

Structure-property relationships in novel polydiacetylene-containing oligoester: Polyolefin blends

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Summary: The paper describes thermal and mechanical properties of a series of novel blends prepared using a two-stage process which involved solution blending a specially-synthesised diacetylene-containing oligoester (DOE) with a semi-crystalline poly[ethylene-co-(vinyl acetate)] (EVA), followed by conversion of the DOE to a polydiacetylene-containing oligoester (cp-DOE) by *in situ* thermal cross-polymerisation during moulding. Moulded blends range from ductile to brittle materials and give intense Raman spectra in which the C≡C stretching band at $\sim 2100\text{ cm}^{-1}$ is well-defined and shifts to lower wavenumber when the blends are subjected to tensile stress. For each blend composition, shifts in wavenumber were used to determine local stress in the cp-DOE component independently of the overall stress applied to blend.

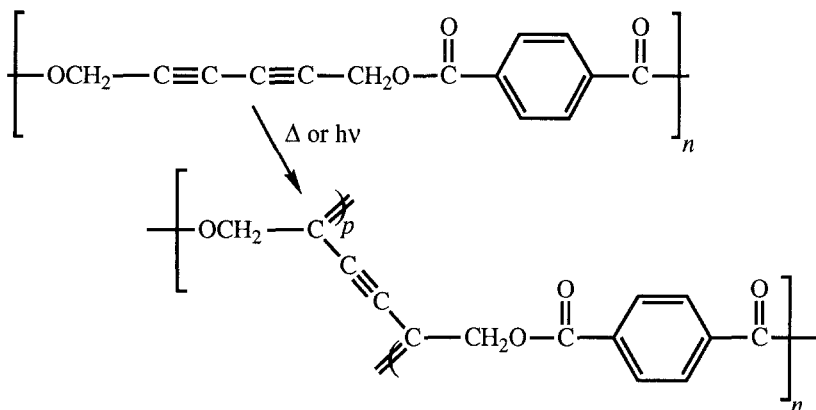
Introduction

Most polymer blends are multiphase materials in which the morphology and interfacial properties are of critical importance [1]. Considerable effort has been devoted to controlling phase morphology and to improving the bonding between incompatible polymers in blends. For example, block and graft copolymers often are used as interfacial agents because they can be designed such that one block is miscible with one component of the blend and the remaining block is miscible with the other blend component. In this way the interfaces can be made stronger and stress transfer between phases can be achieved. However, such stress transfer has previously only been determined indirectly by monitoring changes in the properties of a blend which result from changes in blend composition.

The present paper shows how in model polymer blends comprising as one component a polydiacetylene-containing phase, it is possible to monitor directly stress transfer between phases during tensile deformation of the blends using shifts in the frequencies of the Raman bands of the polydiacetylene sequences. This has been achieved through the synthesis of semi-crystalline, diacetylene-containing oligoesters, DOE's, for use as one of the components in the model blends. The diacetylene units in the DOE's "cross-polymerise" upon heating to form polydiacetylene crosslinks (see Scheme 1) which possess optical properties similar to those of polydiacetylene single crystals [2] and produce intense resonance Raman spectra. The spectra of the resulting crosslinked polymers show particularly strong Raman signals for C=C and C≡C stretching. The positions of these Raman bands shift to lower frequencies as tensile stress in the crosslinked polymer increases, the shifts being proportional to the stress in the bonds.

Through control of molar mass and crystallinity, a DOE has been prepared which is capable of solution-blending with a semi-crystalline poly[ethylene-co-(vinyl acetate)], EVA, to give blends which can be compression-moulded, cross-polymerisation of the diacetylene units in the DOE taking place during moulding. The morphological, thermal and mechanical properties of blends covering the complete composition range are briefly described in this paper. In particular it is shown that using shifts in wavenumber for the C≡C Raman band of

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Scheme 1. Cross-polymerisation of the diacetylene-containing oligoester

the cross-polymerised DOE phases, stress transfer between EVA and cross-polymerised DOE can be monitored.

