Silane crosslinking of polyolefins: observations on the tin catalyst employed

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*FT*i.r. has shown that the dibutyltin dilaurate catalyst employed in silane crosslinking of polyolefins exists in true equilibrium. The position of this equilibrium is highly dependant upon the polarity of the surrounding medium, which in turn may have a profound effect on the rate of crosslinking in such systems.

(Keywords: crosslinking; polyolefins; catalyst)

Introduction

Dibutyltin dilaurate (DBTDL) is a catalyst employed during the silane crosslinking of polyolefin materials, in particular polyethylene and polyethylene copolymers. The original work pioneered by Dow Corning was a two-stage process, the so-called 'Sioplas' process[1], which has since been developed jointly by BICC Cables Ltd and Maillefer Co. Ltd into a one-stage 'Monosil' process[2].

In both processes a suitable peroxide is broken down by heat and the shear action of extrusion, to act as a source of free radicals. Once formed, these radicals abstract a proton from the polymer backbone, giving a reactive site for subsequent grafting of a silane, normally vinyltrimethoxysilane. Hydrolysis of one or more of the now-grafted methoxy groups by water yields an alcohol, which is then free to undergo a catalytic condensation reaction with a methoxy group from a separate, grafted polymer chain to give a chemical crosslink.

Although the true role of DBTDL in this process remains unclear, present theories[3] suggest that DBTDL undergoes partial hydrolysis to give dibutyltin laurate hydroxide (see equation (1)), and that it is this hydrolysis product that is the true catalyst.

$$(C_4H_9)_2\text{-}Sn\text{-}(OCOC_{11}H_{23})_2 + H_2O \rightleftharpoons (C_4H_9)_2\text{-}Sn\text{-}(OCOC_{11}H_{23})OH + C_{11}H_{23}COOH \quad (1)$$

The mechanism of action of this catalyst is thought to proceed via an intermediate containing a weak Sn–O–Si linkage, although evidence for this is scarce.

The purpose of this work was to investigate further the nature of DBTDL itself, and to determine factors that may influence its use as a catalyst in this crosslink reaction.

Experimental

Initial spectroscopic studies were carried out in dilute solutions of hexane and diethyl ether. Both hexane (Fisons >99%) and diethyl ether were distilled until no impurities were visible in the infra-red spectra. DBTDL was used as supplied by Akzo, after drying over molecular sieves for 24 h. Polyethylene BPD 2133 was used as supplied by BP Chemicals, with 10% w/w of DBTDL being mixed in a Brabender Extrusiograph at 140°C, before pressing into thin sheets (0.5 mm) at 150°C. Infra-red spectra were measured on a Perkin-Elmer Lambda 9 FTIR Spectrometer at room temperature.

Results and discussion

Figure 1a shows the carbonyl absorption region in the infra-red spectrum of dried DBTDL, and clearly shows two carbonyl resonances centred at 1740 and 1720 cm^{-1}. The absorption at 1740 cm^{-1} is assigned to the carbonyl absorption in DBTDL, as this value is typical for ester compounds, and it is also the major component in the sample. The absorption at 1720 cm^{-1} is more difficult to assign, but may be due to a carboxylic acid compound, as these tend to absorb at lower wavenumbers than esters. This observation suggests that DBTDL, as supplied, is not a simple material but exists either as a mixture or in dynamic equilibrium with some other species.

Figures 1b and *c* show the carbonyl resonances of 10% DBTDL in hexane and diethyl ether. In hexane it is seen that the absorption at 1740 cm^{-1}, assigned to DBTDL, is now the minor component and the 1720 cm^{-1} resonance is the major component. However, in diethyl ether the situation has reversed: the 1740 cm^{-1} component is the major component and there is only a suggestion of a 1720 cm^{-1} component. This observation supports the existence of a dynamic equilibrium in DBTDL, which is greatly affected by the polarity of the surrounding medium, and it is further proposed that it is the equilibrium already identified with the 1720 cm^{-1} resonance due to either lauric acid, the organotin hydroxide, or both. This result suggests the presence of water in the system, despite rigorous handling procedures being employed to eliminate it. However, as diethyl ether is more polar, and therefore more hydroscopic, than hexane, it could be expected that diethyl ether would result in the equilibrium being pushed further to the right. This is not the case, as DBTDL appears to be the major

