Properties of PETG/EVA blends:
2. Study of reactive compatibilization by n.m.r. spectroscopy and linear viscoelastic properties

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The reaction product of both methylbenzoate and dimethylphthalate with dibutyltin oxide was determined to be an 1-alkoxy-3-acyloxy distannoxane by multinuclear n.m.r. spectroscopy (^{1}H, ^{13}C and ^{119}Sn) in solution. Dibutyltin oxide promotes ester interchange reactions. It was used to compatibilize the immiscible blend of polyethylene terephthalate glycol (PETG) with the ethylene vinyl acetate (EVA) copolymer. The linear viscoelastic properties of the compatibilized blend were determined and analysed in light of the n.m.r. results. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Adding dibutyltin oxide, Bu_2SnO, to the immiscible PETG/EVA system is susceptible to promote the compatibility through transesterification reactions[1]. It has been shown that Bu_2SnO was not a catalyst, in the common sense, but the precursor of a distannoxane structure[2]. This intermediate favours ester interchange reactions at processing temperatures. The organometallic compound leads either to the formation of a copolymer PETG-*g*-EVA and/or to the co-crosslinking of both phases, as illustrated in *Figure 1*.

Results concerning the morphological analysis and the rheological properties of unmodified PETG/EVA blends have been reported in the first article[3]. We also discussed minor changes in the morphology of the blends when 1.2 wt% Bu_2SnO is added. This second article is devoted to the study of chemical reactions caused by the Bu_2SnO addition with the objective of clarifying the mechanisms involved in the compatilization strategy and explaining major changes observed in the rheological measurements.

The alkoxytrialkyltin compounds (R_3SnOR') promote ester–alcohol or ester–ester interchange reactions[4]. It has been shown that organometallic compounds such as Bu_2SnX_2 (with $X = OCOCH_3$ or Cl), as in the cases of Bu_2SnO and Bu_2SnS, were good catalysts for

ester–alcohol interchange reactions[5]. More recently, it has been shown that the distannoxane compound (R_4Sn_2XYO) is more efficient[6–8]. In that case, the catalytic mechanism is explained by the alkoxydistannoxane structure formation resulting from the reaction with the alcohol in excess, followed by the alkoxy groups interchange reaction between the ester and the alkoxydistannoxane previously formed. Finally it has been established[9] that aliphatic monoesters RCOOR' (octylacetate and methylnonaoate) react with dibutyltin oxide and give an alkoxyacetoxy 1,3 distannoxane with a dimeric structure even in dilute solution. In this work, reactions between aromatic model mono- and diesters and Bu_2SnO in solution have been carried out and analysed by multinuclear n.m.r. spectroscopy (^{1}H, ^{13}C and ^{119}Sn). The linear viscoelastic properties of a chemically modified PETG/EVA blend have been determined and interpreted in the light of chemical mechanisms elucidated by n.m.r. analysis on the model compounds.

EXPERIMENTAL

The preparation of the blends and the pertinent information related to the morphological and rheological measurements have been described in part I[3]. The various reactants used for modelling the action of Bu_2SnO were commercial products. Methylbenzoate, dimethylphthalate and dibutyltin oxide were supplied by Aldrich whereas the tetrachloroethylene (TCE) was

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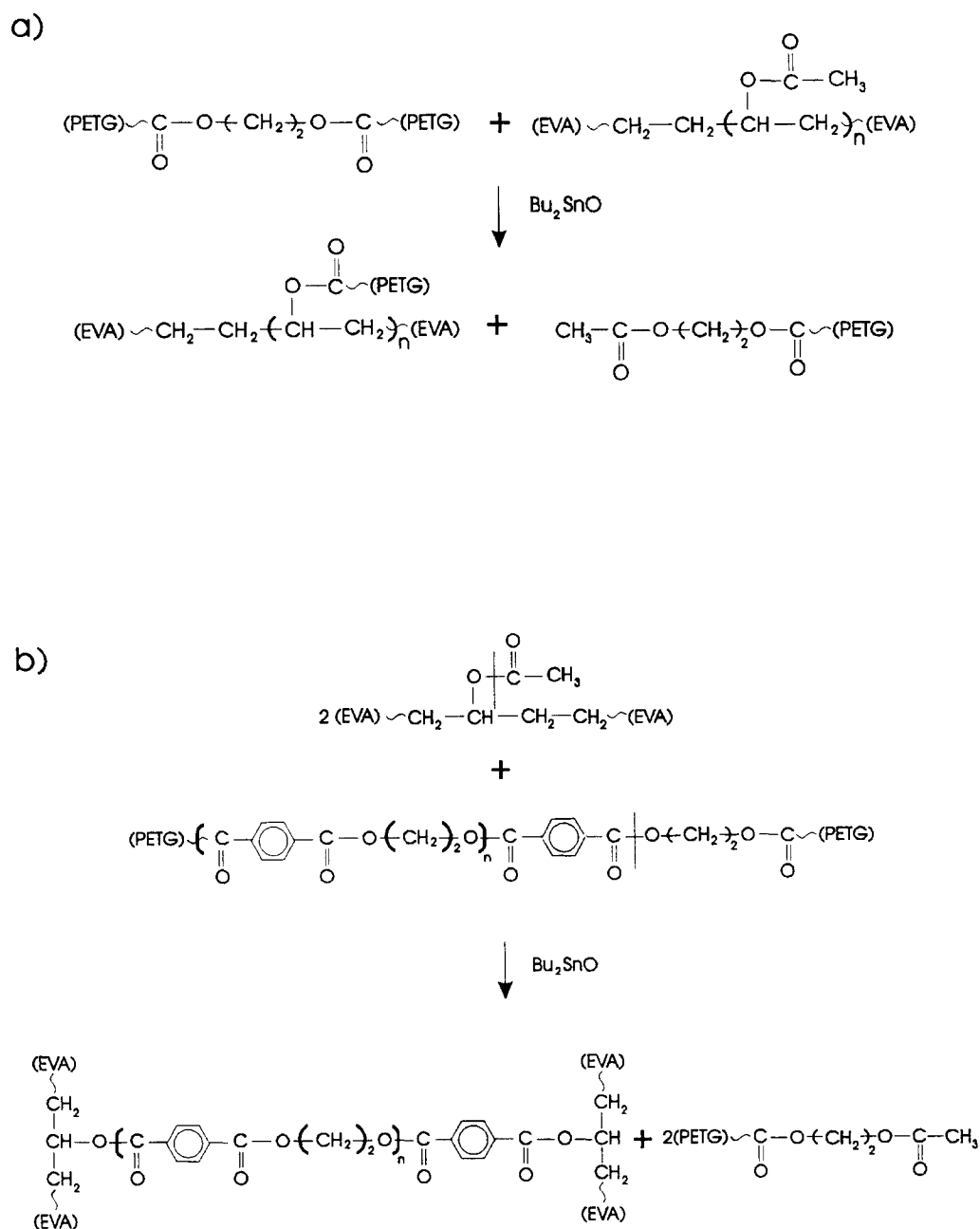†To whom correspondence should be addressed