Experimental

Preparation of the diacetylene-containing oligoester (DOE)

The DOE used for blending was prepared at 0 °C by reaction of hexan-2,4-diyne-1,6-diol (1.1066 g, 10.00 mmol) with a mixture of terephthaloyl chloride (1.4286 g, 6.98 mmol) and benzoyl chloride (0.8485 g, 6.03 mmol) in solution in N-methylpyrrolidone (50 ml), employing pyridine (5 ml) as HCl acceptor. After 5 h reaction, methanol (2 ml) was added and the oligoester isolated by precipitation in a large excess of 60% (v/v) aqueous methanol solution. The product was washed with 0.1 M HCl to remove excess pyridine and then with copious quantities of water to remove HCl. The oligoester, in the form of a white powder, was dried under vacuum at room temperature and stored in the dark in a refrigerator.

Preparation and Moulding of the Blends

A series of blends of the DOE with a commercial EVA material (Exxon Chemical Grade UL00206) were prepared and moulded in two stages as follows. The DOE was first blended in the appropriate proportion with the EVA by dissolution in a 50:50 tetrahydrofuran:toluene mixture at 80 °C, followed by co-precipitation into a large excess of 20:80 methanol:water mixture which was at room temperature. The resulting blend, in powder form, was dried to constant weight under vacuum in the dark at room temperature and then placed in a purpose-designed mould which enabled the blends to be compression-moulded into tensile bars under nitrogen at 120 °C for 6 h, which were the optimum conditions with respect to the intensity of the Raman signals from the cross-polymerised DOE. During moulding the blends attained the deep purple colour which is characteristic of the polydiacetylene crosslinks in cross-polymerised DOE.

Characterisation of the Materials

Gel permeation chromatography, GPC, was carried out using 0.1% (w/v) solutions in tetrahydrofuran, THF. Each solution (70 μ L) was injected into the THF flowstream of a GPC system operating at 30 °C, and the polymer separated on a series of three columns of 10 μ m PL gel with porosities of 500, 10⁴, 10⁶ Å using a flow rate of 1 cm³ min⁻¹. Polystyrene standards (Polymer Laboratories) were used for calibration. Wide-angle X-ray diffraction, WAXS, measurements were made using a Phillips PW1710 instrument with Cu K α radiation. Differential scanning calorimetry, DSC, was performed under nitrogen at a heating rate of 20 °C min⁻¹ using a DuPont 2000 Thermal Analyst instrument with a DuPont 910 cell base

equipped with a DSC cell. Surfaces revealed by fracture of mouldings which had been cooled in liquid nitrogen, were sputter-coated with gold and then analysed by scanning electron microscopy, SEM, using a Phillips 505 instrument at 10 kV.

Raman Spectroscopy

Resonance Raman spectra were recorded during deformation of tensile bars using well-established apparatus and procedures [3,4] with the 632.8 nm line of a 10mW He-Ne laser. Overall strains were independently measured using a strain gauge accurate to 0.0014 %.

Results and Discussion

A range of DOE's with different molar masses were prepared from hexan-2,4-diyne-1,6-diol and terephthaloyl chloride with benzoyl chloride as molar mass regulator in order to achieving the optimum balance between ease of processing, crystallinity and the intensity of the C≡C Raman band in the cross-polymerised material. Low molar masses were essential in order to ensure the melting temperature was below the temperature for cross-polymerisation, thereby facilitating moulding of the material. The optimum DOE prepared for use in the model blends was found to have a number-average molar mass of 1.3 kg mol^{-1} by GPC and was estimated to be 24% crystalline from WAXS measurements. The DSC trace for this material shows a melting endotherm (2 J g^{-1}) at $119 \text{ }^\circ\text{C}$ and an intense cross-polymerisation exotherm (650 J g^{-1}) which begins at $157 \text{ }^\circ\text{C}$, has a maximum at $205 \text{ }^\circ\text{C}$ ($T_{\text{cp,DOE}}$) and is complete at $219 \text{ }^\circ\text{C}$. The resonance Raman spectrum of cp-DOE shows strong bands due to the C=C and C≡C stretching modes of the polydiacetylene crosslinks (see Figure 1).

