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Influence of Thickness and Modulus on the Environmental Degradation of Vulcanised NR Latex Films

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The microbial degradation of rubber products has been variously linked to curing conditions and rubber formulations crosslink density, carbon black loading or to rubber shapes In this study the degradative behaviour of NR latex films with a range of thicknesses (0 09 mm – 0 79 mm) and varying moduli (8 5 MPa – 16 MPa at 700% elongation) was examined Dipped film pieces were buried in soils for 24 weeks and the materials analysed for residual mass, swelling tensile properties and spectral examination by FTIR-ATR spectroscopy The morphology of the soil-degraded film surfaces was examined by a low vacuum scanning electron microscope Degradation of the prevulcanised NR latex films was significantly decreased when either the thickness or modulus increased Within this general trend the residual mass of the buried films were noticeably affected by the interactions between material thickness and moduli The thinner latex films degraded faster than thicker films within the same moduli The appearance of carbonyl and hydroxyl groups as a consequence of polyisoprene oxidation from surface analyses of the samples occured across all film thicknesses but was more severe with the low modulus films SEM visualisation of the soil-buried films showed that irrespective of thickness and moduli the surfaces were characterised by cracks typical of bulk disintegration and mesovoids from where bacteria and fungi colonised to penetrate the fractured areas

Key words environment, degradation, thickness, FTIR, ATR, soil, NR, latex films, modulus, SEM, bacteria, fungi

Knowledge on the potential microbial degradation of rubber products is important from the viewpoint of waste disposal, or in the prolongation of usage[1] The microbial disintegration of rubber products has been studied with respect to curing conditions and rubber formulations[2 4], crosslink density and carbon black loading[1] or to rubber shapes[1 5]

Vulcanisation introduces crosslinks at various points along a polymer chain The crosslink density of NR vulcanisates is generally related to the vulcanisates' stiffness or hardness Thus a measure of stiffness (modulus) allows the estimation of the apparent crosslinks in the vulcanisates[6] Since modulus increases with increasing

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crosslink density, a high modulus value indicates a high crosslink density.

In stirred flask cultures, Tsuchii *et al.*[8] showed that the thickness, length and width of rubber glove pieces influenced an actinomycete strain (*Nocardia* sp. 835A) colonisation and degradation of rubber products. NR latex products such as balloons, condoms and varieties of gloves are generally thin products. It follows that thin rubber products of different crosslink densities will have different modulus that affect their susceptibility to environmental degradation. In the current study, we examine the degradation of NR latex films with a range of thickness and modulus grade in soil.

MATERIALS AND METHODS

Preparation of Latex Films

Dipped NR latex films were prepared from commercial prevulcanised NR latex mixes of different modulus grades [high modulus (HR); medium modulus (MR) and low modulus (LR)] by dipping calcium nitrate coated glass plates into the latex mix. The commercial latex had properties as shown (*Table 1*). The thicknesses prepared from each modulus grade were meant to approximate the average thicknesses of condoms (0.08 mm), examination gloves (0.15 mm), surgical gloves (0.25 mm), household gloves (0.40 mm) and industrial gloves (1.0 mm). To achieve the different film thickness for the study, the immersion, dwelling and withdrawing of the glass plates out of the latex mixture were carefully controlled. The dipped films were stripped from the glass plates after drying at room temperature and dusted with talc.

Estimation of Film Thickness

Film thickness was determined using light microscopy. The films were cut into smaller pieces (0.5 cm × 0.5 cm) and embedded in Paraplast® tissue embedding medium (Oxford Labware, St. Louis, MO) at 56°C. Thin slices were cut from the embedded sub-pieces and the mean thickness determined from 100 sub-pieces at 40 × magnification.

Soil Burial Test

Sandy soil. Pre-weighed rectangular pieces (10×7 mm^2) from films of varying thickness and modulus treatment combinations were placed in nylon-net mesh bags (38 μm pore size) and buried vertically in 4 replications in a soil burial test as previously described[9]. Each

TABLE 1. SOME PROPERTIES OF THE COMMERCIAL NR PRE-VULCANIZED LATEX MIXES[a]

Properties	Modulus grade LR	MR	HR
Tensile strength (MPa)	30	30	26
Elongation at break (%)	1000	900	800
Unaged modulus at 700% elongation (MPa)	8.5	11	16

[a]As cast films tested at 23°C and 50% RH

bag contained one film piece. Smaller cut pieces (2 cm × 2 cm) were similarly buried for microscopic examination of stained surfaces. The coarse sandy clay-loam soil used (Rengam series soil; Typic Kandiudult) was collected at 0-30 cm depth from the RRI Experiment Station, Sg Buloh. Soils were limed to pH 6.5, supplied with nutrients (100 mg L^{-1} N and 150 mg L^{-1} P) and dispensed into large rectangular containers (27 kg soil/container). After burial of the film pieces, the containers were kept in a room at 25°C and watered weekly to 40% field capacity throughout the course of the experiment.

All film pieces were retrieved from soils after 24 weeks, washed in running water and dried prior to weighing.

Clayey soil. In an earlier soil burial test, 14 cm × 4 cm films of two thicknesses (0.15 mm and 0.30 mm) and three moduli were evaluated in a limed clayey soil (Munchong series, Tropeptic Haplorthox) under the incubation conditions described.

Schiff's Reagent Staining

Schiff's reagent prepared from basic fuchsin (BDH, Poole) and a source of sulphurous acid was used to stain the surfaces of the latex film pieces. The purplish-red colour developed allowed instant macroscopic visualisation of degraded rubber areas characterised by accumulation of isoprene oligomers containing aldehyde groups[8,10].

Tensile Properties

The tensile strength, modulus and elongation at break values were determined according to *ASTM D412*.

Swelling Measurements

Cut test pieces weighing 0.2 g were immersed in pure toluene to attain swelling equilibrium at 40°C±3°C. At equilibrium, excess toluene was blotted off with filter paper and the swollen material weighed in a closed vessel. The swollen test piece was then placed under vacuum and de-swollen to constant weight. The swelling ratio is the ratio of the difference between the swollen weight and the initial weight to that of initial weight.

