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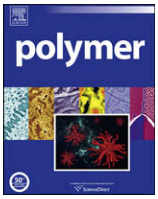

Diallyl orthophthalate as a reactive plasticizer for improving PVC processability, Part III: Curing, properties, and phase separation

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ABSTRACT

Diallyl orthophthalate (DAOP) is investigated as a reactive plasticizer to aid the processing of PVC by reducing the melt's viscosity and thus minimizing the processing temperature so that decomposition of PVC can be effectively avoided during time-consuming processing operations such as rotational moulding. A range of PVC/DAOP blends have been prepared with dicumyl peroxide (DCP) or cumyl hydroperoxide (CHP) as radical initiators, and their chemorheology, properties and morphology have investigated by dynamic rheometry, DMTA, SEM and solvent resistance. DCP was found to be a better initiator than CHP for polymerization of DAOP in blends with PVC because the former's high decomposition temperature matches well with the processing temperature of the PVC/DAOP blends. DMTA indicates that the T_g of the cured PVC/DAOP blends are very close to that of PVC and have a higher storage modulus at the rubbery region. SEM images show that phase separation occurs during cure of the blend and that solid poly(DAOP) nano-particles are embedded in the PVC continuous phase when the PVC content is more than 30 wt%. This cure and phase separation of DAOP from the PVC matrix can successfully recover the PVC's thermal-resistance properties.

1. Introduction

The blending of thermosets and thermoplastics was introduced during the 1980s as a way of toughening thermosets without the loss in modulus observed when elastomeric particles are used for this purpose [1], and interest in the properties and morphology of thermoset–thermoplastic blends has continued to develop. Some thermoplastics are difficult to process, especially when reinforced with nano-fillers, and are likely to suffer degradation during processing operations. Traditional methods of enhancing processability such as reducing the molecular weight, adding inert plasticizers, and blending with a more processable polymer usually result in a reduction in the properties. Recently a new strategy has been developed [2–7] in which the processing temperature is lowered by adding a small amount of a crosslinkable monomer. This monomer acts as a reactive plasticizer during processing by lowering the glass transition temperature and viscosity but it can be subsequently polymerized into a thermoset phase in the thermoplastic matrix, possibly regaining the original mechanical properties of the matrix. So far, the main reactive plasticizers used have been epoxy prepolymers [3–8], however the relatively high viscosity of these resins and their immiscibility with some thermoplastics affect their universal use as reactive plasticizers.

Polyvinyl chloride (PVC) is widely used due to its high properties/cost ratio, but it is also a relatively intractable thermoplastic caused by the high polarity of the C–Cl bond, which necessitates a processing temperature (at least 220 °C) which is similar to its decomposition temperature [9]. As a result, the processing of PVC is rather limited and so is not normally used in processes that require long cycle times such as rotational moulding or powder coating, unless it is plasticized by the addition of an inert plasticizer such as dioctyl phthalate to lower its processing temperature [10]. Unfortunately the plasticizer lowers the glass transition temperature (T_g) of the final product and thus impairs its thermal-resistance [11]. In order to solve this processability problem, we have recently [12–14] proposed extension of the ideas of Lemstra and others [2–6,15,16] on thermoset–thermoplastic blending to long cycle time processes. In contrast to the conditions required for injection moulding and extrusion such as rapid cooling, the use of reactive plasticizers is ideal for processes such as rotational moulding or powder coating because they afford sufficient time for polymer flow before cure occurs at the processing temperature.

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In earlier papers of this series, we have chosen a reactive plasticizer, diallyl phthalate (DAOP), with a chemical structure which is very similar to traditional PVC plasticizers. Upon cure, the final blend should have a high thermal-resistance because the cured DAOP has a T_g around 200 °C [17], compared with PVC's T_g of 95 °C [12] and DAOP's T_g of −90 °C [14]. We have previously investigated the miscibility of PVC and DAOP [12], studied the polymerization kinetics of DAOP in the presence and absence of PVC [12], and have studied the rheology of the uncured and curing blends [18]. In the present paper, the reactivity of DAOP and the processing conditions of PVC/DAOP blends are further investigated and the thermo-mechanical properties and the phase separation in the cured blends are presented.