The EVA was chosen as the second component for the blends because of its low melting point ($107 \text{ }^\circ\text{C}$ by DSC). This facilitated solution blending of the two components at $80 \text{ }^\circ\text{C}$ and subsequent moulding of the blends at $120 \text{ }^\circ\text{C}$, during which conversion of the DOE to a polydiacetylene-containing oligoester (cp-DOE) was effected by *in situ* thermal cross-polymerisation. In this way, a range of blends comprising 20, 40 60 and 80 wt% cp-DOE were obtained as moulded test specimens. Additionally, both blend components were

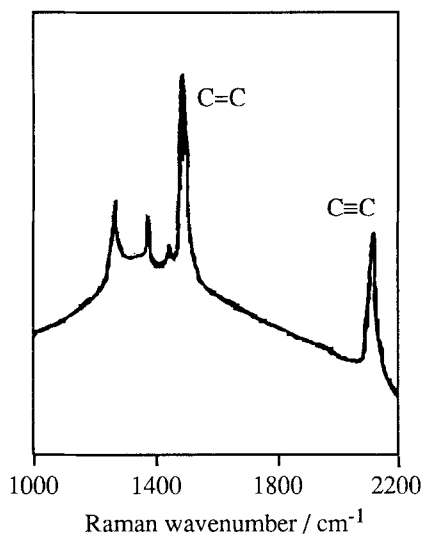


Figure 1. Resonance Raman spectrum of cp-DOE showing the strong C=C and C≡C stretching bands.

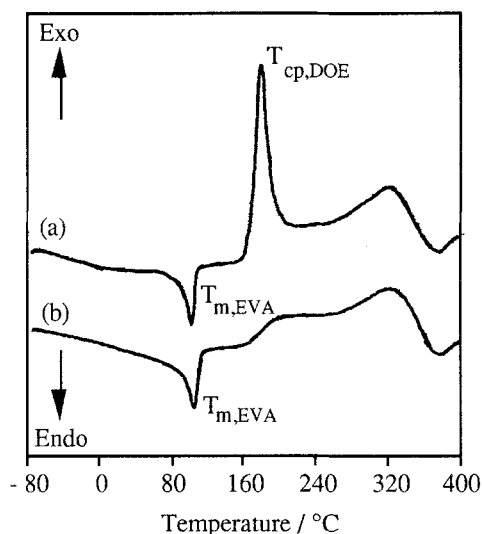


Figure 2. Representative DSC traces. Blend comprising 40% cp-DOE: (a) before moulding, and (b) after moulding.

moulded individually.

Figure 2 shows DSC traces which are representative of all the blends. Before moulding, the blends showed the melting endotherm for EVA, at $T_{m,EVA} = 107\text{ }^{\circ}\text{C}$, and a very intense cross-polymerisation exotherm with a maximum at $T_{cp,DOE} \approx 180\text{ }^{\circ}\text{C}$. (The thermal events above $240\text{ }^{\circ}\text{C}$ are due to degradation processes.) After moulding, only a small residual exotherm was observed at $180\text{ }^{\circ}\text{C}$ showing that cross-polymerisation of the DOE was achieved during the moulding process.

Analysis of the blends using SEM revealed a range of morphologies. Blends comprising 20 and 40 wt% cp-DOE had a dispersed cp-DOE phase with particles of cp-DOE in the approximate size range 2-6 μm . SEM of the blend comprising 60 wt% cp-DOE indicated a co-continuous morphology, an observation which was confirmed by selective solvent extraction of EVA from a moulding using hot toluene; this resulted in complete removal of the EVA without causing the moulding to disintegrate. The blend with 80 wt% cp-DOE had a discontinuous EVA phase.

