

## The Extraction of Admixed Polymers from Natural Rubber Vulcanizates

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### INTRODUCTION

In the preparation of block or graft polymers there is usually present some of the ungrafted homopolymers. The mixtures may usually be separated by fractional precipitation<sup>1</sup> or by extraction with suitable solvents.<sup>2</sup>

These methods can give concordant results under carefully controlled conditions, but in some cases their precision is open to question.<sup>3,4</sup> Moreover, for certain compositions, e.g., polystyrene (PS)-rubber grafts, selective extraction with solvents is not very satisfactory, unless the rubber and rubber graft polymer are vulcanized prior to extraction.<sup>5,6</sup> This is because the best solvents for polystyrene, e.g., benzene and carbon tetrachloride, are also solvents for rubber. Methyl ethyl ketone, which should extract polystyrene from rubber, was found to be not very satisfactory, owing to the sensitivity of rubber to oxidative degradation in its presence. When samples were vulcanized prior to extraction with benzene it was found that variable results were obtained, dependent on the conditions of extraction and vulcanization, particularly in the case of high molecular weight polystyrene. In view of this, rubber-polymethylmethacrylate (PMMA) graft polymers, in which the contents of free homopolymer were known, were vulcanized with sulfur chloride and extracted. Yields of homopolymer were low even after two or four days of extraction.

In order to establish the conditions for quantitative extraction of the uncombined homopolymers, a number of vulcanizates were prepared from rubber-PS and rubber-PMMA graft copolymers, and from mixtures of rubber and the separate polymers.

### EXPERIMENTAL

Graft polymer latices from natural rubber with methyl methacrylate or styrene were prepared as described previously.<sup>7</sup>

Latices of polymethyl methacrylate and polystyrene were prepared at 50°C., employing sulfated methyl oleate (4%) as emulsifier, and potassium persulfate (0.25%) as catalyst. The polymers were of high molecular weight:  $[\eta] = 6.60$  and  $7.45$  respectively (intrinsic viscosity measurements in benzene, 100 ml./g.).

A low molecular weight polymethyl methacrylate ( $[\eta] = 1.60$ ) latex was made at 50°C. with *p*-nitrobenzene diazonium *p*-chlorobenzene sulphonate (0.5%) as catalyst and potassium oleate (4%) as emulsifier.

Cast films from the rubber and polymer latices were prepared and were vulcanized by the following methods.

A. Immersion in sulfur monochloride, 0.1%, 0.5%, or 1.0% v/v in hexane, at room temperature for 60 min. The films were then washed with alcohol and dried *in vacuo*.

B. Press cure with dicumyl peroxide (5%) for 1 hr. at 135°C.

C. Accelerated sulfur vulcanization by the following recipe (parts by weight):

Polymer	100
Sulfur	2.5
Santocure	0.5
Stearic acid	2.0
Zinc oxide	5.0

Cure 1 hr. at 135°C.

D. Exposure to  $\gamma$ -radiation from cobalt-60. Samples were protected from gross oxidation by being wrapped in cellophane foil, but it was clear that during irradiation there was some slight ingress of oxygen. One sample was irradiated in high vacuum.

Samples for extraction were cut into small cubes or passed through mill rolls to obtain a fine crumb. Extracts were dissolved in chloroform, filtered, treated with ozone to remove traces of rubber and unsaturated compounds, in the presence of *n*-butyl sulfide as protective agent,<sup>8</sup> and precipi-