The swollen fraction in the swollen network (V_r) was calculated by using the following equation[11]:

$$V_r = (D\rho_p^{-1})/(D\rho_p^{-1} + A_o D\rho_s^{-1}) \qquad \ldots 1$$

where D is the de-swollen weight; A_o is the weight of the sample; ρ_p is density of NR and ρ_s is the solvent density.

The crosslink density (M_c) as determined *via* the Flory-Rehner equation[12]:

$$M_c = \rho_p V_s (V_r)^{1/3} / \ln(1 - V_r) + V_r + \chi V_r^2 \qquad \ldots 2$$

where V_s is the molar volume of the solvent and χ is the solvent-polymer interaction parameter[13].

Scanning Electron Microscopy

The morphology of the degraded film samples were observed using a JEOL model JSM-5610LV Low Vacuum Scanning Electron Microscope (LV SEM). The LV SEM provided a unique freeze drying method where wet biological samples can be dried in the specimen chamber of the SEM within an hour, compared to drying by either critical point dryer or freeze drier that takes about a day to prepare. The process is outlined as follows The surface of a specimen stub was first roughened, a piece of conductive carbon double-sided tape stuck to the surface and the rubber sample was adhered to the carbon tape Some water is then dropped on to the surface of the rubber sample As rubber has quite high surface tension, the water need to be evenly spread on the surface manually The stub was next dipped into liquid nitrogen for 3 min – 5 min, with care taken not to submerge the rubber sample After the water on the rubber was completely frozen, the stub was transferred into the SEM chamber and the chamber evacuated to around 40 Pa At this pressure, ice will sublime to become gas, and the sample will be completely dried in about 20 min – 30 min Once dried, the image can be observed using Backscattered Electron Detector or Low Vacuum Secondary Electron Detector As the sample was freeze-dried, it was removed from the specimen chamber and went through sputter coating with gold

FTIR-ATR Spectroscopy

The analysis was carried out on a Perkin Elmer Spectrum 2000 spectrometer utilising a Benchmark Series Horizontal ZnSe ATR (50 × 20 × 10 mm) The control samples were washed with distilled water to remove traces of powder and left to dry overnight at room temperature Sixty four scans were accumulated with a resolution of 4 cm^{-1} Samples were purged sufficiently with purified nitrogen prior to each scan

RESULTS

Thickness Measurements

In most cases, there was a tendency for thickness to decrease slightly from low to medium moduli grade films when prepared, but then increased from medium to high moduli (*Table 2*) The divergence of the 0 25 mm and 1 0 mm films from the expected values was readily apparent

Soil Degradation

Sandy soil In the soil burial test, the overall degradation as determined by residual weight loss was significantly decreased when the main effect of thickness, or modulus, increased ($P<0\ 001$) (*Table 3*) There was a strong interaction effect between thickness and modulus ($P<0\ 01$) in influencing the trend of degradation, *i e* for a particular thickness, films of differing moduli degraded differently The effects were demonstrated clearly at a mean thickness of ≤0 17 mm, where the low and medium moduli films behaved similarly and degraded significantly more than the high modulus film At a thickness of 0 20 mm, only the low modulus film degraded significantly more than the medium and the high moduli films

At 0 40 mm thickness, degradation was statistically unaffected by the moduli range but at 0 79 mm, only the low modulus film degraded significantly more than the high modulus film

Clayey soil In the other soil burial test, degradation losses were also significantly affected by modulus but only for films at the lower thickness (*Table 4*) As with the 0 40 mm thick film in the previous soil test, degradation of the 0 30 mm thick film was unaffected by moduli

Schiff's Reagent Staining

Schiff's reagent (parasoaniline and its analogues, rosanilin and magenta II) is widely used

TABLE 2 THICKNESS MEASUREMENTS OF DIPPED FILMS

Presumed thickness (mm)	Modulus grade Low	Medium	High	Mean
0 08	0 084 ± 0 002	0 080 ± 0 002	0 094 ± 0 002	0 086
0 15	0 169 ± 0 002	0 160 ± 0 002	0 194 ± 0 002	0 174
0 25	0 193± 0 002	0 184 ± 0 002	0 218 ± 0 002	0 198
0 40	0 420 ± 0 003	0 396 ± 0 002	0 383 ± 0 003	0 400
1 00	0 787 ± 0 003	0 774 ± 0 003	0 819 ± 0 003	0 790

TABLE 3 MEAN PERCENT INITIAL WEIGHT REMAINING OF DECOMPOSING LATEX FILMS AFTER 24 WEEKS OF SOIL BURIAL (SANDY SOIL)*

Actual thickness (mm)	Modulus grade Low	Medium	High	Thickness mean
0 09	48 2 *ij*	39 8 *j*	59 8 *fg*	49 3 *E*
0 17	48 8 *hi*	56 7 *gh*	67 3 *ef*	57 6 *D*
0 20	57 8 *g*	67 3 *ef*	66 5 *ef*	63 9 *C*
0 40	71 2 *de*	77 0 *cd*	70 4 *de*	72 9 *B*
0 79	80 0 *bc*	86 9 *ab*	94 4 *a*	87 1 *A*
Modulus (mean)	61 2 C	65 5 B	71 7 A	

*Means of 4 replications Values within a row, column or across rows and columns not followed by common letters are significantly different (P<0 05) Analyses based on untransformed data
Significance Thickness (T), P<0 001, Modulus (M), P<0 001, T × M, P<0 01, CV = 8 9%

TABLE 4 MEAN PERCENT INITIAL WEIGHT REMAINING OF DECOMPOSING LATEX FILMS AFTER 24 WEEKS OF SOIL BURIAL (CLAYEY SOIL)*

Presumed thickness (mm)	Modulus grade Low	Medium	High	Thickness mean
0 15	22 1 *c*	30 6 *c*	50 1 *b*	34 2 *B*
0 30	58 7 *ab*	63 9 *a*	61 4 *a*	61 3 *A*
Modulus (mean)	40 4 A	47 2 AB	55 7 A	