2. Experimental

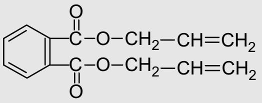
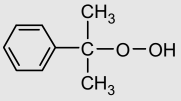
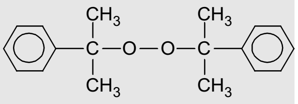
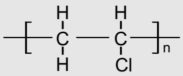
2.1. Materials

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 pre-mixed with 2 wt% calcium stearate (Australian Vinyls Corp) and 1 wt% zinc stearate (Australian Vinyls Corp) as the heat stabilizers. The reactive plasticizer, diallyl orthophthalate (DAOP), the thermal initiators, dicumyl peroxide (DCP), and cumyl hydroperoxide (CHP), and the tetrahydrofuran (THF) solvent used as an etchant for cured PVC/DAOP samples, were all supplied by the Sigma–Aldrich. The materials were used without further treatment, and their chemical structures are listed in Table 1.

2.2. Sample preparation

DAOP was manually mixed with 3 wt% of DCP or CHP to form a homogeneous solution. Dynamic mechanical thermal analysis (DMTA) specimens of cured DAOP/initiator were prepared in silicone moulds at 170 °C for 30 min followed by post-curing at 220 °C for 30 min. For differential scanning calorimetry (DSC) and Fourier-transform infrared, DAOP was manually mixed with 3 wt% of DCP or CHP to form a homogeneous solution. Dynamic mechanical thermal analysis (DMTA) specimens of cured DAOP/initiator were prepared in silicone moulds at 170 °C for 30 min followed by post-curing at 220 °C for 30 min. For differential scanning calorimetry (DSC) curing studies, DAOP and initiator were mixed with a concentrated solution of PVC (with stabilizers) in THF before evaporation of the THF under vacuum.

Table 1
Raw materials used.

Raw material	Full name	Structure
DAOP	Diallyl phthalate	
CHP	Cumyl hydroperoxide	
DCP	Dicumyl peroxide	
PVC	Poly(vinyl chloride)	 $\left[-\mathrm{CH_2}-\mathrm{CHCl}- \right]_n$

The PVC/DAOP blends for all other experiments were prepared by manually pre-mixing DAOP with the stabilized PVC powders. In some studies, no initiator was present in the DAOP and these PVC/DAOP samples were used to determine the DMTA behaviour of the uncured blends. In all other cases where the curing of the blends was intended, the DAOP contained 3 wt% CHP or DCP. The PVC/DAOP blend was added to the hopper of a micro-extruder (Thermo Electron, Haake MiniLab, Germany) and was rapidly extruded at 100 rpm by a pair of tapered screws (L/D linearly changed from 10 to 20, with screw length 100 mm) – the residence time during the extrusion was estimated to be *ca.* 1 min. The pre-set temperatures of the barrel and die ranged from 220 °C for neat PVC down to 140 °C for PVC/DAOP blends. The extrudate was then rapidly transferred into a micro-injection moulding machine (DSM Research, Netherlands), pre-set to the same operating temperature as the extruder, and was injected into a rectangular (2 mm × 5 mm to 10 mm × 80 mm) steel mould held at room temperature. All specimens were transparent. The unplasticized PVC injection moulded specimen had a brown colour, suggesting PVC decomposition but the PVC/DAOP specimens varied in appearance from slightly yellowish to colourless, suggesting these blends had not undergone significant decomposition. The injection moulded specimens containing initiator were further cured at 160 °C in an oven for 30 min to polymerize the DAOP in the blend.

The blends are described by the notation: wt% PVC/wt% DAOP/wt% initiator where the wt% initiator refers to the amount of DCP or CHP added to the DAOP – this coding differs from that used in an earlier paper [12] where the initiator concentration was expressed in parts per hundred of the PVC/DAOP blend. Thus, in the current paper, the code of PVC/DAOP/DCP(60/40/3) identifies the sample containing 60 wt% PVC, 40 wt% DAOP and with 3 wt% of initiator added to DAOP so that the blend contained a total of 1.2 wt% DCP.