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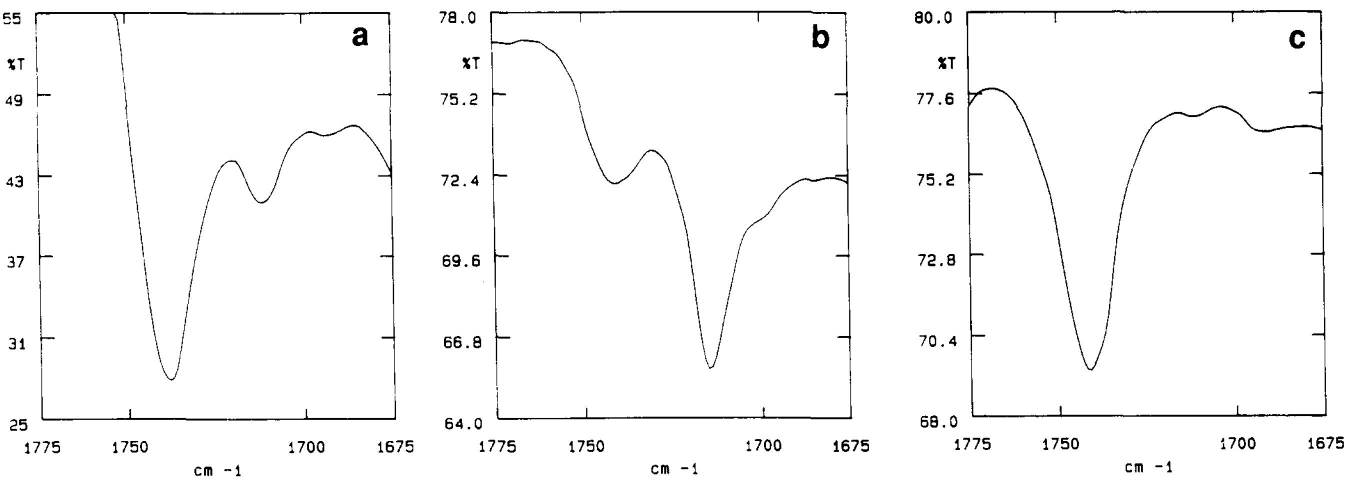

Figure 1 Carbonyl absorption region of infra-red spectra of (a) dried DBTDL; (b) 10% DBTDL in hexane; (c) 10% DBTDL in diethyl ether

