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An NMR and Mössbauer spectroscopic study of antifouling rubbers containing organotin compounds

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An NMR study of the carbon tetrachloride and benzene extracts of bis(tributyltin) oxide-impregnated neoprene and natural rubbers revealed the presence of tributyltin chloride, tributyltin stearate and dibutyltin distearate in the former, and bis(tributyltin) sulphide and tributyltin stearate in the latter. The implications of these findings together with ^{119m}Sn Mössbauer parameters for the formulated rubbers are discussed.

Keywords: ^{119}Sn, ^{13}C NMR ^{119m}Sn Mössbauer, tributyltin, antifoulant, neoprene, natural rubber

INTRODUCTION

The use of tributyl- and, to a lesser extent, triphenyl-tin compounds as toxic additives in antifouling paints and coatings for the protection of ships' hulls and sea-water cooling pipes from the attachment of barnacles, algae, sea grass and other marine organisms, consumes some 3500 tonnes per annum of these compounds.[1] Comprehensive reviews on this topic have recently been published.[1,2]

Originally the triorganotin biocide was simply mixed into a paint matrix and the protective action was produced by leaching of the organometallic toxicant. The main disadvantage with these paint formulations was their relatively short service life of 1–2 years. Increased life-times of 4–5 years were achieved by chemically binding the active triorganotin moiety onto a polymer backbone, e.g. poly(tributyltin methacrylate/methylmethacrylate). Such slow release polymers undergo hydrolysis to release the triorganotin species.

A third antifouling system involves the incorporation of the organotin compound into an elastomeric matrix. Such antifouling coatings were originally developed to overcome the fouling problems associated with rubber domes used to encase sonar equipment. Antifouling paints applied to these domes provided little protection, owing to surface cavitation arising from transmission of the acoustic signals. These problems were eradicated when the concept of adding a toxicant directly to the moulded rubber dome was found to be feasible. Typically a tributyltin species is incorporated into a neoprene, natural or nitrile rubber from which the active organotin species is then slowly released by what is believed to be a diffusion-dissolution mechanism. Such elastomeric systems have been reported to give protection for more than 7 years.[1]

To date there have been very few studies of the chemical nature of the triorganotin species within the elastomers. It has been suggested that the active agent released is a mixture of unreacted bis(tributyltin) oxide ($(Bu_3Sn)_2O$), tributyltin chloride (Bu_3SnCl) and various tributyltin carboxylates resulting from the vulcanising reaction.[3] In addition, it has recently been reported that the major organotin constituent of tributyltin/neoprene-based elastomers is tributyltin chloride, irrespective of the tributyltin compound which is used in the original formulation.[4] We too have been examining the fate of organotin toxicants in neoprene rubber and, also in natural rubber. Thus, the object of this paper is to comment on and expand the previous work[4] and to report the results of our studies with natural rubber.

EXPERIMENTAL

Samples of both neoprene and natural rubbers formulated with bis(tributyltin) oxide were supplied by the Admiralty Research Establishment, Holton Heath, Dorset. The main components of the rubbers are shown in Table 1.

Table 1 Main components of the antifouling rubbers studied

Neoprene	Natural
Neoprene	Smoked sheet
Carbon filler	Carbon filler
Stearic acid	Stearic acid
'Octamine'[a]	Sulphur
$(Bu_3Sn)_2O$ (2.6% w/w)	$(Bu_3Sn)_2O$ (3.2% w/w)

[a] Reaction product of diphenylamine and diisobutylene.

Bis(tributyltin) sulphide ($(Bu_3Sn)_2S$)[5], tributyltin stearate,[6] tris(disbutyltin sulphide) ($(Bu_2SnS)_3$)[7] and dibutyltin distearate[8] were all prepared following previously published procedures. All other chemicals were obtained commercially and used without further purification.

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd, Oxford) with a 512-channel data store. A 5 mCi $Ba^{119m}SnO_3$ source was used at room temperature and samples were cooled to 80 K, using a liquid nitrogen cryostat. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔEq) parameters is $\pm 0.05\ \mathrm{mm\,s^{-1}}$.

NMR spectra were recorded on a JEOL FX60Q spectrometer, with field frequency lock to external D_2O. ^{119}Sn spectra were recorded under nuclear Overhauser suppressed conditions, and, to obtain quantitative results, a pulse repetition time of 10 s was used. ^{119}Sn and ^{13}C chemical shifts (δ ^{119}Sn and δ ^{13}C) are relative to Me_4Sn and Me_4Si respectively and are accurate to $\pm$0.1 ppm.