*Means of 4 replications Values within a row, column or across rows and columns not followed by common letters are significantly different (P<0 05) Analyses based on untransformed data
Significance Thickness (T) P<0 001, Modulus (M), P<0 05, T × M, P<0 05, CV = 14 2%

in the histological staining of biological tissues and colour aldehydes brownish red In this study, the darkly-stained areas due to the reagent were prominent over a wider area of the thinner film pieces (0 09 mm, 0 17 mm) than on the remaining thickness, irrespective of moduli (*Figure 1*) Such observations were however not related to the degree of film mass loss

Microscopy

Microbial colonisation and morphological changes of the polymer surfaces were observed in the degraded areas of the films Irrespective of film thickness and moduli, the surfaces were characterised by cracks typical of bulk disintegration and mesovoids from where bacteria and fungi grew adhesively and penetrated the fractured areas (*Figure 2*)

Swelling Measurements

For any modulus grade, the thinner films possessed a higher crosslink density than thicker latex films (*Table 5*) As film thickness increased, crosslinking decreased When aged at room or elevated temperatures, or left buried in soils, the crosslink densities were also reduced This was expected since a thick rubber component aged less rapidly than a thinner one due to the depth of penetration of oxidative ageing[14] Thus thinner films with higher initial crosslink density resisted ageing better than thicker films with relatively lower initial crosslinks

Tensile Properties

Films prepared from the high modulus grade prevulcanised latex showed consistently lower tensile strength values than the films prepared from medium and low modulus grades (*Table 6*) However, the high moduli latex films had consistently lower elongation at break values compared to that of the other moduli films The crosslinking network in sulphur-vulcanised NR latex films is predominantly a polysulphidic type[14-16], and during ageing at moderate temperatures, autocatalytic free-radical chain reactions are expected to occur This scissioning of crosslinks during ageing is reflected by the reduction in the vulcanisates' crosslink density

FTIR-ATR Spectroscopy Analysis

The FTIR-ATR analysis was used to indicate the generation of bands pertinent to the hydroxyl and carbonyl groups evolved as products of degradation[18] The oxidation of rubber to carbonyl groups proceeds through intermediary hydroperoxidic groups which overlap the band of hydroxyl[19] As such, the ratio of the amounts of hydroxyl to carbonyl groups reflects the decomposition that occurred and the extent of the rubber network disintegration *via* oxidative chain scissions (*Figure 3*, *Table 7*) Carbonyl bands appear in a very broad range of 1600 cm^{-1} – 1800 cm^{-1} and the stretching vibrations of ketones, aldehydes, esters and carboxylic acids appear between 1700 cm^{-1} – 1750 cm^{-1} In this study, a major band attributed to aldehydes at 1640 cm^{-1} could be observed Degradation occurred across all film thicknesses and in most cases, the ratios obtained indicated that degradation was more severe with the low modulus films than with the medium and high modulus samples

DISCUSSION

The processes of natural polymer breakdown, as they occur by thermal oxidation, photo-oxi-

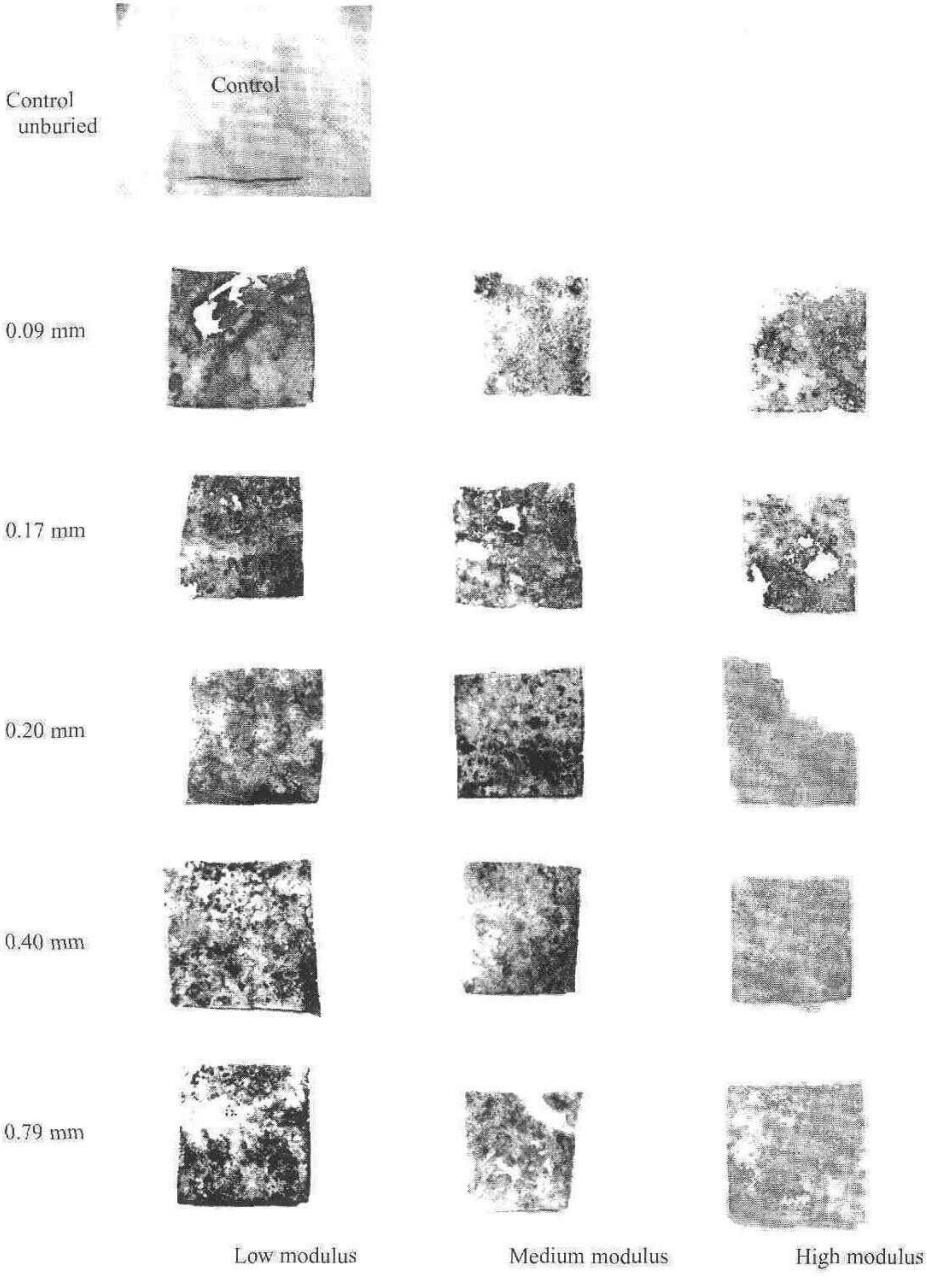


Figure 1. Surfaces of glove pieces of different thickness and moduli stained with Schiff's reagent after soil burial for 24 weeks.