Tensile stress-strain data are presented in Figure 3 for all materials. The individual components show extremes in tensile properties: cp-DOE shows brittle Hookean behaviour and is of high tensile modulus ($E = 3.45\text{ GPa}$) compared with EVA which has a modulus of 0.20 GPa and is highly ductile (failure strain $\approx 220\%$). Moulded blends containing 80 and 60 wt% cp-DOE were brittle, whilst those containing 40 and 20 wt% cp-DOE were ductile but had failure strains substantially less than that of EVA.

Resonance Raman spectra of the moulded blends show the same bands as those in the spectrum of cp-DOE (i.e. as shown in Figure 1). Moulded specimens of cp-DOE and each of the blends were subjected to simultaneous resonance Raman spectroscopy and tensile deformation measurements. The wavenumber for the $\text{C}\equiv\text{C}$ Raman band was observed to shift to lower values with increasing overall strain, as is shown in Figure 4. Raman shift factors ($\delta(\Delta\nu)/\delta\epsilon$) were taken as the slopes of least squares lines through the data and are tabulated in Figure 4. The tensile stress-strain curve and Raman shift factor for cp-DOE were used to convert the wavenumber shifts for each of the blends into the local stresses in the cp-DOE

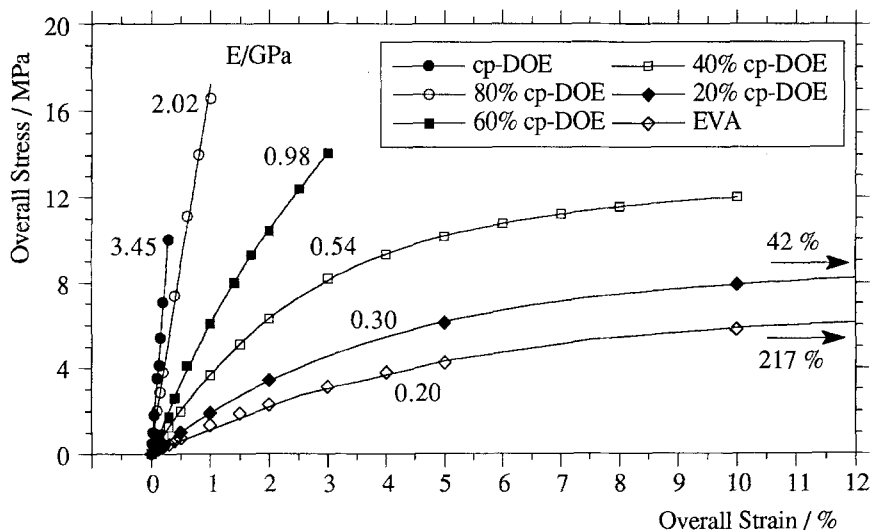


Figure 3. Mean tensile stress-strain curves for cp-DOE, EVA and their blends.