2.3. Instruments

The steady shear rheological properties of the uninitiated blends were measured using a Physica MCR 501 rheometer (Anton Paar, Germany) in parallel plate mode at 180 °C, except for the neat PVC which was measured at 220 °C due to its low flowability. Sections of the extruded bar specimens were placed on the heated circular parallel plates of the rheometer and the molten polymer was sandwiched to give a gap of 0.5 mm, and the chosen plate diameter ranged from 15 mm (for neat PVC, 90/10, and 80/20), to 25 mm (for 60/40), to 40 mm (for 40/60), and to 50 mm (for 20/80).

The chemorheology of DAOP/CHP and DAOP/DCP during cure was monitored at various temperatures with an ARES rheometer (Rheometric Scientific, USA) using parallel plate geometry 8 mm diameter and 0.5 mm gap. The average strains were varied according to the storage modulus value (G'), ranging from 100% for $G' < 10^2$ Pa, to 1% for $G' > 10^5$ Pa. The dynamic real modulus and $\tan\delta$ were measured at various frequencies, ranging from 0.1 to 10 Hz, and the gel times of DAOP were obtained by the frequency independence of $\tan\delta$ [19]. In addition, an operational definition was also employed to estimate the gel time [20], as the stage where the development of the network caused the real modulus to rise to a certain but low value (here we used 10 Pa at a frequency of 1 Hz). Both methods gave very similar results but since the latter was found to be more precise, it was used as the primary method to determine the gel time.

Dynamic DSC curing studies of DAOP and PVC/DAOP blends were performed on ca. 10 mg samples sealed in aluminium pans with vented lids using a Perkin Elmer Pyris 1 fitted with a Flexicool

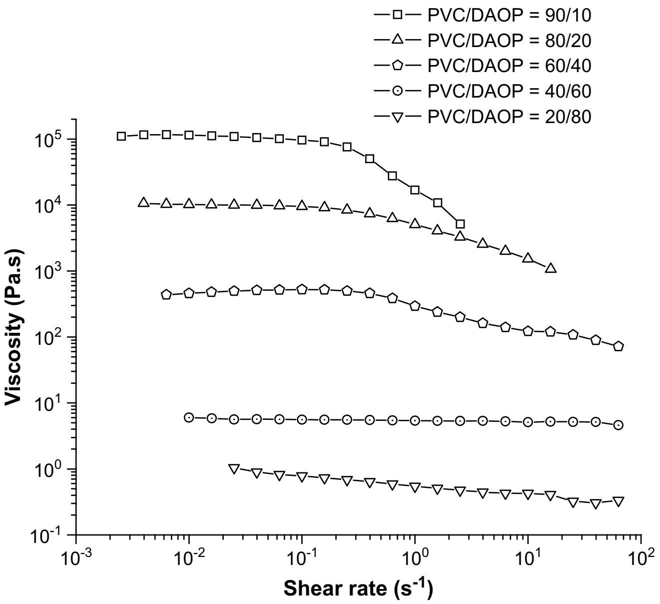


Fig. 1. Steady shear viscosities of various PVC/DAOP blends at 180 °C as a function of shear rates.

(ETS system) cooling system. The samples were heated at 10 °C per min from 50 °C to 200 °C under a nitrogen gas purge at 20 ml/min.

Isothermal cure kinetics were monitored by Fourier-transform IR spectroscopy (FTIR) via a Perkin Elmer 1600 Series FTIR using a drop of DAOP with 3%DCP sample sandwiched between circular KBr plates and placed in a Specac temperature-controlled cell. The characteristic peak in the FTIR spectrum for the allylic group is 1647 cm^{-1} which can be attributed to the stretching vibration of $C=C–H$ in the allyl group [21] while the peaks at 1577 and 1598 cm^{-1} are due to benzene ring [21] and can be used as references because their intensities do not change very much during the cure of DAOP. The ratio of the area under the allylic absorption peak to the area under the benzene ring peaks was used to calculate the conversion of the allylic groups.

A DMTA (model IV, Rheometric Scientific, USA) was used in duel cantilever bending mode at 1 Hz with 0.05% strain to measure the glass transition region of uncured and cured PVC/DAOP blends, over the temperature range of −120 to 250 °C at 2 °C per min with bar-type specimens of dimension 20 mm × 5 mm × 1.5 mm. The glass transition temperature T_g was defined as the temperature corresponding to the maximum in tanδ.