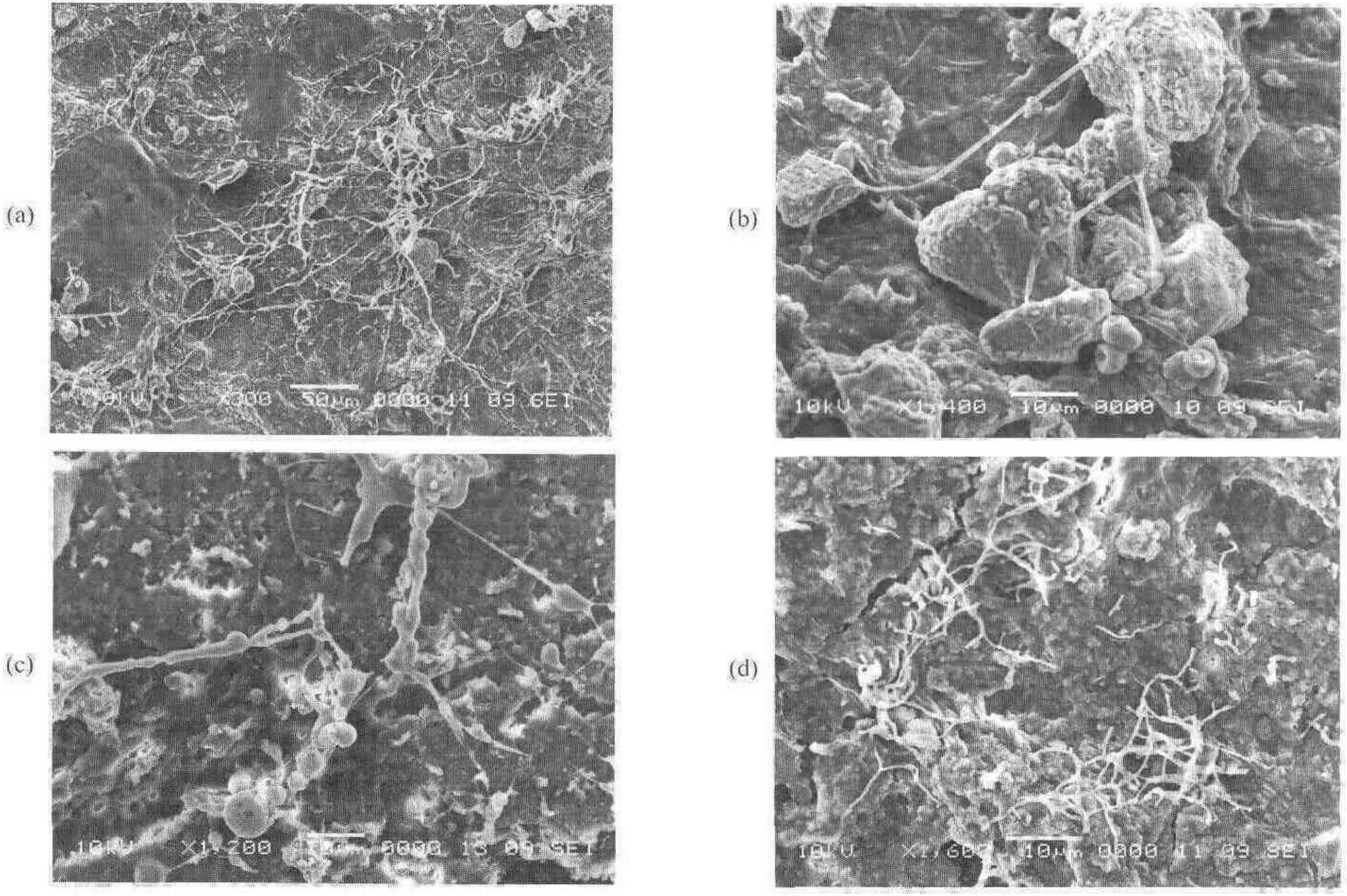


Figure 2. SEM micrographs of degraded NR film pieces after soil burial. Mycelial mass of diffuse spreading hyphae on film surface (a: × 300) typical of soil fungi (b: × 1400). Disintegrating surface colonised by soil fungi showing mesovoids (c: × 1200). Actinomycetes colonising film pieces penetrating cracks and mesovoids (d: × 1600; e: × 3000). Deteriorated film pieces may harbour the occasional soil nematodes, invertebrates that live on organic residues and soil bacteria (f: × 400) and unicellular diatoms with siliceous skeletons (g: × 2000). Cracks and fractures are typical of bulk disintegration of the surfaces and are usually extensively colonised by bacteria and mycelial strands of actinomycetes (h: × 4000). A sparse population of rod-shaped bacteria on film surface (I: × 6500; j: ×25,000). Bars represent 1 µm (j), 2 µm (i), 5 µm (e, h), 10 µm (b, c, d, g) and 50 µm (a, f).

