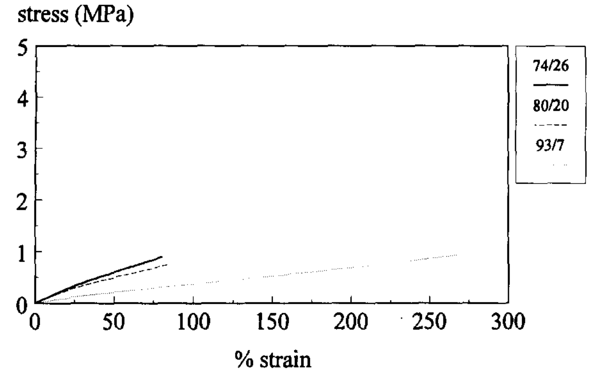

Figure 12 Stress–strain curves for several PHOUs sulfur vulcanized with DPTT

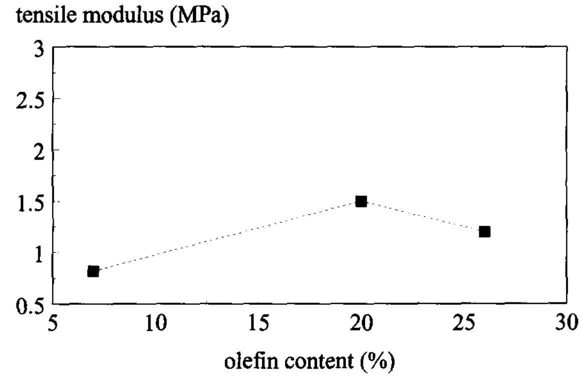

Figure 13 Tensile modulus as a function of olefin content. Samples were vulcanized with 4.5 phr DPTT and 0.5 phr BZ. The strain rates ranged from 1 to 25 s^{-1}. The standard deviation is 20%

equilibrium shear modulus values for the samples tested. From equation (4) in the previous paper, the corresponding molecular weights between crosslinks (M_c) can be calculated, and the calculated M_c scale is included in *Figure 14*.

Increasing the vulcanizing agent concentration increases the equilibrium shear modulus. A dramatic increase in the modulus was noted when the olefin content of the polymer was increased from 7 to 20%. This corresponded to a drop in M_c from approximately 20000 to approximately 6500 g mol^{-1}. An increase to 26% olefin content did not alter the modulus of M_c value significantly above the 20% value. In other words, higher vulcanizing agent concentrations and higher olefin content polymers give a higher crosslink density, as shown by a decrease in M_c.

An interesting calculation revealed that if all the olefin groups in PHOU(80/20) resulted in crosslinks, the resulting M_c should be approximately 750 g mol^{-1}. Since M_c was determined to be between 5500 and 8500 g mol^{-1}, the results indicate that only 10–15% of all olefin groups reacted during sulfur vulcanization. Perhaps many of the olefin groups are somehow prevented from participating in the reaction. This suggestion would be supported by the concept of reduced chain mobility occurring after partial crosslinking.

Ageing

A long term crystallization study on PHO has been published elsewhere[8]. The study indicated that crystallization was very slow and annealing occurred over the long term since the glass transition temperature of PHO is approximately −35°C. Sulfur-vulcanized PHOU also has a glass transition temperature well below room temperature (see *Figure 9*). Therefore, annealing or ageing effects may be possible even with chemical crosslinks present.

One important question which arose in this work was whether or not a sulfur-vulcanized sample which was devoid of crystallinity would remain that way. To answer this question, PHOU(91/9) which had been sulfur vulcanized with DPTT and BZ was re-evaluated for crystallinity using the impulse technique approximately 11 months after vulcanization. The equilibrium modulus dropped significantly after the material was heated above the melting point and allowed to cool to room temperature, implying that crystallization had occurred over the 11 months.

CONCLUSIONS

Several sulfur vulcanization reagent combinations were successful in producing crosslinked PHOUs. As the olefin content in the copolymer was increased, the extractable sol decreased, a lower level of crystallinity was detected (if at all) and a lower molecular weight between crosslinks was observed. These same trends were observed as the vulcanizing agent concentration was increased for PHOU with a specific olefin content. *Table 6* summarizes the results for sulfur-vulcanized PHOUs.

The tensile modulus and tensile strength of the cured materials were dramatically reduced compared to the

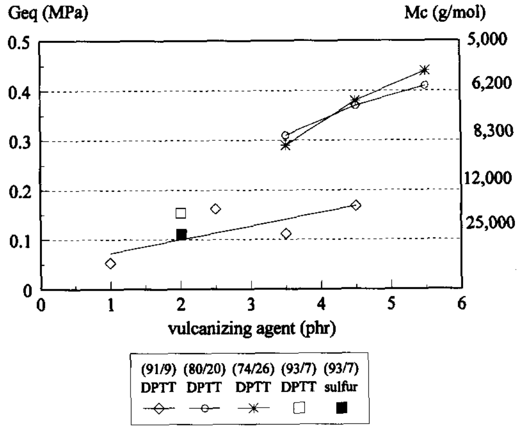

Figure 14 Shear equilibrium modulus G_{eq} and molecular weight between crosslinks M_c as functions of the vulcanizing agent concentration for several systems

Table 6 Sulfur vulcanization results

Cure chemistry	Sol content (%)	Crystallization detected	$10^3 M_c{}^a$ (g mol^{-1})
DPTT and BZ	10–30	Yes to no[b]	6–34
DPTT and ZBUDX	10–20	Yes to no[b]	20–28
S and ZBUDX		Yes	
DPTT and BBTS	33	Yes	
S and BBTS	100	Yes	
DPTT and MBTS	12	Yes	18
S and MBTS	10	Very low	25

[a] Molecular weight between crosslinks

[b] Dependent on concentration of crosslinking agents

non-modified PHOU. However, material integrity was left intact and ultimate mechanical properties were determined. In addition, the goal of improving the elastic response through vulcanization was successful because the materials exhibited less than a 5% tensile set even after 200% elongation.

Improvement of the material properties may be possible by using fillers such as fumed silica or carbon black. The use of fillers to improve mechanical properties is common practice in synthetic rubbers[3].

Ageing effects were observed because annealing continued at room temperature after cure. The result was that crosslinking, which had at first disrupted crystallinity, eventually occurred over long times. This ageing effect hardened the vulcanized copolymer. Higher olefin content PHOUs which had produced a tighter network upon vulcanization are being investigated after long times to determine if the higher crosslink density prevents ageing effects, namely crystallization, from ever occurring.

Sulfur crosslinking requires the use of many reagents, which brings up the concern of environmental fate when (and if) the crosslinked microbial polyesters biodegrade. Investigations are underway to determine if sulfur vulcanization affects the biodegradability of the copolymers.

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