RESULTS AND DISCUSSION

^{119}Sn NMR investigations of a CCl_4 soxhlet extract from a neoprene rubber, formulated with $(Bu_3Sn)_2O$, revealed the presence of three major organotin constituents (Table 2). The two high frequency peaks at 142.9 and 81.3 ppm were assigned to Bu_3SnCl and Bu_3Sn(stearate) on the basis of their chemical shifts. The former compound presumably arises due to reaction of $(Bu_3Sn)_2O$ with HCl produced from the dehydrochlorination of the base polymer under curing conditions. With regard to the formation of Bu_3Sn(stearate), rubber formulations frequently contain a carboxylic acid which acts as a lubricant. In the rubber studied the lubricant was stearic acid which is known to react rapidly with $(Bu_3Sn)_2O$ at elevated temperatures, as would be encountered during processing.

The chemical shift (−170.8 ppm) of the third organotin species observed in the NMR spectrum is typical of a diorganotin dicarboxylate, and is therefore assigned as $Bu_2Sn(stearate)_2$. From Table 2 it can be seen that the chemical shift of an authentic sample of this compound in CCl_4 (10% w/v) was −151.4 ppm. The difference of approximately 19 ppm from the observed value in the extracted solution may be explained by the fact that diorganotin dicarboxylates autoassociate to form dimers, and so shift differences are frequently observed, dependent upon the position of equilibrium in solution.[10,11]

In order to check that CCl_4 was a suitable solvent for this study, a soxhlet extraction was carried out on a second rubber sample using C_6H_6. After concentration, a ^{119}Sn NMR spectrum of this solution was recorded (Table 2 and Fig. 1) and revealed the presence of the same three organotin compounds. In fact, a ^{119}Sn NMR spectrum of a solution containing a mixture of authentic samples of these organotin derivatives was recorded and the chemical shifts observed were in excellent agreement with those of the extracted solution (Table 2). Although some differences in signal integrals, compared to the CCl_4 extract, were obtained (Table 2), essentially the organotins were found to be present in similar relative amounts as before.

It is possible that, with both CCl_4 and C_6H_6 solvents, not all of the organotin is extracted from the rubber. However, total tin contents of the rubber before (0.7% as Sn) and after extraction (CCl_4–0.3% as Sn; C_6H_6–0.1% as Sn) suggest that the majority was removed.

Bu_3SnCl was reported by Allen et al.[4] to be the major component, detected by ^{119}Sn NMR, in a CH_2Cl_2 extract from a neoprene rubber and was believed to be the predominant organotin species within the rubber. Our results from both the CCl_4 and C_6H_6 extracts, indicate, on the basis of integrated NMR signals (Table 2), that although Bu_3SnCl constitutes approximately 45% of the total extracted organotin content it is not the only organotin compound contained in the rubber, as previously implied,[4] but that Bu_3Sn(stearate) and $Bu_2Sn(stearate)_2$ are present in appreciable levels as well.

To ensure that Bu_3Sn(stearate) was not pro-

Table 2 ^{119}Sn NMR chemical shifts

Compound	Solvent	Concentration (% w/v)	$\delta\,^{119}$Sn (ppm)[a]
$(Bu_3Sn)_2O$	Neat		81.7
	CCl_4	10	84.7
	C_6H_6	5	83.7
Bu_3SnCl	Neat		143.0
	CCl_4	10	143.5
	C_6H_6	15	144.8
$(Bu_3Sn)_2S$	Neat		81.9
	CCl_4	10	82.4
	C_6H_6	5	81.6
Bu_3Sn(stearate)*	CCl_4	25	89.5
	CCl_4	10	90.2
	C_6H_6	10	91.2
Bu_2Sn(stearate)$_2$	CCl_4	10	−151.4
$(Bu_2SnS)_3$	Neat		126.9
Bu_3SnCl	C_6H_6	15	143.5
Bu_3Sn(stearate)		30	88.6
Bu_2Sn(stearate)$_2$		25	−168.0
Bu_3Sn(stearate)	C_6H_6	10	91.2
$(Bu_3Sn)_2S$		5	81.6
Soxhlet extract from neoprene rubber sample	CCl_4	[b]	142.9 (48%) 87.3 (38%) −170.8 (14%)
	C_6H_6	[b]	143.4 (42%) 88.8 (46%) −167.5 (12%)
Soxhlet extract from natural rubber sample	CCl_4	[b]	89.9 (62%) 82.2 (38%)
	C_6H_6	[b]	90.3 (71%) 81.2 (29%)

[a] Percent compositions, where appropriate, obtained from integral values are shown in brackets, [b] Not determined.