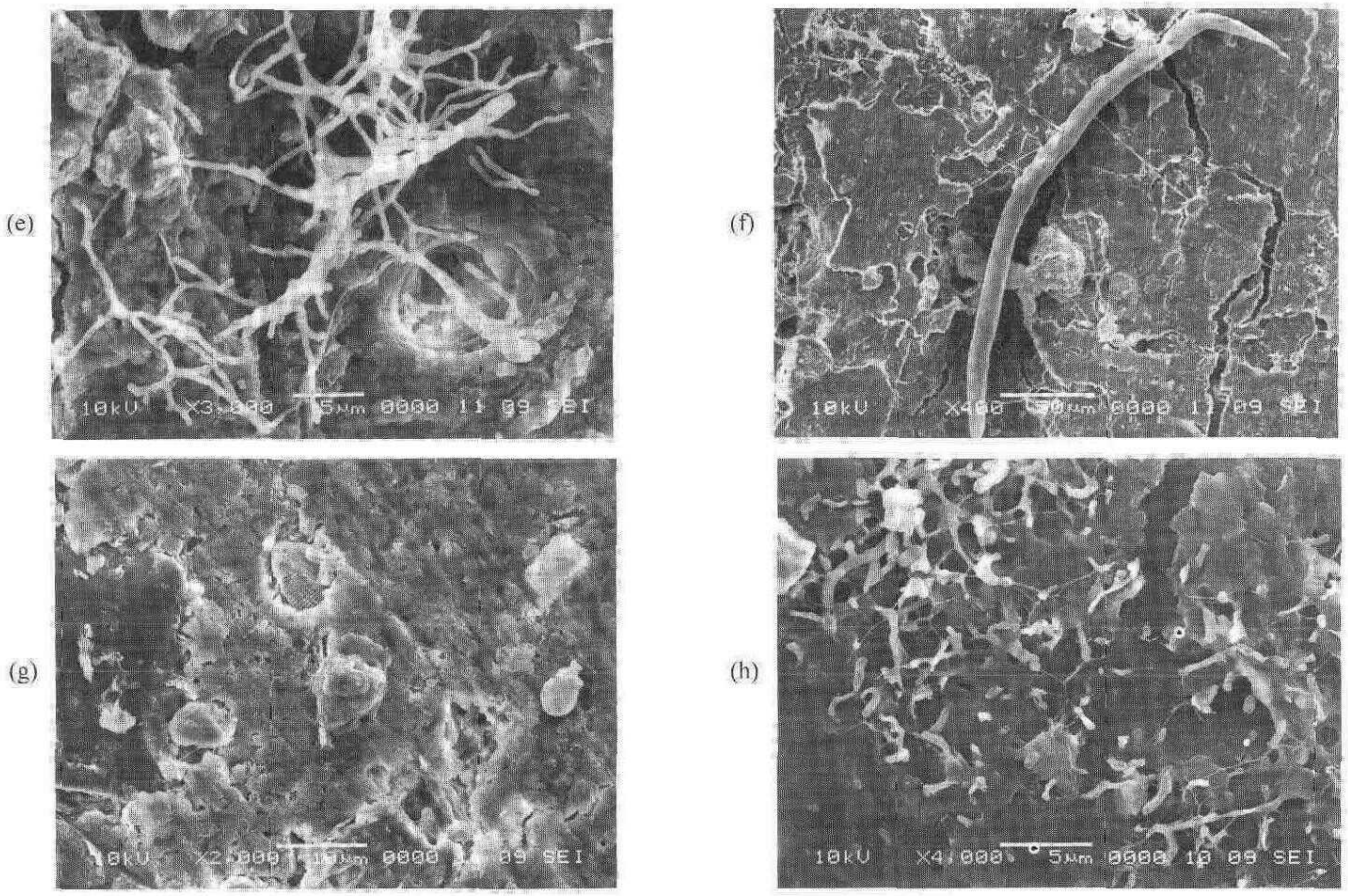
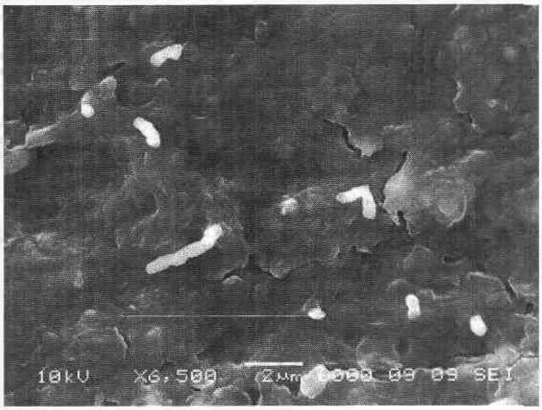
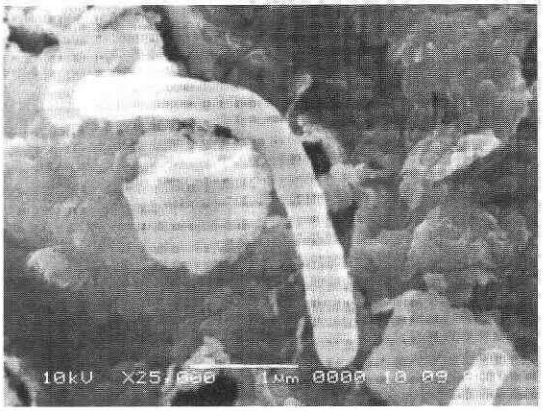


Figure 2 cont. SEM micrographs of degraded NR film pieces after soil burial. Mycelial mass of diffuse spreading hyphae on film surface (a: × 300) typical of soil fungi (b: × 1400). Disintegrating surface colonised by soil fungi showing mesovoids (c: × 1200). Actinomycetes colonising film pieces penetrating cracks and mesovoids (d: × 1600; e: × 3000). Deteriorated film pieces may harbour the occasional soil nematodes, invertebrates that live on organic residues and soil bacteria (f: × 400) and unicellular diatoms with siliceous skeletons (g: × 2000). Cracks and fractures are typical of bulk disintegration of the surfaces and are usually extensively colonised by bacteria and mycelial strands of actinomycetes (h: × 4000). A sparse population of rod-shaped bacteria on film surface (I: × 6500; j: ×25,000). Bars represent 1 μm (j), 2 μm (i), 5 μm (e, h), 10 μm (b, c, d, g) and 50 μm (a, f).



(i)



(j)

Figure 2 cont. SEM micrographs of degraded NR film pieces after soil burial. Mycelial mass of diffuse spreading hyphae on film surface (a: × 300) typical of soil fungi (b: × 1400). Disintegrating surface colonised by soil fungi showing mesovoids (c: × 1200). Actinomycetes colonising film pieces penetrating cracks and mesovoids (d: × 1600; e: × 3000). Deteriorated film pieces may harbour the occasional soil nematodes, invertebrates that live on organic residues and soil bacteria (f: × 400) and unicellular diatoms with siliceous skeletons (g: × 2000). Cracks and fractures are typical of bulk disintegration of the surfaces and are usually extensively colonised by bacteria and mycelial strands of actinomycetes (h: × 4000). A sparse population of rod-shaped bacteria on film surface (I: × 6500; j: ×25,000). Bars represent 1 μm (j), 2 μm (i), 5 μm (e, h), 10 μm (b, c, d, g) and 50 μm (a, f).