a)

b)

Figure 1 Transesterification mechanisms between the polyester and acetate groups from EVA: (a) copolymer formation; (b) co-crosslinking of EVA and PETG chains

supplied by Merck. The same following procedure was applied to synthesize the reaction product of the model esters and Bu_2SnO: 0.5 mol Bu_2SnO were mixed with 0.5 mol of the corresponding ester in a tricol equipped with reflux condenser and magnetic stirrer; 5 ml TCE was used as solvent for the reaction so as well as for n.m.r. measurement. The reaction was carried out for 5 h at 120°C. The solvent was introduced in a quantity just sufficient to allow the stirrer to rotate. The reflux action was stopped rapidly and temperature increased to 135°C and stabilized. After 40 min, the Bu_2SnO powder suspension disappeared and the mixture became temporarily liquid. At the end of the reaction, the mixture was yellow and oily. N.m.r. spectroscopy was carried out using a Bruker AC 250 working at 250 MHz for ^1H and 62.9 MHz for ^{13}C. A Bruker AC 200 spectrometer was used for ^{119}Sn working at 74.6 MHz. The solvent used was a mixture of TCE/deuterated benzene (C_6D_6) 2/1 by

volume. The tetramethylsilane (TMS) was taken as the reference for the chemical shifts value (δ) in ppm for ^1H and ^{13}C n.m.r. In the case of ^{119}Sn n.m.r. tetramethyltin was used as reference for the chemical shifts.

RESULTS AND DISCUSSION

N.m.r. analysis

The co-crosslinking between ethylene vinylacetate (EVA) and ethylene methylacrylate (EMA) copolymers when adding Bu_2SnO in the molten state has been investigated recently through model reactions in solution using multinuclear n.m.r. spectroscopy[10]. This work follows a previous paper[9] which dealt with the analysis of model compounds obtained by reaction of *n*-octylacetate and methylnonaoate with Bu_2SnO. It has been shown that the main product of these reactions was a dimer of 1,3 acyloxy alkoxy distannoxane (*Figure 2*). These
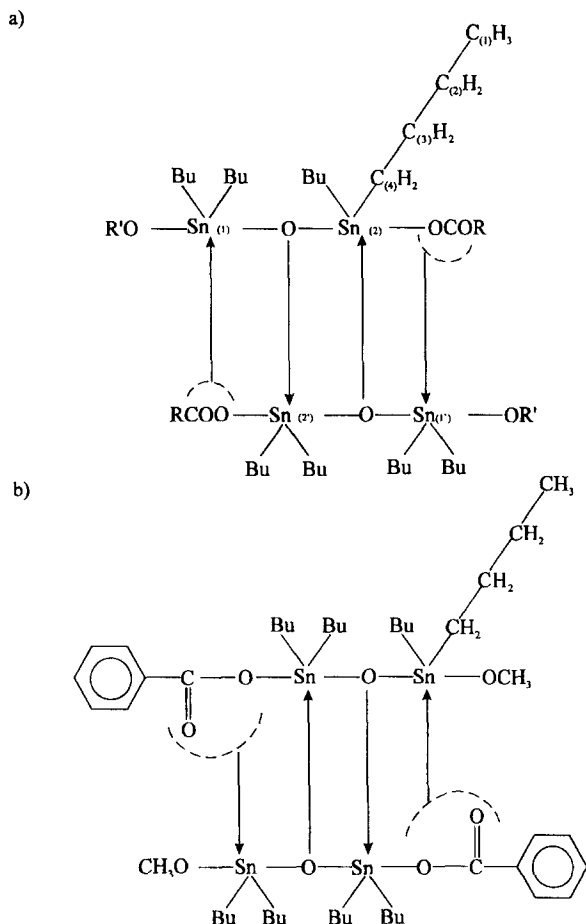
a)

b)

Figure 2 (a) Schematic representation of the dimeric 1-alkoxy-3-acyloxy tetrabutyl distannoxane structure; (b) reaction product of methylbenzoate in excess and dibutyltin oxide

reactions were carried out in the bulk and using stoichiometric quantities. Under less severe conditions (in solution) and with ester in excess in order to avoid the presence of residual butyltin oxide, interchange ester reactions have been investigated[10]. The chosen model esters, in the frame of the present work, methylbenzoate and dimethylphthalate, were the simplest structures most resembling the PETG hydrocarbon skeleton. Taking into account the previous results[2,9,10] we will verify if the organometallic compound action is similar with an aromatic monoester and a diester and if it leads to the formation of a distannoxane structure. As shown in *Figure 2a*, the distannoxane structure is characterized by two different tin sites. Thus, coupling ^{119}Sn and ^{13}C n.m.r. to ^{1}H n.m.r. results can give sufficient information to determine the structure of the resulting reaction products.

