

Diallyl orthophthalate as a reactive plasticizer for improving PVC processibility. Part I: Polymerization kinetics

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Abstract

The thermal radical curing of four diallylic monomers were studied and was found to be very similar. Dynamic DSC of diallyl orthophthalate (DAOP) showed a strong correlation between the cure rate and the half life temperature of the initiator employed. The extent of allylic cure was found by DSC to be very dependent on the reactivity of the initiator due to a dead-end effect, and to rise towards a plateau value with increasing initiator levels. DAOP was blended with poly(vinyl chloride) (PVC) in various weight ratios by both solution and melt compounding. The compatibility between DAOP and PVC was analysed by measuring the glass transition temperatures of mixtures with dynamic mechanical thermal analysis which showed that DAOP monomer and PVC were fully miscible regardless of the composition. The cure rate of the DAOP/PVC blends was found by dynamic DSC and isothermal NIR to increase with higher levels of PVC due to a gel effect accentuated by grafting to the PVC, while the final extent of cure decreased because of topological constraints.

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1. Introduction

Poly(vinyl chloride) (PVC) is one of the most widely used plastic in the world due to its favourable cost/property benefits, however, it is difficult to process – usually PVC is processed up to 220 °C due to its high melt viscosity, but thermal decomposition with the release of toxic hydrogen chloride occurs at a relatively low temperature [1]. A traditional method to reduce the processing temperature is to add an inert plasticizer such as dibutyl phthalate or dioctyl phthalate [2], however, the addition of such plasticizers reduces the elastic modulus and glass transition temperature (T_g), and causes the long-term changes in the properties due to the migration and evaporation of the inert plasticizer [1].

Recently a new strategy to improve the processibility of intractable plastics without impairing their inherent properties

has been developed in which the processing temperature is greatly reduced by adding a small amount of a crosslinkable monomer. This monomer acts as a reactive plasticizer during processing (e.g. rotomoulding) but it can be subsequently polymerized into a dispersed thermoset phase in the thermoplastic matrix thus retaining its original mechanical properties. A suitable reactive plasticizer requires a high boiling point, a relatively low reactivity at the melt processing temperature, and miscibility with the processed thermoplastic. Currently, epoxy prepolymers are the most widely used reactive plasticizer in processing the aromatic polymers, such as polyphenylene ether (PPE) [3–6]. Some limited studies have been undertaken with the use of an allylic monomer as a plasticizer for PVC [7] and PPE [8].

In the present study, diallyl orthophthalate (DAOP) has been chosen as a free-radical crosslinkable reactive plasticizer because DAOP has a high boiling temperature (290 °C [9]), a relatively low reaction rate due to its degradative chain transition reaction and cyclization [10–13], a high gel point (up to 21% [9]) which means that it can be processed up to this point

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without any difficulty, and a structural similarity to traditional inert phthalate plasticizers for PVC which should result in the high compatibility. In this paper the polymerization kinetics of DAOP in the presence of various PVC contents using various thermal initiators with different half-time decomposition temperatures are studied by means of the dynamic differential scanning calorimetry (DSC), near infrared spectroscopy (NIR) and solvent extraction, and the thermal-mechanical properties of uncured PVC/DAOP blends are investigated by dynamical mechanical thermal analyser (DMTA). An investigation of the properties of cured PVC/poly(DAOP) will be reported in part II of this work [14].

2. Experimental

2.1. Materials

The poly(vinyl chloride) (PVC) powder was supplied by Australian Vinyls Corp under the trade name Corvic 5716 with \overline{M}_w at 8.6×10^4 , and was mixed with 2 wt% calcium stearate (CaSt, Australian Vinyls Corp) and 1 wt% zinc stearate (ZnSt, Australian Vinyls Corp) as the heat stabilizers. Diallyl orthophthalate (DAOP), diallyl isophthalate (DAIP) and diallyl terephthalate (DATP) were supplied by Daiso Co Ltd while diethylene glycol di(allyl carbonate) (DEGDAC) was supplied by PPG Industries. A variety of initiators, including azobis-isobutyronitrile (AIBN, Aldrich), benzoyl peroxide (BPO, Aldrich), di(4-*tert*-butylcyclohexyl)peroxydicarbonate (BCHPC, Akzo Nobel), *tert*-butylperoxy-2-ethylhexanolate (TBPEH, Interlox), cumyl hydroperoxide (CHP, Interlox), and azobutane (AB, Aldrich) and dicumyl peroxide (DCP, Aldrich), were used to cure the diallyl phthalate monomers. In some cases, the solvent tetrahydrofuran (THF, Aldrich) was used to aid mixing of PVC with the monomers. All raw materials were used without further treatment except for BPO which was pre-dried in a desiccator to remove the water. The chemical structures of initiators are shown in Table 1.