*Stearic acid, $CH_3(CH_2)_{16}COOH$.

duced by reaction of $(Bu_3Sn)_2O$ with stearic acid during the soxhlet extraction process, a further sample of the rubber was taken and the organotin extracted by passing cold CCl_4 over the sample contained in a column. A subsequent ^{119}Sn NMR spectrum of this solution again indicated the presence of the same species, thereby demonstrating that products were not being formed in this solvent at higher temperatures.

Mössbauer spectra were recorded of the neoprene rubber formulated with $(Bu_3Sn)_2O$. The data for the unextracted rubber (Table 3) are in accord with those reported by Allen et al.[4] and were previously interpreted as being due to the presence of Bu_3SnCl. However, the ΔE_Q value does not correspond to that of the pure compound and this was explained in terms of Bu_3SnCl occupying a pseudopolymeric five coordinate site within the rubber matrix. Consequently, it would appear that a discrepancy arises due to the NMR evidence showing the presence of three organotin compounds, and the Mössbauer spectrum apparently indicating only one species. If, however, the Mössbauer parameters of pure Bu_3SnCl and pure Bu_3Sn(stearate) are compared (Table 3), it is seen that they are almost identical. Therefore, if both of these compounds exist

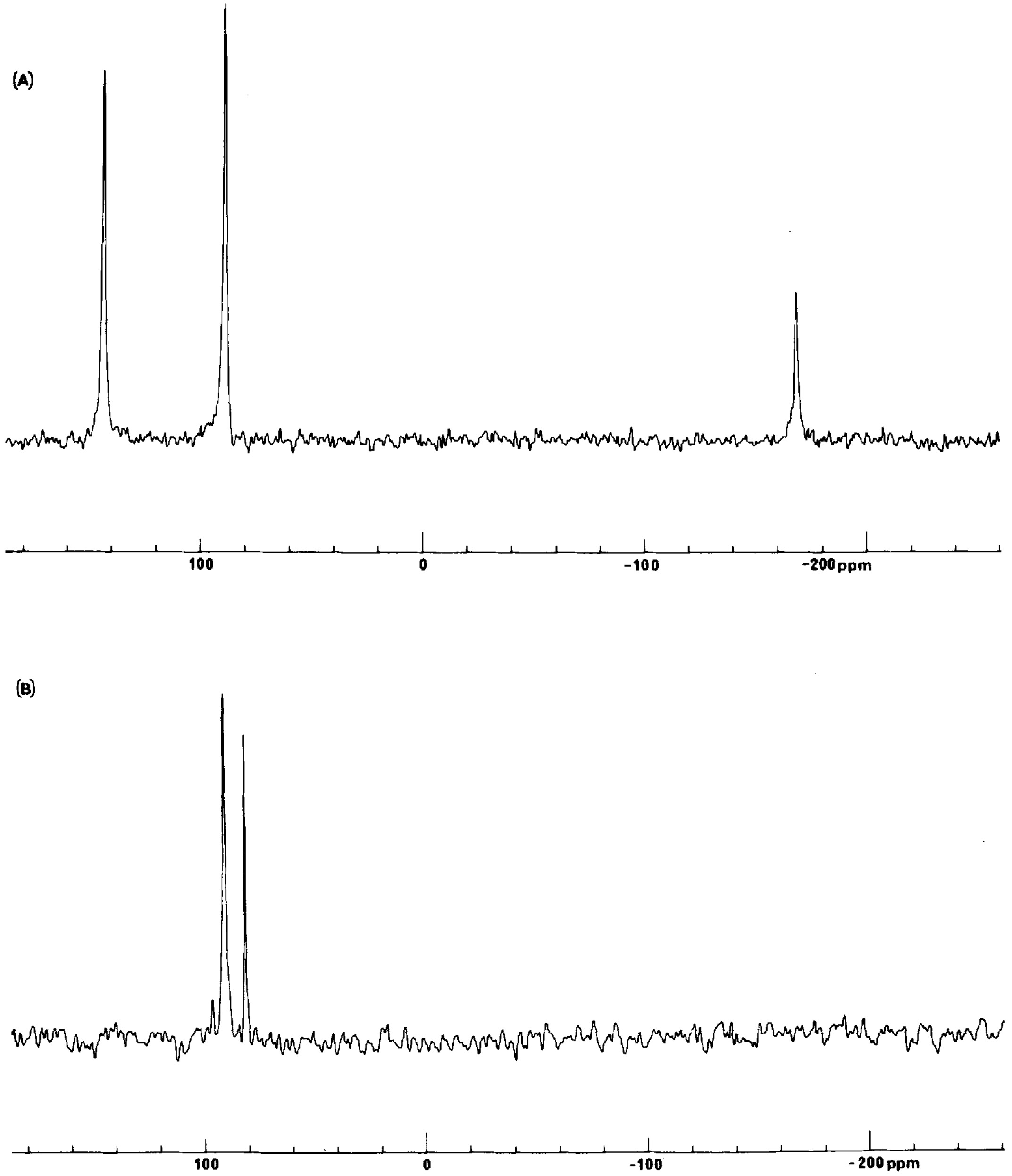

Figure 1 ^{119}Sn NMR spectra of the C_6H_6 extracts from (A) neoprene and (B) natural rubbers.

within the rubber in a similar environment it would be expected that their Mössbauer parameters would still remain practically identical. Consequently, we suggest that it would be extremely difficult to identify the presence of this particular mixture by Mössbauer spectroscopy. Similarly, the parameters of $Bu_2Sn(stearate)_2$ are very close to those of the two triorganotin compounds, and, especially when the lower concentration of this species is considered, it would again be expected that this compound, in mixture within the rubber matrix, would not be readily identified by Mössbauer spectroscopy.

In a similar manner we have studied the organotin species present in a natural rubber formulated with $(Bu_3Sn)_2O$. Soxhlet extractions

Table 3 ^{119m}Sn Mössbauer parameters