Reaction between methyl benzoate and Bu₂SnO. As shown by the ^{119}Sn spectrum of *Figure 3*, a reaction between methylbenzoate and Bu₂SnO has taken place. The resulting product is characterized namely by two major tin resonances, $\delta = -180.6$ ppm and $\delta = -215.9$ ppm, whereas pure Bu₂SnO possesses only one single ^{119}Sn resonance at -172.2 ppm. This spectrum suggests, as in the preceding studies, the presence of two tin sites of equal populations with different environments. The ^{119}Sn spectrum will be discussed in the following sections in the light of ^{1}H and ^{13}C n.m.r. results.

^{1}H n.m.r. *Figure 4* compares the ^{1}H n.m.r. spectra of pure methylbenzoate and of the product coming from the reaction with Bu₂SnO. Four different chemical shift regions can be extracted from this spectrum.
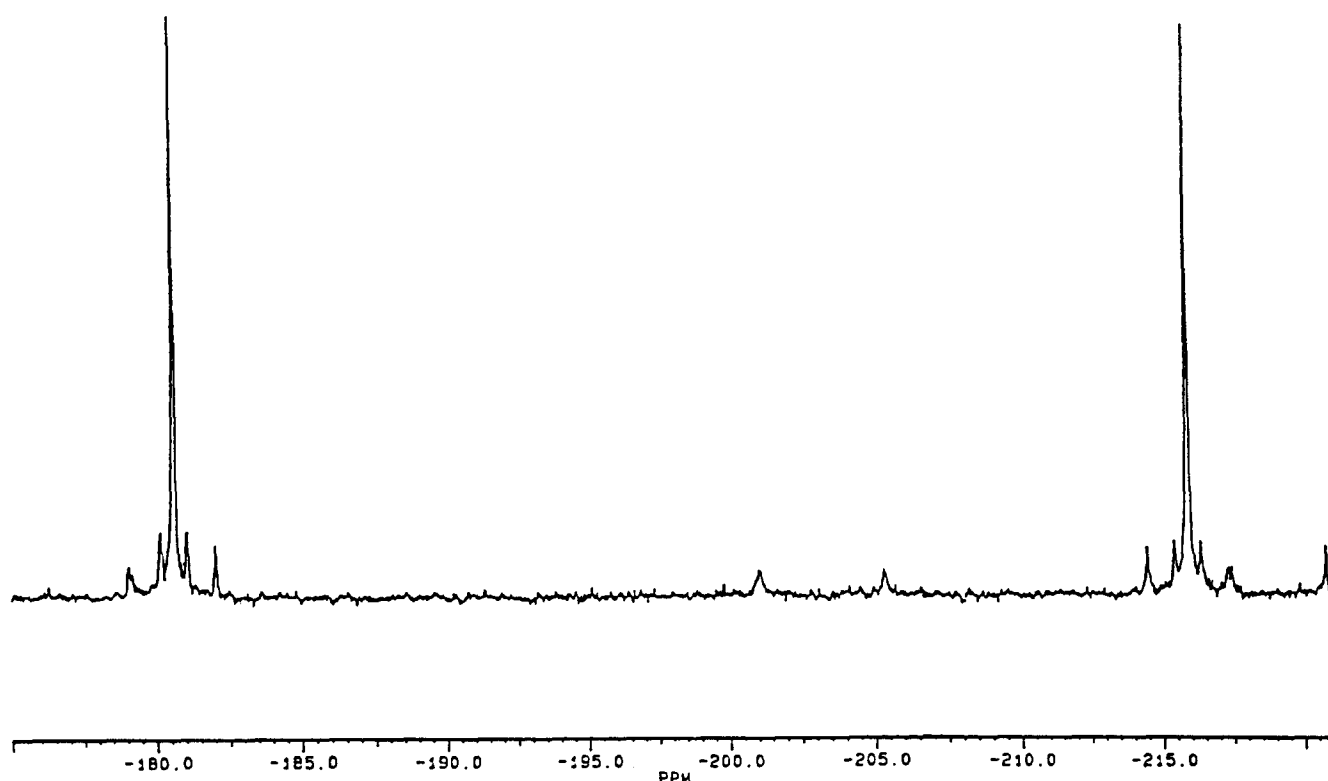

Figure 3 ^{119}Sn n.m.r. spectrum of the reaction product of Bu₂SnO with methylbenzoate at 120°C after 5 h