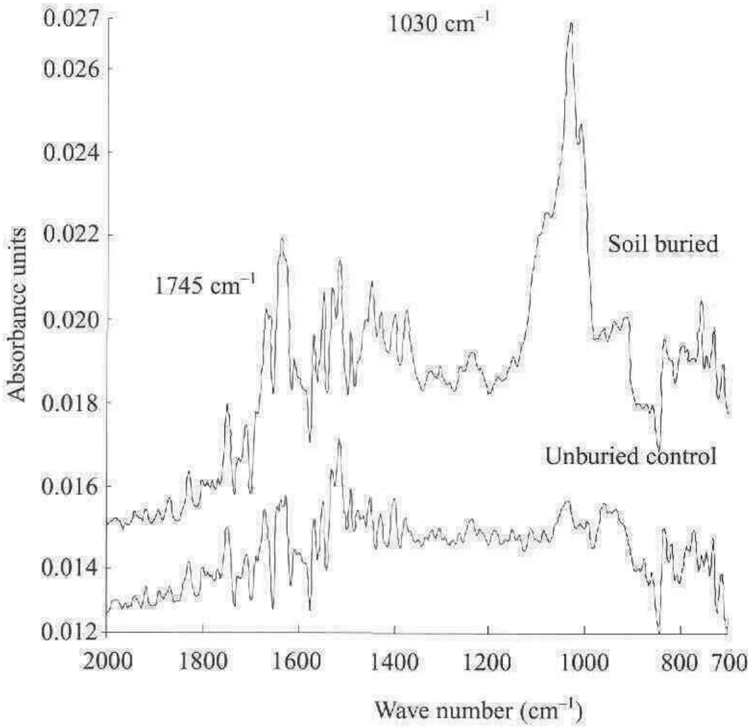


Figure 3. Changes in a typical FTIR-ATR spectra of soil buried NR latex films. A thin film (0.09 mm, low modulus) was compared to an unburied sample.

TABLE 5 NETWORK CROSSLINK DENSITY OF VULCANISED NR LATEX FILMS OF VARYING THICKNESS AND MODULUS

Thickness (mm)	Crosslink density ($1/2 M_c \times 10^{-5}$ mol/g rubber)* Unaged	Room temperature	Soil-buried	Heat-aged 70°C	Heat-aged 100°C
(a) Low modulus					
0.09	4.52	3.55	3.67	3.49	3.88
0.17	3.43	3.50	3.14	3.11	2.52
0.20	3.28	3.20	1.71	2.16	2.64
0.40	2.98	2.92	1.60	2.91	2.33
0.79	2.14	2.66	2.00	1.72	0.52
(b) Medium modulus					
0.09	7.51	5.12	6.31	4.18	2.31
0.17	3.93	4.10	5.84	3.86	3.48
0.20	3.89	3.92	5.58	3.78	2.85
0.40	3.34	3.41	2.90	3.63	2.54
0.79	3.18	3.08	2.10	3.36	2.10
(c) High modulus					
0.09	6.46	4.86	7.54	5.43	2.47
0.17	4.74	4.44	3.80	5.95	2.96
0.20	4.58	4.13	2.38	4.97	2.87
0.40	3.86	3.89	2.82	3.88	2.70
0.79	2.34	3.29	2.36	3.48	1.60

*Values are means of two determinations; Unaged = unaged samples at start of experiment; Room temperature = samples stored for 6 months at room temperature; Soil-buried = samples buried for 6 months in soil; Heat-aged = samples heat-aged at 70°C for 7 days and at 100°C for 24 hours.

dation and biodegradation, rely on a high surface area to volume ratio, and thus thin industrial products tend to break down more than thicker ones[20,21]. Once fragmentation has occurred, the surface area available for further oxidation is considerably increased. Polymer products should physically disintegrate after discard through the influence of the environment and be chemically transformed *via* initial peroxidation into low molecular weight oxidation products normally found in nature for microbial bioassimilation[22].

The experiment reported here demonstrated that degradation of the prevulcanised NR latex films was significantly decreased when either the thickness, or modulus, increased. Within this general trend, the residual mass of the buried films was noticeably affected by the interaction between the thickness and the modulus of the material. At mean thicknesses of <0.20 mm, the high modulus films degraded significantly less than the low modulus films. The effects were less clear when mean film thicknesses were ≥0.20 mm, where degradation was either unaffected by the modulus range tested (0.30 mm and 0.40 mm films) or that only the low modulus films degraded significantly more than the higher modulus grades (0.20 mm and 0.79 mm films). These results extend the conclusions from earlier experiments by Tsuchii *et al.*[8] who found that

TABLE 6. PHYSICAL PROPERTIES OF UNAGED DIPPED PREVULCANISED NR LATEX FILMS[a]

Thickness (mm)	Modulus	Property		
		TS (MPa)	EB (%)	M300% (MPa)
0.09	Low	19.00 (0.67)	936 (28)	1.62 (0.67)
	Medium	20.47 (0.45)	872 (20)	1.68 (0.47)
	High	12.28 (2.00)	644 (143)	1.17 (0.07)
0.17	Low	23.00 (0.45)	946 (9.3)	1.09 (0.02)
	Medium	19.51 (1.50)	1074 (30)	0.73 (0.03)
	High	17.80 (0.54)	826 (8.1)	1.34 (0.03)
0.20	Low	22.36 (0.47)	944 (17)	1.07 (0.04)
	Medium	22.75 (0.38)	942 (15)	1.18 (0.03)
	High	18.01 (0.55)	878 (4.4)	1.15 (0.26)
0.40	Low	22.04 (0.12)	974 (17)	1.01 (0.01)
	Medium	22.69 (1.18)	922 (8)	1.23 (0.01)
	High	17.28 (0.06)	862 (5.0)	1.29 (0.02)
0.79	Low	25.10 (0.92)	1108 (29)	0.75 (0.01)
	Medium	29.00 (0.84)	986 (12)	1.00 (0.001)
	High	25.10 (0.60)	938 (14)	1.22 (0.06)

[a]Mean of 5 test pieces; TS = tensile strength; M300% = modulus at 300%, EB = elongation at break (%); values in parentheses are standard deviation values.