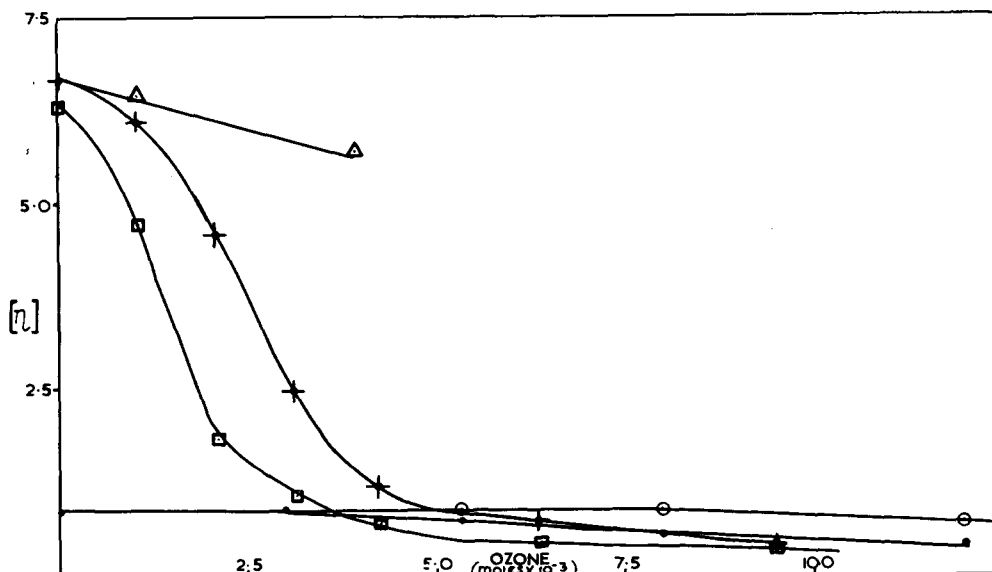


Fig. 1. Influence of ozone on polymethyl methacrylate (chloroform solution at  $-25^\circ\text{C}$ ), PMMA and additive respectively, in moles  $\times 10^3$ : ( $\bullet$ ) 2.5, di-*n*-butyl sulfide 1.7; ( $\bullet$ ) 5.0, di-*n*-butylsulfide 2.9; ( $\Delta$ ) 2.5, di-*n*-butyl sulfide 6.9; ( $\circ$ ) 5.0, di-*n*-butyl sulfide 8.7; ( $\square$ ) 2.5, di-*tert*-butyl disulfide 1.4.

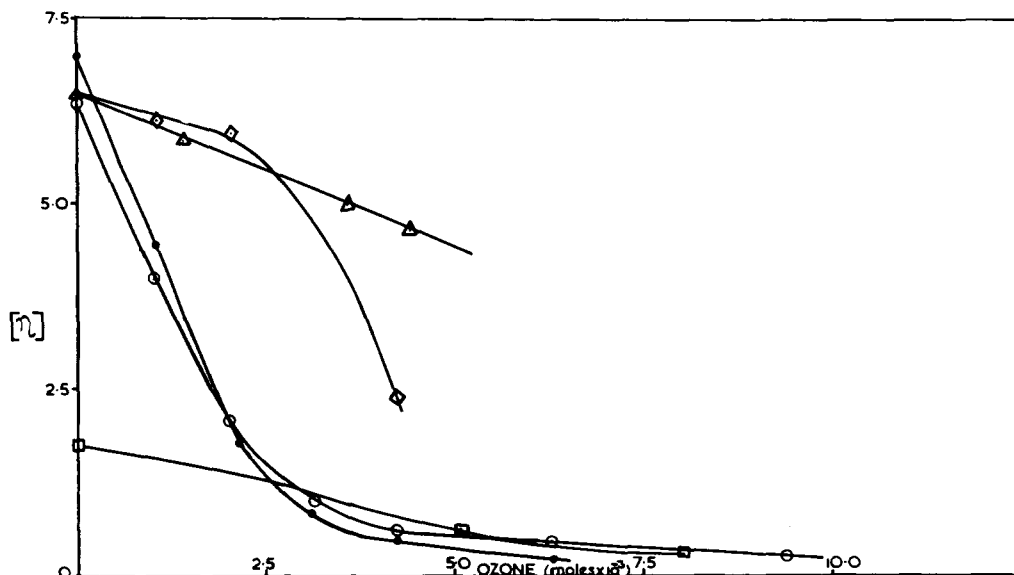


Fig. 2. Influence of ozone on polystyrene (chloroform solution at  $-25^\circ\text{C}$ .), PS and additive respectively, in moles  $\times 10^3$ : ( $\square$ ) 1.9, di-*n*-butyl sulfide 1.45; ( $\bullet$ ) 2.3, di-*n*-butyl sulfide 1.45; ( $\diamond$ ) 2.3, di-*n*-butyl sulfide 6.9; ( $\Delta$ ) 2.3, natural rubber 1.45 and di-*n*-butyl sulfide 3.5; ( $\circ$ ) 2.3, di-*tert*-butyl disulfide 1.2.

tated with ethanol. With low molecular weight PMMA it was necessary to employ 75:25 ethanol-water as precipitant.