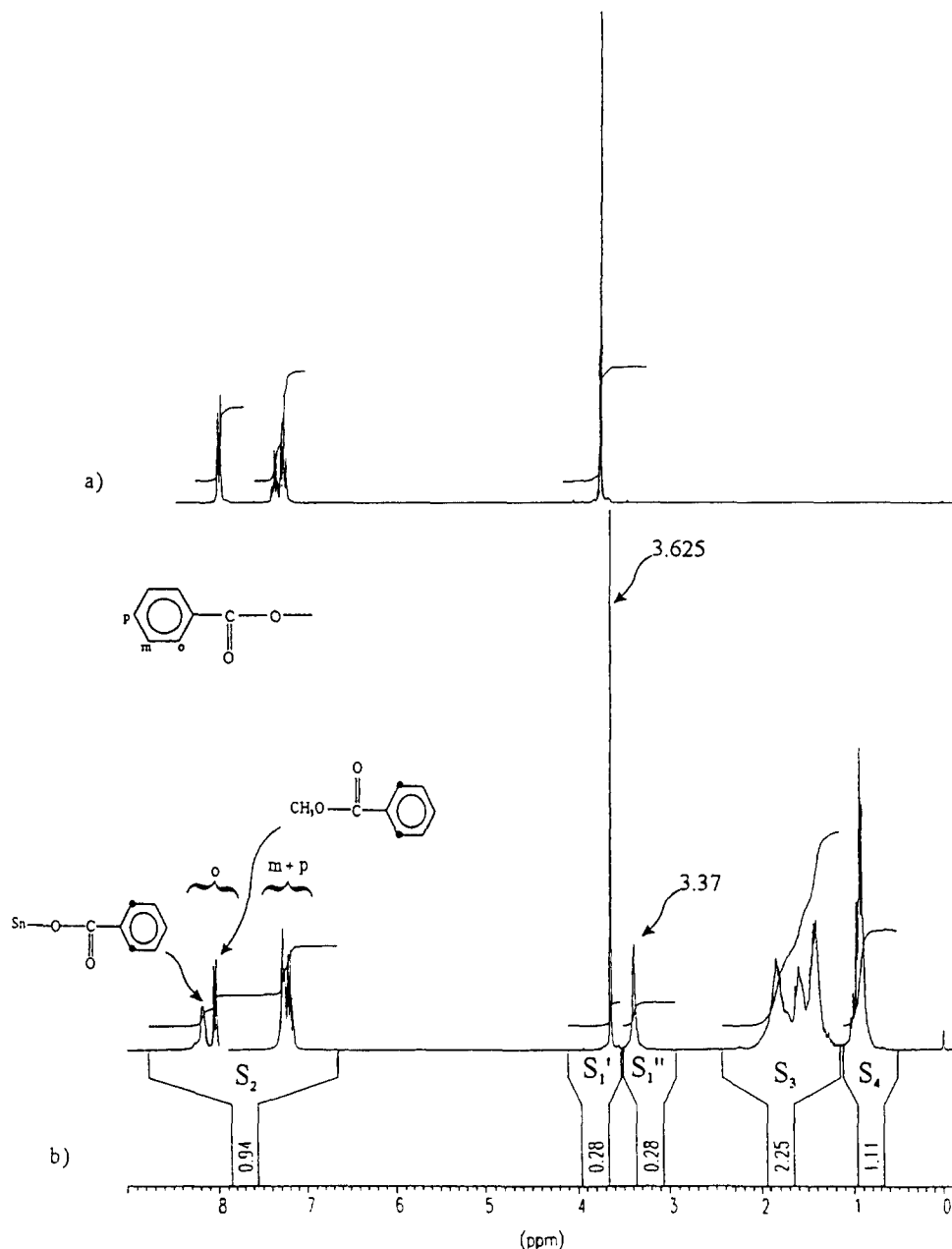**Figure 4** ^{1}H n.m.r. spectra: (a) of the initial methyl benzoate; (b) of the reaction product of dibutyltin oxide with methylbenzoate at 120°C after 5 h

The S_1 region between 2.45 and 3.9 ppm is composed of two singlets. S_1' at $\delta = 3.625$ ppm corresponds to the methyl proton resonances from the residual ester (O–C$\underline{H}_3$) whereas the methyl proton resonances from the reacted ester (Sn–OC$\underline{H}_3$) at 3.37 ppm represent the S_1'' region.

The aromatic proton resonances lie between 6.6 and 8.5 ppm in the S_2 region. This zone corresponds to the residual and reacted ester aromatic resonances. The protons in *meta* and *para* positions appear at higher field while the two well resolved peaks at lower fields correspond to the aromatic protons in *ortho* position to the acyl group. The large and more deshielded resonance corresponds to a SnOCOΦ compound (Φ designating the aromatic ring).

The S_3 zone, from 1.2 to 2.45 ppm, corresponds to all the methylene (–CH$_2$–) proton resonances of the soluble butyltin compound whereas the S_4 region, 0.5 to 1.1 ppm, is assigned to the methyl proton resonances of butyltin groups.

The formation of alkoxytin groups (Sn–OR′) and acyloxytin groups (Sn–OCOR) with R and R' coming from the reacting ester is one of the features of the tin compound obtained. These groups are also evidenced by ^{13}C and ^{119}Sn n.m.r. analysis.