	δ	ΔE_Q (mm s^{-1})	$\Gamma_1{}^a$	$\Gamma_2{}^a$
$(Bu_3Sn)_2O$/Neoprene	1.40	2.86	0.98	1.02
$(Bu_3Sn)_2O$/Neoprene^{b,c}	1.40	2.82	1.09	1.09
Bu_3SnCl/Neoprene^{b,c}	1.41	2.78	1.05	1.05
Bu_3Sn(stearate)/Neoprene^{b,c}	1.44	2.82	0.99	0.99
$(Bu_3Sn)_2O$/Natural rubber^d	1.47	3.46	1.17	1.03
	1.47	1.83	1.26	0.88
$(Bu_3Sn)_2O$	1.17	1.46	0.89	0.93
Bu_3SnCl^c	1.52	3.42	1.06	1.06
Bu_3Sn(stearate)	1.42	3.59	0.96	0.89
Bu_3Sn(stearate)^c	1.45	3.65	0.95	0.95
$(Bu_3Sn)_2S$	1.42	1.63	0.87	0.75
Bu_2Sn(stearate)$_2$	1.45	3.54	0.82	0.84
$(Bu_2SnS)_3$	1.45	1.86	1.01	0.91
$(Bu_2SnS)_3{}^c$	1.46	2.18	—	—

^{a}Full line width at half maximum, ^{b}2.6% Organotin w/w, ^{c}Reference 4, ^{d}Computer-fitted as two unresolved doublets, ^{e}Reference 9.

Table 4 ^{13}C NMR chemical shifts of the butyl-carbon atoms

Compound	(C-2)	(C-3)	(C-1)	(C-4)
Bu_3Sn(stearate)	28.2	27.3	16.6	13.7
$(Bu_3Sn)_2S$	29.1	27.4	16.2	13.8
$(Bu_3Sn)_2O$	28.6	27.6	16.8	13.9
Bu_3Sn(stearate)/$(Bu_3Sn)_2S$	28.3	27.3	16.7	13.7^a
	29.1	27.4	16.2	
Bu_3Sn(stearate)/$Bu_3Sn)_2O$	28.4^b	27.4^b	16.6^b	13.8^b
C_6H_6 extract from natural rubber	28.3	27.3^a	16.2	13.8^a
	29.2		16.7	

^{a}Two peaks coincident, ^{b}See text.

of the organotin compounds, using both CCl_4 and C_6H_6, subsequent concentration, and ^{119}Sn NMR investigation, revealed the presence of two organotin compounds (Fig. 1 and Table 2). The peaks at 89.9 and 90.3 ppm in the CCl_4 and C_6H_6 solution respectively were ascribed to Bu_3Sn(stearate) and those at 82.2 and 81.2 ppm, again in the CCl_4 and C_6H_6 solutions respectively, are typical of both $(Bu_3Sn)_2O$ and $(Bu_3Sn)_2S$. However, inspection of the ^{13}C NMR spectrum of the C_6H_6 solution, and comparison with ^{13}C spectra of solutions containing authentic Bu_3Sn(stearate)/$(Bu_3Sn)_2O$ and Bu_3Sn(stearate)/$(Bu_3Sn)_2S$ mixtures (Table 4) confirmed the presence of $(Bu_3Sn)_2S$. It is interesting to note that the ^{13}C spectrum of the solution containing both $(Bu_3Sn)_2O$ and Bu_3Sn(stearate) showed only one set of butyl resonances. Similarly, the ^{119}Sn NMR spectrum of this solution showed only one broad resonance centred at approximately 88 ppm. Thus, the Bu_3Sn moiety is probably undergoing exchange between the oxide and carboxylate sites.