2.2. Sample preparation

Samples for DSC studies of the polymerization kinetics of the monomers were prepared by dissolving various amounts of the initiators into the monomers. As discussed below, due to the similar curing behaviour of the four allylics, only DAOP with DCP was chosen to mix with PVC by either solvent or melt blending. In the solvent blending method, DAOP was mixed with a 20 wt% of neat PVC solution in THF at room temperature – for DSC and near infrared (NIR) studies of the cure of DAOP in the presence of PVC, DCP was also added. The mixtures were cast on glass plates to form films which were evaporated at room temperature for several hours to remove most of solvent before final drying under vacuum either at room temperature for 4 days (for glass transition temperature measurements) or at 60 °C for 2 days (for studies of the DSC or NIR curing kinetics).

For melt blending of PVC with DAOP, the PVC with the stabilizers was pre-mixed by hand with DAOP (containing

2 pph, or parts per hundred, of DCP for cured samples used in solvent extraction studies, or without DCP for T_g measurements of the uncured blends), followed by blending in a Haake Rheocord 90 melt blender at a pre-set temperature for *ca.* 3 min. The processing temperature was 180 °C for neat PVC resin but this was decreased to 140 °C for the 80 wt% PVC/20 wt% DAOP blend and down to 100 °C for the 50 wt% PVC/50 wt% DAOP. The resulting blends were then compression-moulded at the blending temperature into flat sheets (*ca.* 1.5 mm thick) between Teflon coated sheets, using an aluminum spacer and steel backing plates. For gel content determination, DAOP/PVC/DCP samples with various PVC contents were cured at 140 °C for 6 h and post-cured at 160 °C for 30 min.

The blends are described by the notation, wt% PVC/wt% DAOP/pph DCP, so that the code of 90/10/2 identifies the sample containing 90 wt% PVC, 10 wt% DAOP and 2 pph of DCP added to the blend.

2.3. Equipment

Differential scanning calorimetry (DSC) curing studies were performed on *ca.* 10 mg samples sealed in aluminum pans using a Perkin Elmer DSC7 and nitrogen as the purge gas. Usually heating scans were performed at 10 °C per min, although the curing of DAOP was also performed at 2, 5, 10, and 20 °C per min to determine the activation energy. Some samples and DSC pans were prepared and sealed in a nitrogen dry-box to study the effect of cure inhibition by oxygen.

Isothermal cure kinetics were also monitored by Fourier transform near-IR spectroscopy (NIR) via a Perkin Elmer Spectrum GX FTIR using thin samples sandwiched between KBr plates and cured in a Graesby–Specac temperature-controlled cell at a range of temperatures. The characteristic peaks in the NIR for the allyl group was 6135 cm^{-1} which can be attributed to the overtone absorption due to stretching vibration of C=C–H bond in the allyl group [15]. The area under the allyl absorption peak was used directly to calculate the conversion of the C=C groups as a function of time.

A Rheometric Scientific Mark IV model dynamic mechanical thermal analyser (DMTA) was used in dual cantilever bending mode to measure the glass transition temperature of uncured PVC/DAOP mixtures, over the temperature range from –100 to 150 °C at 2 °C per min at 1 Hz with bar-type specimens of dimension 20 mm × 5 mm × 1.5 mm. The T_g was defined as the temperature corresponding to the maximum in $\tan \delta$.

Gel contents in the cured PVC/DAOP/2 pph DCP samples were determined by solvent extraction and gravimetry. Samples with various PVC contents (cured as described above), were cut into small pieces, and subjected to Soxhlet extraction for 48 h refluxing with THF – preliminary studies showed that there was little difference in the gel content between 24 h and 48 h extraction periods. The insoluble gel was dried in a vacuum oven to remove the residual solvent and then was weighed. The PVC content in the gel was determined by mid-infrared spectroscopy with a Perkin Elmer Spectrum GX FTIR, using the ratio of the peak at 1730 cm^{-1} due to

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