^{13}C n.m.r. By comparing the ^{13}C n.m.r. spectra of pure and reaction products and knowing specific shifts from the previous studies[2,9,10], it was possible to assign all the peaks. The ^{13}C n.m.r. spectrum of *Figure 5a* shows resonances at 51.15 ppm of methoxytin (Sn–OC$\underline{H}_3$) whereas the corresponding resonance in the residual ester lies at $\delta = 51.50$ ppm. In the typical chemical shift region of carbonyl groups the peak at $\delta = 166.25$ ppm corresponds to the residual ester ΦC$\underline{O}$OCH$_3$. The tin atom gives rise to a deshielded carbonyl resonance as shown in previous studies[10]; this allows us to assign the peak at $\delta = 171.90$ ppm to Sn–OC$\underline{O}$Φ. Comparing ^{13}C n.m.r. spectra with those obtained in previous studies allows us to determine all the carbon resonances from
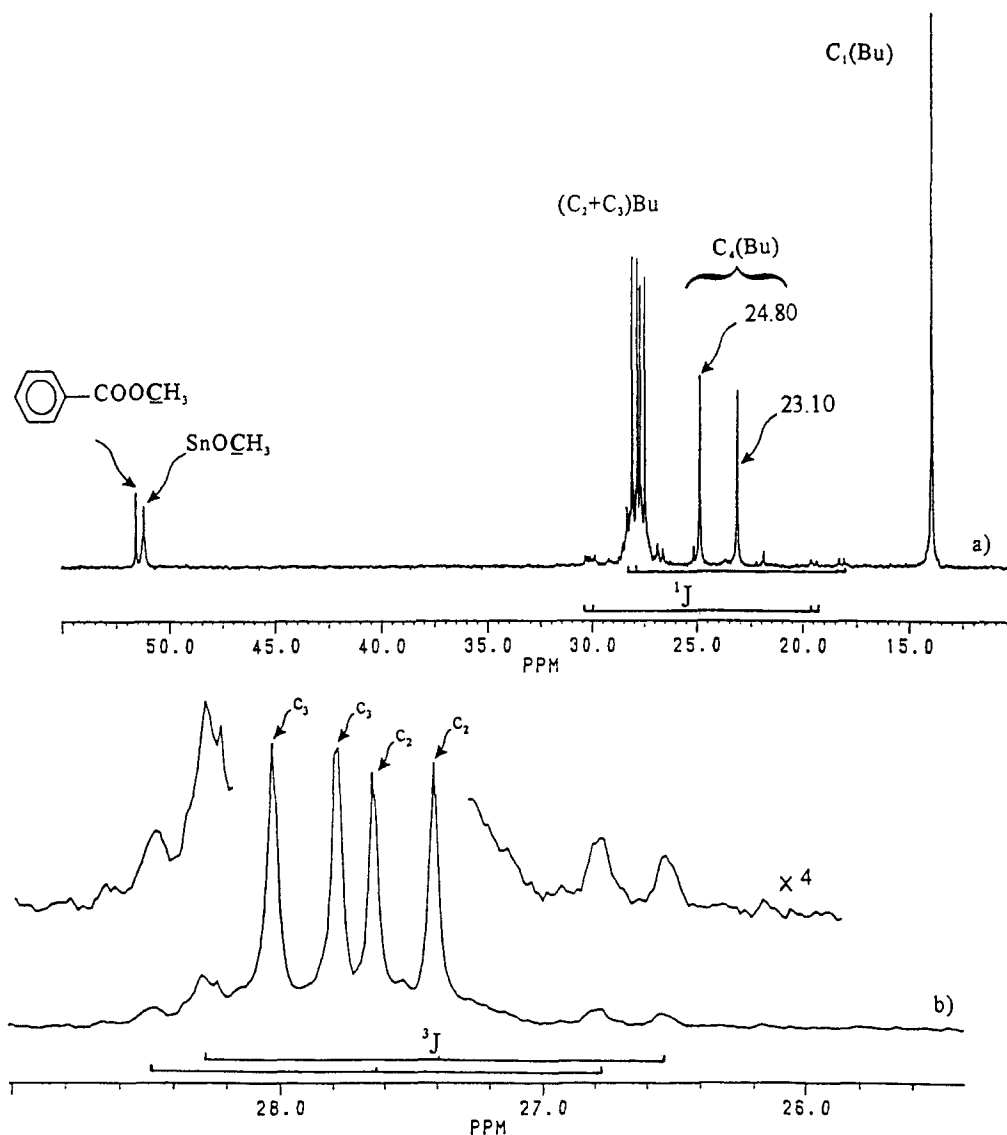
Figure 5 ^{13}C n.m.r. spectra of dibutyltin oxide with methylbenzoate (initial oxide/ester ratio = 1/1): (a) methoxy and butyl carbon resonances; (b) enlargement: C_2 and C_3 of butyl groups

two different butyltin groups: at 13.85 ppm, the methyl carbons are not resolved, the two peaks at 23.10 and 24.80 ppm are assigned to the methylenic carbons (C_1) in the α position to the tin. This proves that two tin atoms of the reaction product possess two different chemical environments. The resonances at 27.40 and 27.65 (C_2), 27.80 and 28 ppm (C_3) characterize the carbons respectively in the β and γ positions with respect to the tin atom. These chemical shifts are very close to those obtained in the case of the reaction between Bu_2SnO and methylnonaoate and octylacetate[9]. The different butyltin groups are an important feature of the tin compound obtained, and are characteristics of a distannoxane structure as in the case of the product obtained with methylnonaoate and the octylacetate[9,10]. The coupling constant values ^1J, ^2J and ^3J (particularly $^1J(^{119}Sn-C)$ and $^1J(^{117}Sn-C)$) are typical of the penta-coordination state of the tin sites and, moreover, of the dimeric structure of the distannoxane (see *Table 1* and references 2, 9, 10). It was also possible to determine the ^2J and ^3J coupling constants from the spectrum enlargements as shown in *Figure 5b*. The results are reported in *Table 1*. From the knowledge of these

coupling constants, the two peaks at 27.40 and 27.65 ppm are assigned to the C_2 carbons whereas the chemical shifts at 27.80 and 28 ppm characterize the carbons in the C_3 position.