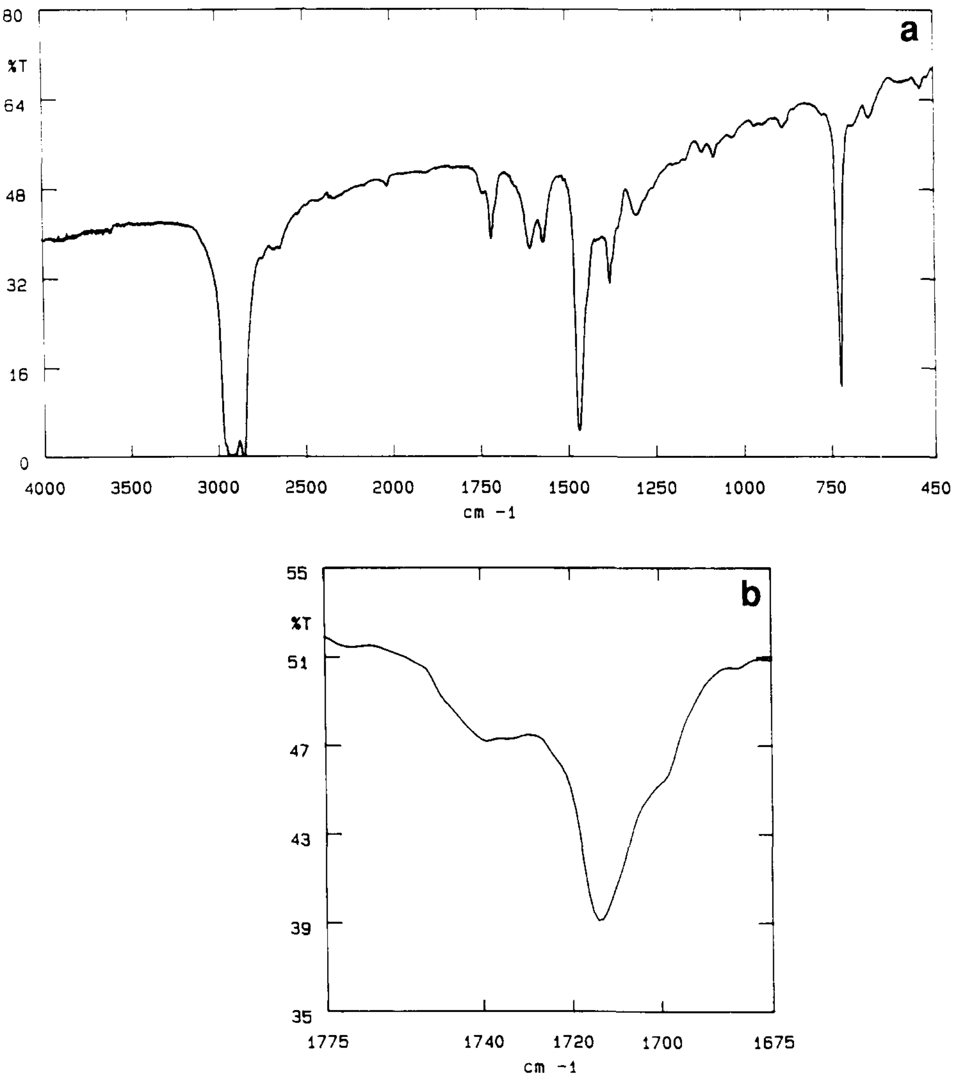

Figure 2 (a) Infra-red spectrum of 10% DBTDL in polyethylene; (b) carbonyl absorption region of (a)

component in diethyl ether. Thus, it is concluded that there is a true equilibrium at work in DBTDL, which is dependent upon the polarity of the surrounding medium.

Observations in mixed solvents show that this is not a gradual change in equilibrium on changing solvent polarity, but that the solvent needs to be essentially non-polar before the 1720 cm^{-1} resonance becomes significant. This again supports the idea of an equilibrium having been set up.

This shows that simply changing the polarity of the medium surrounding DBTDL results in a change in the equilibrium position. If this equilibrium is real then we see that formation of the so-called 'true' catalyst is favoured in non-polar media. Thus, for efficient catalytic action a non-polar medium is preferred.

Extending these observations into solid polymer materials allows some predictions to be made, assuming that the same mechanisms operate in the solid state. It may be expected that in non-polar polymers (e.g. polyethylene) the major component will be the active catalyst, but in polar polymers (e.g. ethylene vinyl acetate (EVA)) DBTDL will be more favoured. This in turn may have some implications for the silane crosslinking process in terms of different rates of reaction, due to the fact that in non-polar polymers the active catalyst is already present and does not need subsequent hydrolysis. This may result in a faster cure for non-polar polymers.

Figure 2 shows the infra-red spectrum of 10% DBTDL in polyethylene and, as anticipated from the solution studies, shows that the 1720 cm^{-1} resonance is the major component present. Thus, it appears that simply adding DBTDL to polyethylene alters the equilibrium in favour of the proposed active catalyst. This may be advantageous in the crosslinking reaction, as subsequent hydrolysis of DBTDL to the proposed active catalyst is no longer necessary in polyethylene. Unfortunately, further information using i.r. methods to study polar, EVA copolymers was not possible due to the carbonyl resonances from the vinyl acetate groups masking the regions of interest. However, subsequent work using other methods has shown similar trends to that observed in solution.

References

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2 BICC/Maillefer, British Patent 1 526 398, 1978
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