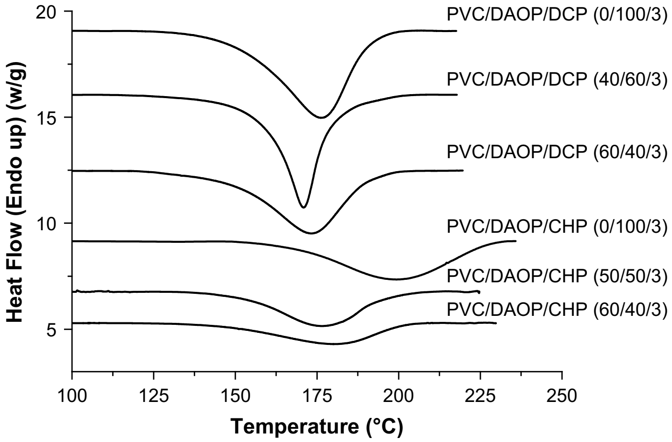


Fig. 2. Dynamic DSC curves (at 10 °C per min) of the polymerization in neat DAOP and in PVC/DAOP blends using either DCP or CHP (3 wt% based on the monomer).

Table 2
DSC curing data for DAOP and PVC/DAOP with DCP and CHP.

Initiator	0/100/ 3DCP	40/60/ 3DCP[a]	60/40/ 3DCP	0/100/ 3CHP	50/50/ 3CHP	60/40/ 3CHP
ΔH (kJ/mol)	79.3	66.4	59.8	49.4	35.8	24.8
T_{peak} (°C)	176 ± 1	171 ± 1	173 ± 1	199 ± 1	177 ± 1	180 ± 1

[a] 40/60/3DCP stands for PVC/DAOP/DCP (40/60/3).

Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6300F instrument operating at 15 kV. The cured blend specimens were fractured in liquid nitrogen, and in some cases the fracture surface was etched in THF for 3 min with stirring, before gold-sputter coating of the surface.

3. Results and discussion

As mentioned above, the addition of DAOP significantly decreased the processing temperature for the PVC/DAOP blends by lowering the mixing torque required, and as a result decomposition of the PVC was greatly reduced as indicated by the low colouration in the blends. Quantification of this improved processability is given in Fig. 1 which shows the steady shear rheology of PVC/DAOP blends versus shear rate. An increase in the DAOP concentration of the blend causes a substantial reduction in viscosity, so that an increase of ca 20% DAOP in the blend reduced the viscosity by tenfold. Fig. 1

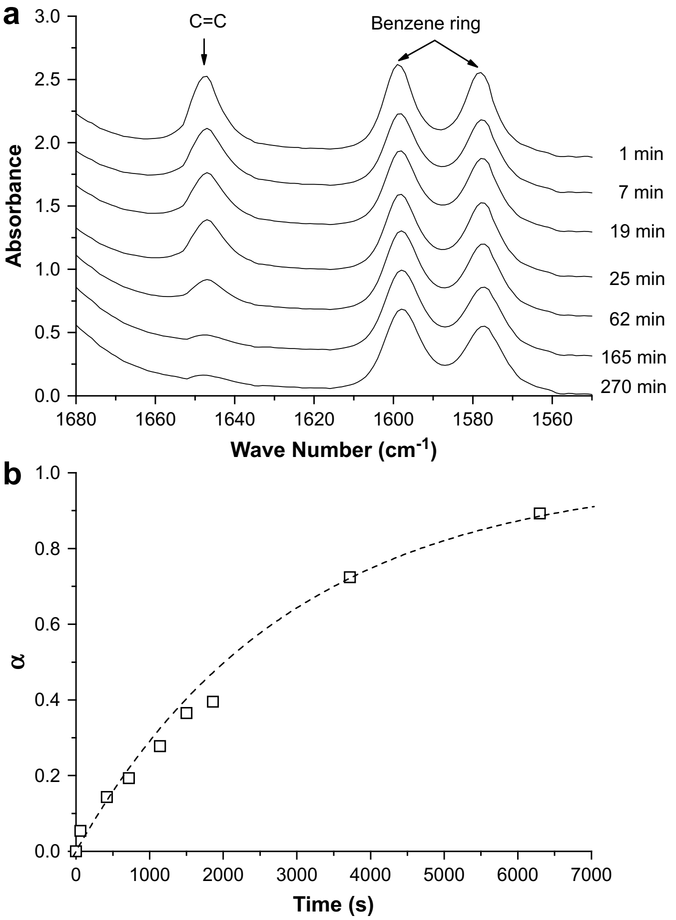


Fig. 3. FTIR spectra during cure of DAOP using 3 wt% DCP as initiator at 130 °C (a), and fits of the dependence of conversion (α) on time, assuming first order kinetics (b).