Complementary information is given by ^{119}Sn spectroscopy. The spectrum obtained (*Figure 3*) is typical of a dimeric distannoxane structure as already evidenced in previous studies[2,9,10]. The two main peaks correspond to equal populations. As expected in this structure (*Figure 2a*), each exocyclic tin site (1 or 1') is coupled through oxygen to two other tin atoms (2 and 2') with different coupling constants. The reverse holds for endocyclic (2 and 2') sites. These are detectable on the spectrum by the doublet satellite peaks (*Figure 3*). The presence of two different butyl groups (^{13}C n.m.r.), as well as new $SnOCH_3$ and $SnOCO\Phi$ chemical bonds (both ^1H and ^{13}C n.m.r.), combined with the proof of a dimeric distannoxane structure (^{119}Sn), allow us to conclude that the reaction product has the structure proposed in *Figure 2b*.

Reaction between dimethylphthalate and Bu_2SnO. The reaction between this diester in excess and dibutyltin

Table 1 Characteristic n.m.r. spectral features of dimeric 1,3 acyloxyalkoxy distannoxane

ester: *methylbenzoate*	ester: *dimethylphthalate*

^{1}H n.m.r.

δ C$\underline{H}_{3(1)}$Bu = 0.910, 0.940	δ C$\underline{H}_{3(1)}$Bu = 0.875, 0.960
δ Sn–OC$\underline{H}_3$ = 3.370	δ Sn–OC$\underline{H}_3$ = 3.325
δ ΦCOOC$\underline{H}_3$ = 3.625	δ C$\underline{H}_3$OCOΦCOOC$\underline{H}_3$ = 3.705
δ –O–CO–$\underline{\Phi}$(ortho) = 8.040	δ SnOCOΦCOOC$\underline{H}_3$ = 3.755
δ –Sn–OCO—$\underline{\Phi}$(ortho) = 8.185	

^{13}C n.m.r.

δ C$_1$Bu = 13.85	δ C$_1$Bu = 13.80, 13.90
δ C$_2$Bu = 27.40, 27.65 (^3J = 108)	δ C$_2$Bu = 27.45, 27.50
δ C$_3$Bu = 27.80, 28 (^2J = 30)	δ C$_3$Bu = 27.70, 27.80
δ C$_4$Bu = 23.10 (^1J = 606, 636)	δ C$_4$Bu = 23.10 (^1J = 609, 636)
δ C$_4$Bu = 24.80 (^1J = 660, 692)	δ C$_4$Bu = 24.20 (^1J = 644, 673)
δ Sn–O$\underline{C}$H$_3$ = 51.15	δ Sn–O$\underline{C}$H$_3$ = 51.10
δ ΦCOO$\underline{C}$H$_3$ = 51.50	δ $\underline{C}$H$_3$O–COΦCOOSn = 51.80
δ $\Phi\underline{C}$OOCH$_3$ = 166.25	δ $\underline{C}$H$_3$OCOΦCOO$\underline{C}$H$_3$ = 52
δ Sn–O$\underline{C}$OΦ = 171.90	δ CH$_3$O$\underline{C}$OΦCOOCH$_3$ = 167.10
	δ CH$_3$–O$\underline{C}$OΦCOOSn = 167.8
	δ CH$_3$–OCO$\Phi\underline{C}$OOSn = 172

^{119}Sn

δ Sn$_{exo}$ = –180.6	δ Sn$_{exo}$ = –180.7
δ Sn$_{endo}$ = –215.9	δ Sn$_{endo}$ = –209.6
(^2J = 67, 221)	(^2J = 70, 224)

oxide has been investigated in the same way as in the case of the monoester. All n.m.r. characteristic features (Table 1) converge to prove the formation of a dimeric distannoxane structure. The ^{119}Sn spectrum of the

reaction products consists of two major sites, coupled to each other. The chemical shift values (*Table 1*) are easily assigned from the previous studies[9,10] which have shown that the endocyclic tin sites are more deshielded than the exocyclic ones in the case of 1-alkoxy-3-acyloxytetrabutyl distannoxane.

The ^{13}C n.m.r. spectrum (*Figure 6* and *Table 1*) shows the presence of two butyltin groups (exo and endo), particularly by the typical C$_4$ resonances. Three different methoxy groups (*Figure 6a*) and three carbonyl groups (*Figure 6b*) indicate the presence of residual diester and of the distannoxane from the monoreacted diester, shown schematically in *Figure 6*.

In summary, it can be concluded that both aromatic mono- and diester model compounds which have been chosen react with Bu$_2$SnO. The resulting products have a dimeric 1-alkoxy-3-acyloxy distannoxane structure in which the alkoxy tin bound is very sensitive to moisture.