TABLE 7. EVOLUTION OF CARBONYL AND HYDROXYL GROUPS AS DERIVED FROM THE ABSORBANCE SPECTRA OF SOIL-BURIED NR LATEX FILMS

Thickness (mm)	Modulus	Absorbance units		
		Carbonyl	Hydroxyl	OH/C=O
0.09	Low	0.011	0.018	1.79
	Medium	0.014	0.023	1.58
	High	0.022	0.025	1.12
0.17	Low	0.007	0.013	1.82
	Medium	0.019	0.026	1.36
	High	0.025	0.047	1.89
0.20	Low	0.011	0.018	1.58
	Medium	0.020	0.024	1.22
	High	0.021	0.021	1.02
0.40	Low	0.016	0.019	1.17
	Medium	0.022	0.025	1.17
	High	0.021	0.020	0.95
0.79	Low	0.012	0.027	2.32
	Medium	0.025	0.036	1.46
	High	0.027	0.040	1.46

the thickness, length and width of rubber glove strips greatly influenced colonisation by a rubber-degrading *Nocardia* sp in stirred flask shake cultures and the subsequent rate of material degradation Elsewhere, it has also been observed that the hydrodynamic function behaviour of a flexible prosthetic heart valve made from biostable polyurethanes is heavily influenced by leaflet thickness but not by material modulus[23] Although most thin latex products (gloves, condoms, balloons) are completely disintegrated within a realistic time scale, the evidence available pointed strongly towards the interactions between material thickness and modulus in determining their environmental fate For instance, the slower environmental degradation rate of used male NR condoms in soils compared to the relatively-thicker examination gloves was due to its higher modulus[24]

The soil-buried thinner latex films were highly crosslinked and tend to degrade significantly faster than thicker films within the same moduli This apparent trend of decreasing crosslink density with increasing thickness at any modulus value was also evident in the unaged and aged film samples This would mean that thinner films were relatively stiffer and less elastic as shown by their lower tensile properties that was to be expected for highly crosslinked latex films It is worth noting that since the dipped NR latex films of various thicknesses were individually prepared from the same prevulcanised NR latex mix, some possibility exists that the process of drying and heating the films caused formation of further crosslinks, strengthening the view that crosslink formation is thickness dependent

It seems generally to be thought that the crosslink density of vulcanisates can affect the resistance of vulcanisates to microbial attack, *i e* the greater the crosslink density, the greater the resistance to degradation[1] Since different crosslink structures in dry rubbers result from different sulphur vulcanisation systems used (polysulphidic, disulphidic and monosulphidic crosslinks), Tsuchii *et al*[1] proposed that the type of crosslink density and the effect of the different types of crosslinks in the vulcanisates require further study The results for NR latex which is predominantly polysulphidic[15,17] showed that highly-crosslinked films were more susceptible to degradation, depending on material thickness and modulus

Polyunsaturated rubbers are oxidised by the well-known free radical chain reaction which precede property change in polymeric materials[25] The analysis of surfaces of the soil-buried films by means of FTIR-ATR spectroscopy yielded further evidences of degradation The absorbance spectra showed bands attributed to regions comprising the absorption of carbonyl (1745 cm^{-1}) and hydroxyl (1030 cm^{-1}) groups, the former corresponding to carbonyl stretching of esters However, such observations may not apply homogeneously throughout the polymer bulk since the degradation thickness profiles may differ The formed carbonyls and hydroxyl groups were calculated to be in a superficial layer of 0 70 µm – 1 2 µm depth

A common SEM surface morphology change on all the films sampled was the formation of cracks and mesovoids that became colonised by soil microorganisms In a twelve-week aseptic culture study on the biodegradation of unvulcanised NR (SMR L) by an actinomycete in packed bioreactors, Azhari *et al*[26] characterised the morphological changes as surface asperities (grooves), voids, striations and bulk disintegration They also showed that mesovoids grew in diameter sizes under the influence of increasing pHs or aeration rates, indicating different mechanisms of degradation In the present study, the formation of cracks and mesovoids could well be the prelude to bulk disintegration in material breakdown In a previous study, Tsuchii et al[7] observed that the formation of cracks and pits of degrading tyre strips in stirred flask cultures occurred only at points of direct contact with the microbial colonies The filamentous growth of their rubber-degrading actinomycete (*Nocardia* sp) on the glove pieces[8], as was growth of the fungi *Fusarium solani* on thin rubber sheets in a different experiment[28], were tightly bound to the rubber pieces indicating that colonisation efficiency as a microbial strategy could be a key factor affecting the degradation rate by microbes However, Linos et al[29,30] described experiments that used several actinomycetes (*Gordonia* sp , *Mycobacterium fortuitum, Micromonospora aurantiaca*) to degrade natural and synthetic rubbers and showed the existence of two groups, one that grew in direct contact with the rubber substrate to give considerable material disintegration, and another belonging to weaker decomposers that did not grow adhesively

Degradable polymers may degrade in many very different environments It is apparent that the degradation rate of thin rubber products depended on the rubber formulations used, the microorganisms present and their interactions with the environment This situation cannot be simple but that their complexity emphasizes the need for further study Among the many important aspects still to be resolved is the role of antioxidants, sulphur and vulcanisation accelerators that had frequently been invoked as detrimental to the process

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REFERENCE

1 TSUCHII, A HAYASHI, K , HIRONIWA T , MATSUNAKA, H AND TAKEDA, K (1990) The Effect of Compounding Ingredients on Microbial Degradation of Vulcanized Natural Rubber *Journal of Applied Polymer Science*, **41**, 1181–1187