When intrinsic viscosities were required to be measured, great care was needed to avoid serious degradation by ozone, particularly in the case of polystyrene. With low molecular weight PMMA di-*n*-butyl sulfide protected the polymer against

the addition of almost an equimolar amount of ozone. With PMMA of high molecular weight, however, slight degradation occurred even in the presence of the protective agent (Fig. 1), and it was therefore necessary to ensure minimum exposure to ozone after the destruction of unsaturated compounds. In the presence of di-*n*-butyl sulfide the ozonolysis products of rubber had no degrada-

tive effect on PMMA. With polystyrene, contrary to Barnard's findings,<sup>8</sup> it was found that di-*n*-butyl sulfide did not afford complete protection against ozone (Fig. 2), and with high molecular weight polymer a fall in intrinsic viscosity occurred even before all the rubber was destroyed. Those polymers treated with the greatest amount of ozone rapidly became insoluble on storing at room temperature—presumably the result of forming a polyozonide. Di-*tert*-butyl disulfide tried as an alternative protective agent appears to be less effective than the monosulfide.

## RESULTS

### Influence of Extraction Conditions

In Figure 3 are shown the results of extractions made with various solvents. Acetone, which extracts all the PMMA from unvulcanized polymer in 48 hr., is much less effective with vulcanizates, and may extract little or no homopolymer even after many days of extraction. (See, e.g., curve 4 in Fig. 3). Benzene or chloroform, which swell the vulcanizates greatly, extract larger amounts, but

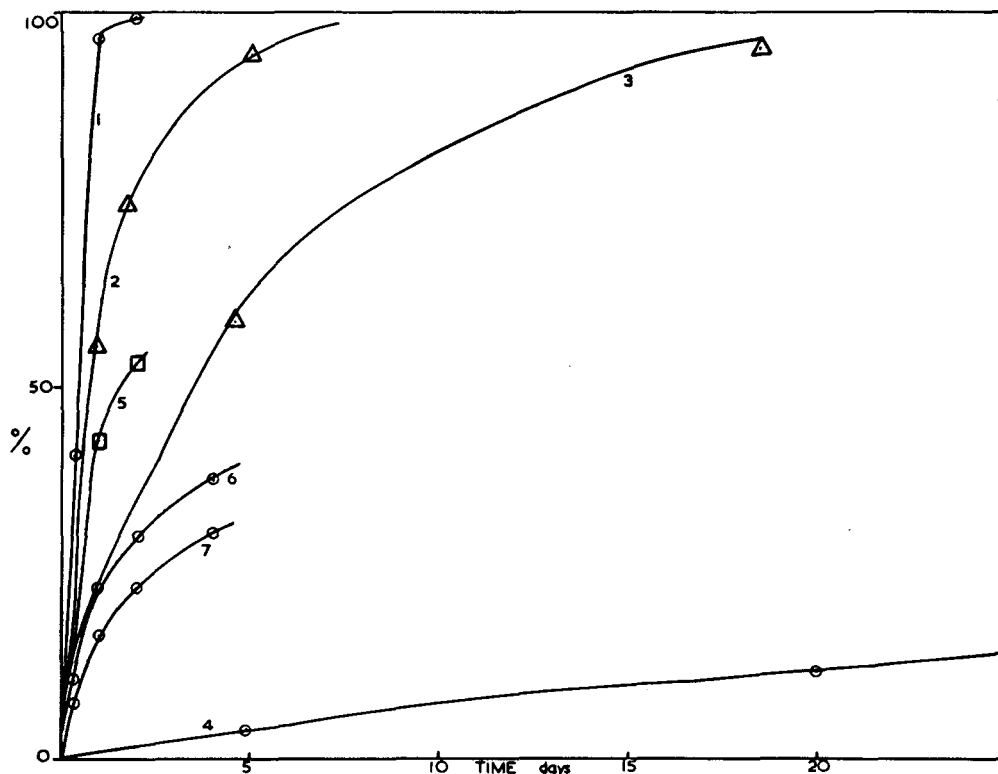


Fig. 3. Extraction of vulcanizates: 1, rubber-PMMA unvulcanized; 2, rubber-PS sulfur-vulcanized; 3 and 4 (Curve 4, 14.6% after 27 days), rubber-PMMA sulfur-vulcanized; 5 and 6, rubber graft PMMA, 0.5%  $S_2Cl_2$ ; 7, rubber graft PMMA, 1.0%  $S_2Cl_2$ . Acetone at 60°C. (○); Benzene at 80°C. (△); Chloroform at 56°C. (◻).