$(Bu_3Sn)_2S$ presumably results in the natural rubber from reaction of $(Bu_3Sn)_2O$ with sulphur which is present in excess in the original formulation. It was in fact found that direct reaction between these two species occurs in refluxing xylene (140°C).

$$2(Bu_3Sn)_2O + \tfrac{2}{n}S_n \rightarrow 2(Bu_3Sn)_2S + O_2. \quad [1]$$

Therefore, it is not surprising that the above reaction (Eqn 1) occurs during processing of the rubber in which temperatures of approximately 150°C are encountered. Prolonged refluxing (approx. 4 h) of $(Bu_3Sn)_2S$ in xylene was found, by ^{119}Sn NMR, to cause debutylation of the tributyltin species with the formation of $(Bu_2SnS)_3$. It should be noted, however, that reaction between $(Bu_3Sn)_2O$ and sulphur does not occur at lower temperatures, e.g. refluxing toluene (110°C).

With regard to the extent of organotin extraction from the natural rubber sample, total tin contents before (1.0% as Sn) and after (CCl_4–0.2% as Sn; C_6H_6 –0.4% as Sn) show that, as with the neoprene rubber, the majority has been removed. Therefore, the evidence obtained by ^{119}Sn NMR spectroscopy shows that both Bu_3Sn(stearate) and $(Bu_3Sn)_2S$ must be present within the rubber in significant amounts.

As stated previously, Allen et al.[4] showed that a change in the Mössbauer ΔE_Q value occurred on incorporation of Bu_3Sn(stearate) into neoprene rubber, compared to the neat compound, which was explained in terms of the presence of a five coordinate tin species. The neoprene rubber contained an amine ('Octamine') and we believe that it is possible that this interacts with the tin compound through electron donation ($N \rightarrow Sn$) to produce the five-coordinate environment. In the natural rubber investigated, no amine electron-donating species was present and so the Mössbauer parameters of the organotin containing sample might be expected to closely resemble those of the pure compounds. In fact, a Mössbauer investigation of the natural rubber formulated with $(Bu_3Sn)_2O$ reveals two quadrupole-split doublets (Table 3) and, on the basis of the above discussion, we assign these to $(Bu_3Sn)_2S$ and Bu_3Sn(stearate), consistent with the NMR data.

CONCLUSION

From these studies, it was found that the incorporation of $(Bu_3Sn)_2O$ into the neoprene rubber led to the formation of a mixture of Bu_3SnCl, Bu_3Sn(stearate) and $Bu_2Sn(stearate)_2$, whereas in natural rubber a mixture of Bu_3Sn(stearate) and $(Bu_3Sn)_2S$ was produced.

Carboxylic acids are added to rubber formulations to accelerate the 'breakdown' of the gum elastomer, i.e. to lower the molecular weight, and thereby allow mixing of the rubber compounds. The acids are termed lubricants and act by coating the broken molecular chains and preventing the re-establishment of bonds between molecules. Since in both the neoprene and natural rubber studied, $(Bu_3Sn)_2O$ had reacted with the carboxylic acid to form the tributyltin carboxylate it is possible that the intended function of the lubricant will not be achieved and so inferior mixing of the rubber compounds may result. In addition, studies[12] using natural rubber have shown that elastomers formulated with $(Bu_3Sn)_2S$ are more effective at controlling fouling than those formulated with $(Bu_3Sn)_2O$. Since the former compound will not readily react with a carboxylic acid, this improved performance may be due to the absence of the tributyltin carboxylate, which perhaps has less favourable leaching characteristics.

The presence of the dibutyltin species in the neoprene rubber, combined with the fact that $(Bu_3Sn)_2S$ degraded on heating, shows that degradation of the parent triorganotin species can occur during processing. Therefore, rubbers which are produced using long processing times at elevated temperatures may possibly show an increased proportion of the dibutyltin derivative and a corresponding reduction in biological activity.

Finally, since the two rubber compositions studied result in the presence of different organotin compounds, it is probable that release rates of the active species will differ, thereby affecting both antifouling effectiveness and lifetime of the coating.

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