Viscoelastic properties

N.m.r. results have shown that Bu$_2$SnO leads to the formation of a dimeric distannoxane structure. The formation of alkoxy tin and acyloxy tin bonds implies that ester bond scissions occur in a first step. Rheological experiments are a powerful tool to assess the Bu$_2$SnO action on phenomena encountered in the molten state, using the n.m.r. results obtained for model

+ residual unreacted ester
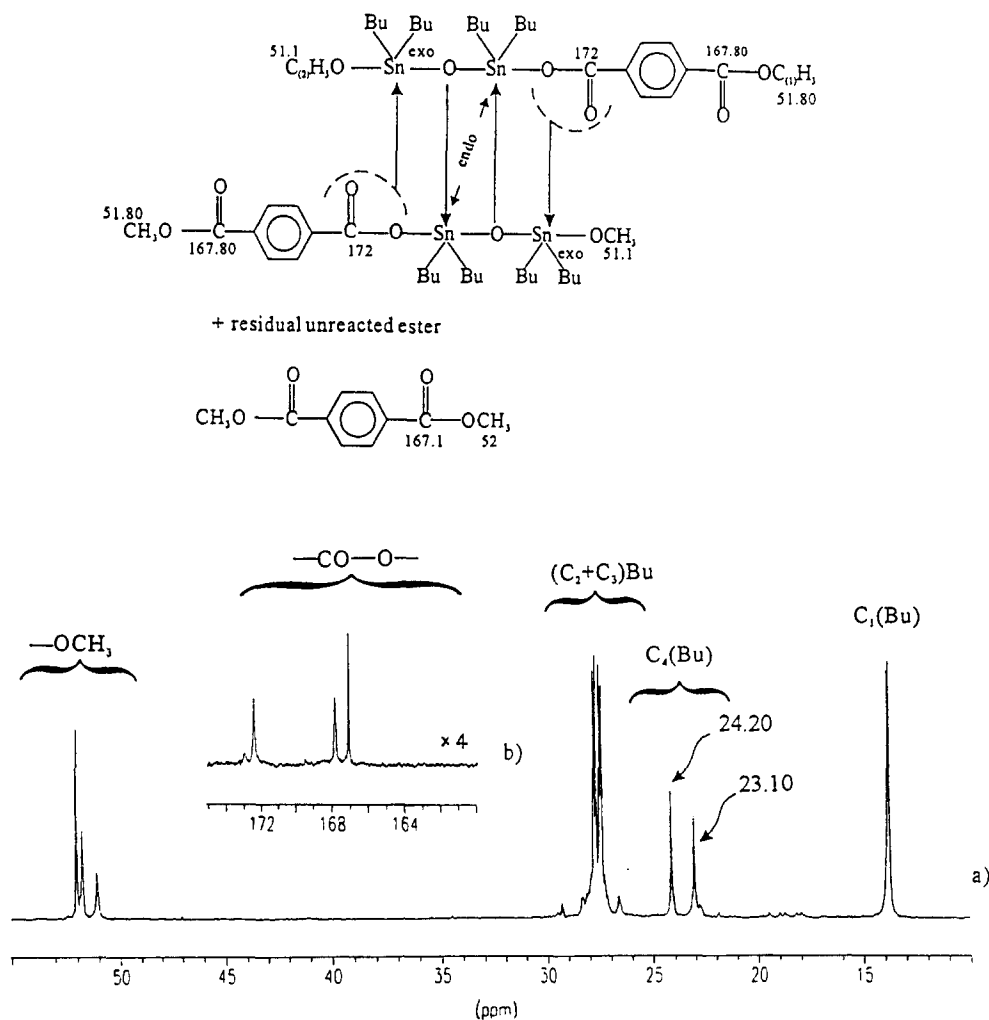
Figure 6 ^{13}C n.m.r. spectra of the reaction product of dibutyltin oxide with dimethylphthalate (1/1 molar ratio): (a) methoxy and butyl carbon resonances; (b) enlargement of carbonyl resonances

compounds. We report here the linear viscoelastic properties for the 90/10 PETG/EVA blend containing 1.2 wt% Bu_2SnO, at a temperature of 210°C. Time sweep experiments at the constant frequency of 1 Hz were conducted to follow the rheological behaviour of the reactive blends with the time. *Figure 7* shows the variation of the complex viscosity with time for the PETG and the 90/10 PETG/EVA blend, both containing 1.2 wt% Bu_2SnO.

It is well known that it is almost impossible to eliminate all traces of water in polyesters and, moreover, alkoxy tin bonds are very sensitive to moisture. The samples were initially predried at a temperature between 80°C and 95°C under vacuum during 12 h. As illustrated in *Figure 7*, time effects for the blend are similar to those observed for the PETG containing Bu_2SnO. Both systems exhibit an initial decrease of the complex viscosity due to hydrolysis of the alkoxy tin bond in the distannoxane in presence of water. A minimum value is reached and the following viscosity increase is explained by further formation of the distannoxane, resulting in a molecular weight increase. However, the magnitude of the complex viscosity for the blend is much larger than that of the matrix, either due to some crosslinking of the dispersed EVA phase[1] or to formation of the PETG-g-EVA copolymer combined with the co-crosslinking of both phases (*Figure 1*). Nevertheless, the effects cannot be quantified because of irreproducibility. In order to improve the reproducibility, the PETG and the 90/10 PETG/EVA blend samples containing 1.2 wt% Bu_2SnO were predried in the same conditions but during 24 h. As illustrated in *Figure 7*, the complex viscosity is considerably affected by the predrying period. For a predrying period of 24 h, the rheological results were reproducible and no further changes were observed for longer predrying. We observe for both the matrix and the blend a very minor initial decrease. This is followed by a substantial increase with time of the complex viscosity for the matrix as observed for the matrix which was dried during 12 h. In the case of the blend, the complex viscosity remains about constant. We note a substantially larger value for the initial complex viscosity of the blend (dried for 24 h). This is attributed to the reaction that took place during the sample preparation. The major difference observed is the magnitude of the complex viscosity compared to that of the samples dried only 12 h.