In the ozonolysis of vulcanizates, attack on the rubber takes place only at the surface of the swollen polymer. Sufficient ozone may persist in the solution to destroy the protective agent and subsequently to degrade the polymer. This was observed even in the case of highly swollen rubber-polymer samples. In such cases it was necessary to reduce the sample to a very small particle size crumb before swelling in chloroform, and to add further quantities of the sulfide during ozonolysis.

the bulk of the polymer can still only be isolated by extraction for many days.\*

It is of importance to note that the vulcanizates swell much more in chloroform or benzene than does the unvulcanized polymer in acetone. In acetone, swelling volumes varied from 130% for

\* Results on mixed polymers are expressed as percentage recovery of the original polymer added to rubber, except for results on graft polymers in Table III, where they are expressed as percentage of the total.

TABLE I  
Effect of Sample Size on Extraction of Polymer

Average size of vulcanizate (mm) <sup>3</sup>	Yield of extract (48 hr. Soxhlet, chloroform), %			
	1	2	3	4
8	16.6	15.0	30.8	17.6
1	46.9	41.9	—	—
0.03	—	57.0	58.5	58.5

<sup>a</sup> Sample: No. 1, rubber-PMMA, 0.1% S<sub>2</sub>Cl<sub>2</sub>; No. 2, rubber-PMMA, 1.0% S<sub>2</sub>Cl<sub>2</sub>; No. 3, rubber-PMMA, sulfur-cured; No. 4, rubber-PS, sulfur-cured.

TABLE II  
Influence of Molecular Weight on Extraction

Polymer	Vulcanization <sup>a</sup>	[ $\eta$ ]	Extract (48 hr., CHCl <sub>3</sub> ), %
Rubber-PMMA	A, 0.1% S <sub>2</sub> Cl <sub>2</sub>	6.60	16
		1.60	50
Rubber-PS	C, sulfur	6.50	58.5
		0.65	79

<sup>a</sup> See text, Experimental.

unvulcanized mixtures to 75% for tightly cross-linked polymers. Chloroform and benzene swelled the polymers to 5–20 times this extent.

In Table I is shown the influence of sample size on the rate of extraction of polymer.

### Effect of Molecular Weight on Extraction

Vulcanized samples of rubber containing homopolymer of differing molecular weights were extracted. The results (Table II) show the greater ease of extraction of low molecular weight polymer.

Further evidence of the greater ease of extraction of low molecular weight polymer was shown by the fact that when degradation of PMMA occurred concurrently with crosslinking (e.g., when high-energy radiation was used), all the homopolymer was extracted within 48 hr. (Table III). It is also relevant that the lower molecular weight fraction of the polymer is first extracted, since the intrinsic viscosity of the homopolymer increased with increase in yield of extract.

TABLE III  
Effect of Method of Crosslinking on Extraction of Homopolymer<sup>a</sup>

Vulcanization (see text)	PMMA			PS		
	Swelling in benzene, w/w <sup>e</sup>	% Extracted	[ $\eta$ ]	Swelling in benzene, w/w <sup>e</sup>	% Extracted	[ $\eta$ ]
Mixed polymers						
A 0.1% S <sub>2</sub> Cl	1565	16.6	1.94	1110	12.1	1.35
1.0% S <sub>2</sub> Cl <sub>2</sub>	470	15.0	0.97	420	3.4	0.07
B Dicumylperoxide	440	32.4	3.1	450	79.5	0.97
C Sulfur	360	30.8	3.4	390	17.6	1.24
D Dose 2.9 × 10 <sup>7</sup> r	790	~100 <sup>b</sup>	0.13	1125	65.2	0.83
2.0 × 10 <sup>8</sup> r	220	~100 <sup>b</sup>	0.07	180	11.6	0.34
3.0 × 10 <sup>7</sup> r <sup>c</sup>	530	95	0.19	—	—	—
Graft polymers						
Unvulcanized	—	9.6 (acetone)	—	—	7.6 (5.6 benzene and 2.0 chloroform) <sup>d</sup>	—
A 1.0% S <sub>2</sub> Cl <sub>2</sub>	475	0.9 (acetone) 3.4 (chloroform)	—	—	7.8 (benzene)	—
A 0.5% S <sub>2</sub> Cl <sub>2</sub>	600	2.0 (benzene)	—	—	11.6 (8.2 benzene and 3.4 chloro- form) <sup>d</sup>	—
A 0.1% S <sub>2</sub> Cl <sub>2</sub>	1285	8.0 (acetone) 9.3 (chloroform)	—	—	7.4 (benzene)	—