2 SIMPSON, K E (1988) Biodegradation of Natural Rubber Vulcanisates *International Biodeterioration*, **24**, 307–312

3 WILLIAMS G R (1986) The Biodegradation of Vulcanized Rubbers *International Biodeterioration*, **22**, 308–311

4 HANSTVEIT, A O , GERRITSE, G A AND SCHEFFERS, W A (1988) A Study of the Biodeterioration of Vulcanized Rubber Pipe-Seals Exposed to Inoculated Tap Water *NR Technology*, **19**, 48–58

5 SEAL, K J (1988) The Biodeterioration and Biodegradation of Naturally Occuring and Synthetic Plastic Polymers *Bideterioration Abstracts*, **2**, 295–317

6 FLETCHER, W P , GEOFFREY, G AND MORRELL, S H (1952) Use of Modulus as a Measure of the State of Cure in Pure Gum Natural Rubber Vulcanisates Quantitative Characterisation of Cure *Transactions, I R I*, 1885–1893

7 GORTON, A D T AND PENDLE, T D (1976) A New Rapid Measurement of Crosslink Density in Compounded Natural Latices, *NR Technology*, **7**, 77–81

8 TSUCHII, A, TAKEDA K SUZUKI, T AND TOKIWA, Y (1996) Colonization and Degradation of Rubber Pieces by *Nocardia* sp *Biodegradation*, 7 41–48

9 IKRAM, A, ALIAS, O, SHAMSUL BAHRI A R FAUZI, M S AND NAPI D (2001) Effects of Added Nitrogen and Phosphorus on the Biodegradation of NR Gloves in Soil *J Rubb Res*, **4(2)**, 102–117

10 BEREKAA, M M, LINOS, A REICHELT, R, KELLER U AND STEINBUCHEL, A (2000) Effect of Pretreatment of Rubber Material on its Biodegradability by Various Rubber Degrading Bacteria *FEMS Microbiology Letters*, **184** 199–206

11 ELLIS, B AND WELDING G W (1964) Estimation from Swelling of the Structural Contribution of Chemical Reactions in Vulcanization of Natural Rubber II Estimation of the Equilibrium Degree of Swelling *Rubb Chem Technol*, **37** 571–575

12 FLORY PJ AND REHNER, J (1943) Statistical Mechanics of Crosslinked Polymer Networks I Rubber-like Elasticity *J Chem Phys*, **11**, 512–520

13 KRAUS, G (1957) Degree of Cure in Filler-Reinforced Vulcanizates by Swelling Method *Rubb Chem Technol* **30**, 928–951

14 LINDLEY, PB AND TEO, S C (1977) High-temperature Ageing of Rubber Blocks *Plastics and Rubber Materials and Applications*, **2** 82–88

15 LOH, A C P (1982) Further Investigations of Prevulcanisation of Natural Rubber Latex Ph D Thesis CNAA NCRT Polytechnic of North London

16 PORTER M (1988) The Influence of Vulcanisate Structure at Physical Properties and Ageing Behaviour *Proc Int Rubb Technol Conf 1988, Penang Malaysia (Amin L L and Lau Kai Thong eds)*, p 26-46 Kuala Lumpur Rubber Research Institute of Malaysia

17 AMIR-HASHIM, M Y AND MORRIS M D (1999) NR Latex Vulcanisation–Prevulcanisation and Post-vulcanisation of Dipped NR Latex Films *J Rubb Res*, **2(2)** 78–87

18 MORAND, J L (1977) Chain Scission in the Oxidation of Polyisoprene *Rubb Chem Technol* **50** 373–396

19 KELLO V, TKAC, A AND HRIVIKOVA, J (1956) A Study of the Aging of Natural Rubber by Means of Infrared Spectroscopy V Aging Accelerated by Heat *Rubb Chem Technol* **29** 1245–1254

20 SCOTT G AND GILEAD, D (eds) (1995) *Degradable Polymers Principles and Applications* London Chapman & Hall

21 SCOTT G (2000) Green' Polymers *Polymer Degradation and Stability*, **68** 1–7

22 SCOTT, G (1999) *Polymers and the Environment* Cambridge The Royal Society of Chemistry

23 BERNACCA, G M O'CONNOR, B, WILLIAMS, D F AND WHEATLEY, D J (2002) Hydrodynamic Function of Polyurethane Prosthetic Heart Valves Influences of Young's Modulus and Leaflet Thickness *Biomaterials* **23** 45–50

24 IKRAM, A (2002) Condom Biodegradation in Soil *Malaysian Rubber Technology Developments*, **2** 15 17

25 SCOTT, G (1997) *Antioxidants in Science Technology Medicine and Nutrition* Chichester Albion Publishing

26 AZHARI, C H, SAAD, A F, WAN YUSOFF W M AND IKRAM, A (2000) Biodegradation of Natural Rubber by Actinomycete #4 in a Continuous Culture

System. *Pakistan Journal of Biological Sciences*, **5**, 329–331.

27. TSUCHII, A., TAKEDA, K. AND TOKIWA, Y. (1997) Degradation of the Rubber in Truck Tires by a Strain of *Nocardia*. *Biodegradation*, **7**, 405–413.

28. KWIATKOWSKA, D., ZYSKA, B.J. AND ZANKOWICZ, L.P. (1980) Microbial Deterioration of Natural Rubber Sheet by Soil Microorganisms. *Proceedings of the Fourth International Biodeterioration Symposium, Berlin (Oxley, T.A., Becker, J. and Allsop, D., eds.)*, pp. 135–141. Pitman Publishing Ltd & The Biodeterioration Society.

29. LINOS, A., BEREKAA, M.M., REICHELT, R., KELLER, U., SCHMITT, J., FLEMMING, H-C., KROPPENSTEDT, R.M. AND STEINBÜCHEL, A. (2000) Biodegradation of *cis*-1,4-Polyisoprene Rubbers by Distinct Actinomycetes: Microbial Strategies and Detailed Surface Analysis. *Applied and Environmental Microbiology*, **66**, 1639–1645.

30. LINOS, A., AND STEINBUCHEL, A. (2001) Biodegradation of Natural and Synthetic Rubbers. *Biopolymers Vol. 2, Polyisoprenoids (Koyama, T. and Steinbuchel, A., eds.)*, pp. 321–359. Weinheim: Wiley-VCH.