Figure 8 compares the storage and loss moduli of the unmodified blend and of the chemically modified blend once equilibrium has been reached. For comparison, the storage modulus data for the 'pure' PETG and the dynamic moduli for the unmodified PETG/EVA blend are represented in the figure by the dashed line and by triangles respectively. The most important effects of adding Bu_2SnO are the large decreases of the dynamic moduli at high frequencies and the completely different rheological behaviour at low frequencies compared to the unmodified PETG/EVA blend. The possible chemical mechanisms shown in *Figure 1* lead in both cases to chain scission of the matrix at the interphase between both components. It must be pointed out that chain scission is part of the chemical mechanism, and this combined with moisture effects leads inevitably to viscosity and moduli decreases. As discussed in the first article[3], the deformability of the EVA droplets in
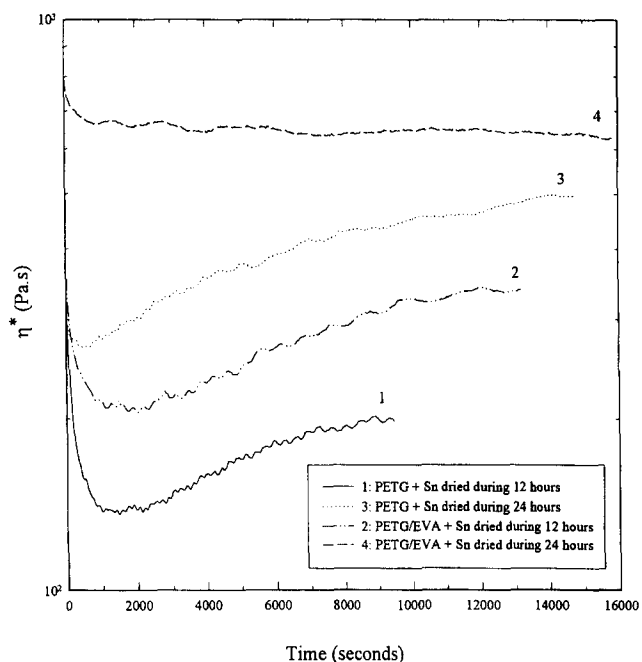
Figure 7 Complex viscosity η^* vs. time for PETG + 1.2% Bu_sSnO and for 90/10 PETG/EVA + 1.2% Bu_2SnO, $T = 210$°C
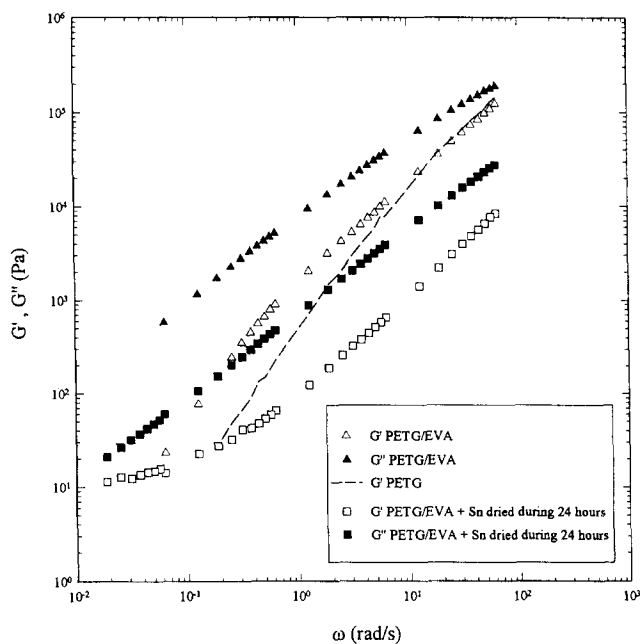
Figure 8 Comparison between the storage and loss moduli G', G'' of 90/10 PETG/EVA without and with 1.2% Bu_2SnO at 210°C. The dashed line represents the G' data of the PETG matrix at 210°C

unmodified blends results in a shift of the terminal zone and the appearance of a shoulder in the storage modulus at low frequencies. At high frequencies, the storage modulus of the blends coincide with that of the matrix. For the chemically modified blend, the low frequency behaviour is characterized by a secondary plateau. Such a plateau is generally associated with a network-type structure. In this case, the copolymer formation can be indeed followed by co-crosslinking of both phases in the interfacial zone and possibly some crosslinking of the dispersed EVA. The copolymer acts as a core-shell structure for the dispersed EVA phase. In

the presence of Bu$_2$SnO, ester interchange reactions occur necessarily in the interphase region. For this reason, the rheological behaviour described in *Figure 8* is attributed to an interfacial network formation. No significant effect can be attributed to the deformability of the suspended particles, nor related to changes in the interfacial tension[3]. Thus, for this chemically modified 90/10 PETG/EVA system, it is impossible to determine the interfacial tension using a rheological method as done in the first article[3]. Compatibilization has to be assessed via other methods, for example using changes in the mechanical properties[1].

CONCLUSION

In the light of the formation of a distannoxane structure shown by multinuclear n.m.r. spectroscopy, the linear viscoelastic behaviour of a PETG/EVA blend, chemically modified by the addition of Bu$_2$SnO, has been explained. Chain scission in the PETG matrix is inherent to the compatibilization mechanism. The initial viscosity decrease as a function of time is due to the redistributive transesterification mechanism and to the sensitivity to moisture of the distannoxane intermediate. Reproducible results could be obtained only for samples predried for at least 24 h. Substantial reaction occurs during the sample preparation and the results indicate preferentially a copolymer formation at the interphase,

and further co-crosslinking of both phases can take place.

ACKNOWLEDGEMENT

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