<sup>a</sup> The mixed polymers were all extracted for 48 hr with chloroform; the graft polymers, with the stated solvents.

<sup>b</sup> Contaminated with ozonolysis products from rubber.

<sup>c</sup> Irradiated *in vacuo*.

<sup>d</sup> Successive extraction following benzene.

<sup>e</sup> Swollen for 3 days at room temperature.

### Influence of Crosslinking

In Table III is given the data for the extraction of the various vulcanizates with the use of different crosslinking systems.

#### DISCUSSION

It is clear from the above data that, in general, the extraction of homopolymer from vulcanizates is slow with high molecular weight polymer. The rate of diffusion of polymer through a highly swollen network might be expected to be greater than extraction from slightly swollen, unvulcanized polymer. That a smaller amount is extracted in a given time is, no doubt, due to the fact that although the diffusion rate of polymer may be faster in the swollen vulcanizate, the distance which a polymer molecule must travel is very much greater. In agreement with this it is found that the percentage of extract is increased by reducing the mesh of the sample. It is not clear, however, why the extraction rate should fall so sharply with increase in crosslinking when the swelling volume, though reduced, is still very much greater than that of the unvulcanized polymer. Vulcanizates prepared with sulfur chloride yield less extract than would be anticipated from the swelling volume. The reason for this is possibly the result of non-uniform crosslinking, the outer surface of the polymer being more tightly cured than the interior and so restricting diffusion of the polymer.

The possibility of attack on the homopolymer during vulcanization, or even of cocrosslinking with the rubber, must always be kept in mind. The latter is unlikely with PMMA, since it is well known that polymethyl methacrylate radicals are incapable of transfer grafting to rubber.<sup>9</sup> There is, however, a very large fall in molecular weight during radiation crosslinking. As far as can be ascertained, sulfur or sulfur chloride vulcanization has little effect on the molecular weight of PMMA, and these probably are the safest methods for this polymer.

With polystyrene the effects of crosslink density, sample size, molecular weight of polymer, and solvent were similar to those observed with PMMA. Intrinsic viscosities of the isolated polymers are low (Table III), but it is uncertain whether this is due to the effect of crosslinking or to the influence of ozone during isolation, although it is probably the latter. Crosslinking by sulfur or by sulfur chloride is also recommended when this polymer is present.

Similar results were obtained by dry-mixing the polymers into rubber, or by imbibing monomer

containing 0.25% of azobisisobutyronitrile into acetone-extracted natural rubber and polymerizing *in situ*, or by using the mixed latices. This proves that the water-soluble components of the latices do not influence the extraction.

Extraction made for many days is very inconvenient. The rate is, of course, greatly increased by raising the temperatures.

As a practical procedure it was found that all the homopolymer (PS or PMMA) was extracted from sulfur vulcanizates by benzene after 4 days at 100°C. The yield of ozone-reactive material was also appreciable and increased with time and temperature of extraction—indicating some oxidative breakdown of the rubber network. This occurred to some extent even when air was expelled from the vessels employed and antioxidant added to the solvent. With graft polymers this led to the uncertainty whether degradation of the vulcanizate might permit the solution of some graft polymer as well as ungrafted polymer.

The work described here relates only to PMMA or PS mixed with rubber, but there is no reason to believe that results on other polymer systems would not be similar. It follows, therefore, that unless polymers of very low molecular weight are involved or the extraction is very prolonged, quantitative results will not be obtained. Molecular weights of partial extracts are not representative of the whole. Separate tests should be made to preclude cocrosslinking or degradation during vulcanization, or degradation of the vulcanizates during extraction of the homopolymer.