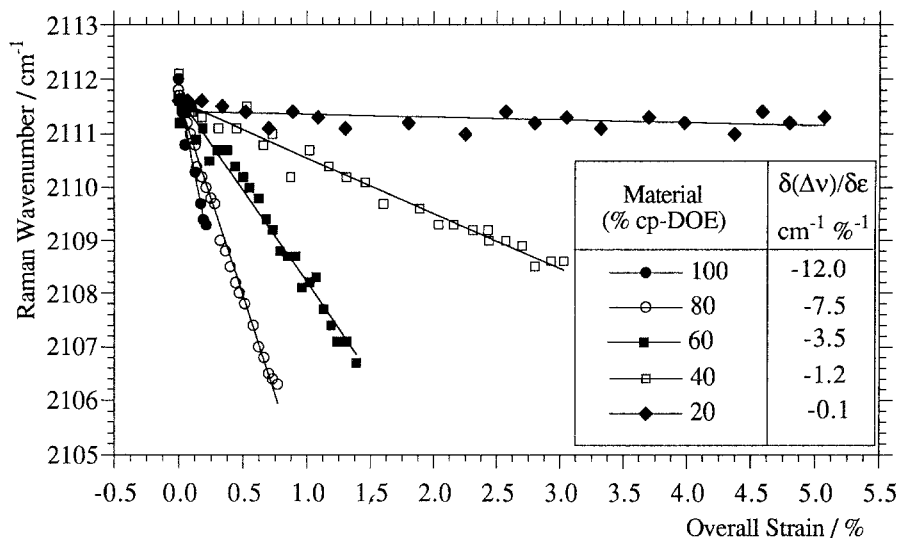


Figure 4. Plot showing the shift in wavenumber of the C≡C Raman band with overall strain for cp-DOE and each of the blends. The inset table gives the Raman shift factors ($\delta(\Delta\nu)/\delta\varepsilon$).

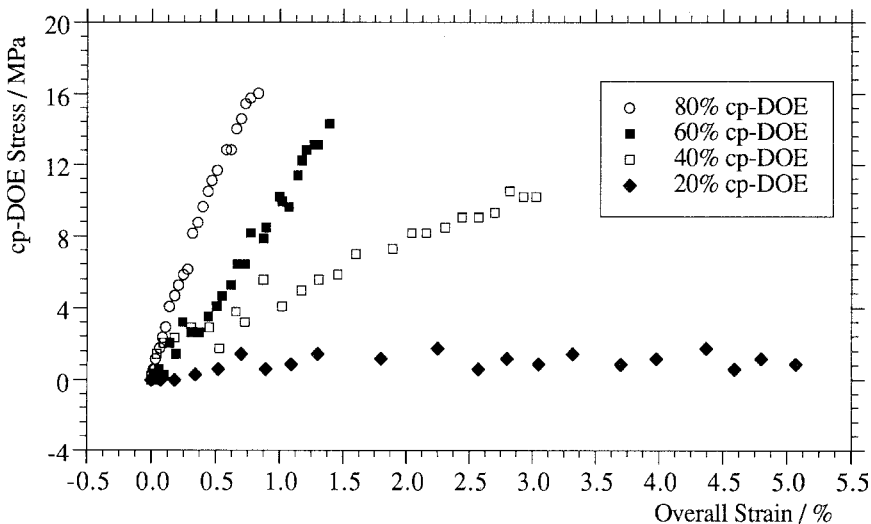


Figure 5. Plot of stress in the cross-polymerised DOE phases as a function of the overall strain in the blends for each blend composition. The stress values were determined from the shifts in the wavenumber of the C≡C Raman band.

component. The data obtained are plotted against overall strain in Figure 5. The data clearly show that there is little stress-transfer from the continuous EVA phase to the discontinuous cp-DOE phase in the blend comprising 20 wt% DOE. For the other materials, stress transfer is efficient and the stress taken by the cp-DOE increases as the cp-DOE content increases. In particular, for a given overall strain on the blend, there is a major increase in the stress within the cp-DOE phase as the blend composition changes from 40 to 60 wt% DOE, corresponding to the transition from a discontinuous to a continuous cp-DOE phase.

Conclusion

The results presented in this paper show that in model blends comprising as one component a polydiacetylene-containing phase, it is possible to monitor the stress in the polydiacetylene-containing phase independent of the overall deformation of the blend using the stress dependence of the wavenumber of the $C\equiv C$ Raman band. In this way, the micromechanics of deformation can be quantified in terms of stress transfer between phases for this range of materials which have widely-differing morphologies. More detailed analyses of the results presented here and of results from studies of the effects of a specially-synthesised compatibiliser on deformation micromechanics will be presented in further papers.

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