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#### References

1. Bateman, L. C., *Ind Eng Chem.*, **49**, 704 (1957).
2. Angier, D. J., and D. T. Turner, *J. Polymer Sci.*, **28**, 265 (1958).
3. Angier, D. J., and W. F. Watson, *J. Polymer Sci.*, **25**, 1 (1957).
4. Cooper, W., and G. Vaughan, *J. Appl. Polymer Sci.*, **1**, 254 (1959).
5. Bevilacqua, E. M., *J. Polymer Sci.*, **24**, 292 (1957).
6. Cooper, W., P. R. Sewell, and G. Vaughan, *J. Polymer Sci.*, **41**, 167 (1959).
7. Cooper, W., G. Vaughan, S. Miller, and M. Fielden, *J. Polymer Sci.*, **34**, 651 (1959).
8. Barnard, D., *J. Polymer Sci.*, **22**, 213 (1956).
9. Merrett, F. M., *Trans. Faraday Soc.*, **50**, 759 (1954).

#### Synopsis

Extraction by solvent of admixed polymethyl methacrylate or polystyrene from natural rubber vulcanizates is de-

pendent on the crosslink density, the solvent, the molecular weight of the polymer, and the size of sample extracted. High molecular weight polymer is extracted very slowly, and in some cases several weeks of continuous extraction have been found necessary. The rate of extraction is increased, as would be expected, by solvents which swell the rubber strongly, and by increase in temperature of extraction. In some cases the vulcanization procedure degrades the polymer, while in others there is a possibility of cocrosslinking the rubber and polymer. Graft copolymers from rubber and methylmethacrylate or styrene possess similar characteristics when vulcanized. In consequence, analysis of the content of free homopolymer is subject to considerable uncertainty. In the analysis of these rubber-polystyrene mixtures by ozonolysis, polystyrene was found to be very susceptible to attack by ozone.

### Résumé

L'extraction par un solvant du polyméthacrylate de méthyle ou du polystyrène incorporé au départ d'une vulcanisat de caoutchouc naturel dépend de la densité de pontage, du solvant, du poids moléculaire du polymère et de la dimension de l'échantillon extrait. L'extraction d'un polymère de poids moléculaire élevé est très lente et on a trouvé que dans certains cas il était nécessaire de procéder à une extraction continue de plusieurs semaines. On accroît la vitesse d'extraction, comme on l'espérait, par des solvant qui gonflent fortement le caoutchouc, et par élévation de la température d'extraction. Dans certains cas, le processus de vulcanisation dégrade le polymère, tandis que dans d'autres

on a la possibilité d'un pontage combiné du caoutchouc et du polymère. Des copolymères greffés de caoutchouc et de méthacrylate de méthyle ou de styrène ont des caractéristiques semblables après vulcanisation. Par conséquent, toute analyse du contenu en homopolymère libre est sujet à une incertitude considérable. Lors de l'analyse de ces mélanges caoutchouc-polystyrène par ozonolyse, on a trouvé que le polystyrène est très sensible à l'attaque par l'ozone.

### Zusammenfassung

Die Extraktion von beigemengtem Polymethylmethacrylat oder Polystyrol aus Naturkautschukvulkanisaten durch ein Lösungsmittel ist von der Vernetzungsdichte, vom Lösungsmittel, vom Molekulargewicht des Polymeren und von der Grösse der extrahierten Probe abhängig. Hochmolekulare Polymere werden langsam extrahiert und in einigen Fällen waren einige Wochen kontinuierlicher Extraktion notwendig. Die Extraktionsgeschwindigkeit steigt, wie zu erwarten, bei Lösungsmitteln, die den Kautschuk stark quellen, und bei erhöhter Extraktionstemperatur an. In einigen Fällen wird durch den Vulkanisationsprozess das Polymere abgebaut, während in anderen Fällen eine Möglichkeit zur Co-Vernetzung des Kautschuks und des Polymeren besteht. Propfcopolymere aus Kautschuk und Methylmethacrylat oder Styrol verhalten sich bei der Vulkanisation ähnlich. Die Bestimmung des Gehalts an freiem Homopolymeren ist daher nur mit grosser Unsicherheit möglich. Bei der Analyse dieser Kautschuk-Polystyrol-Mischungen durch Ozonolyse wurde gefunden, dass das Polystyrol durch Ozon sehr leicht angegriffen wird.