also exhibits typical polymer melt rheology with a low shear rate Newtonian region and a pseudoplastic (shear rate thinning) region at higher shear rates for PVC/DAOP systems with high PVC levels (>40 wt%) as found for other polymer solutions [22,23].

The addition of DAOP to PVC also impairs its heat-resistance properties by reducing the glass transition temperature (T_g) as illustrated in our previous work [12]. Theoretically this plasticization problem can be solved by polymerizing the reactive plasticizer after the processing operation. Previous studies of the curing behaviour of DAOP with a range of peroxide initiators have shown [12] that DCP and CHP can polymerize DAOP to high conversions but at temperatures which would not cause premature cure of the PVC/DAOP blend during processing. Fig. 2 and Table 2 compare the dynamic DSC curing curves of DAOP and PVC/DAOP blends when cured with 3 wt% initiator. DCP caused faster polymerization (lower onset and peak temperatures) and a higher level of conversion (higher heat of polymerization) than CHP. DSC studies with 6 wt% CHP (data not shown here) gave a similar level of cure as 3 wt% DCP but still cured more slowly. Table 2 also shows that the heat of polymerization of DAOP decreases as the concentration of PVC is raised in the blend in agreement with that found previously for PVC/DAOP systems cured with DCP [12]. This was attributed [12] to the reduction in the average monomer concentration in the matrix which interferes with the propagation reaction through a topological effect. In addition (and in contrast to the previous study [12]), in the present study the concentration of initiator in the matrix is also reduced when PVC is added. This reduction in initiator concentration should also reduce the conversion due to premature loss of initiator via dead-end polymerization [24,25] or by degradative chain transfer [26] in which an allylic radical abstracts a hydrogen from an allylic group, thus forming a resonance stabilized and unreactive radical, as previously discussed [12]. The DSC studies of the polymerization of the PVC/DAOP blends show (Table 2) that the peak curing temperature does not show a systematic variation with PVC content. This is probably due to the competition of two effects. The rate should be reduced by addition of PVC to the blend because it reduces the concentration of both DAOP and initiator. However this may be overcome by an increase in the polymerization rate when PVC is added to the blend due to the effect of PVC on the termination rate as discussed previously [12].

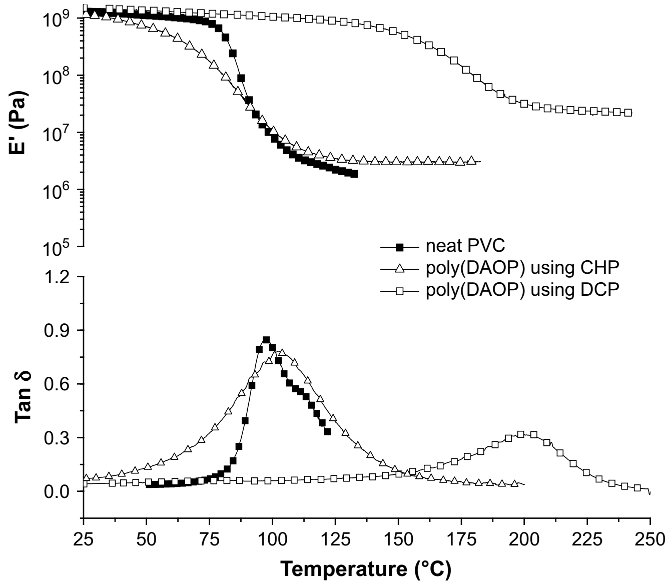


Fig. 5. DMTA of PVC and of poly(DAOP) cured using either 3 wt% CHP or 3 wt% DCP.

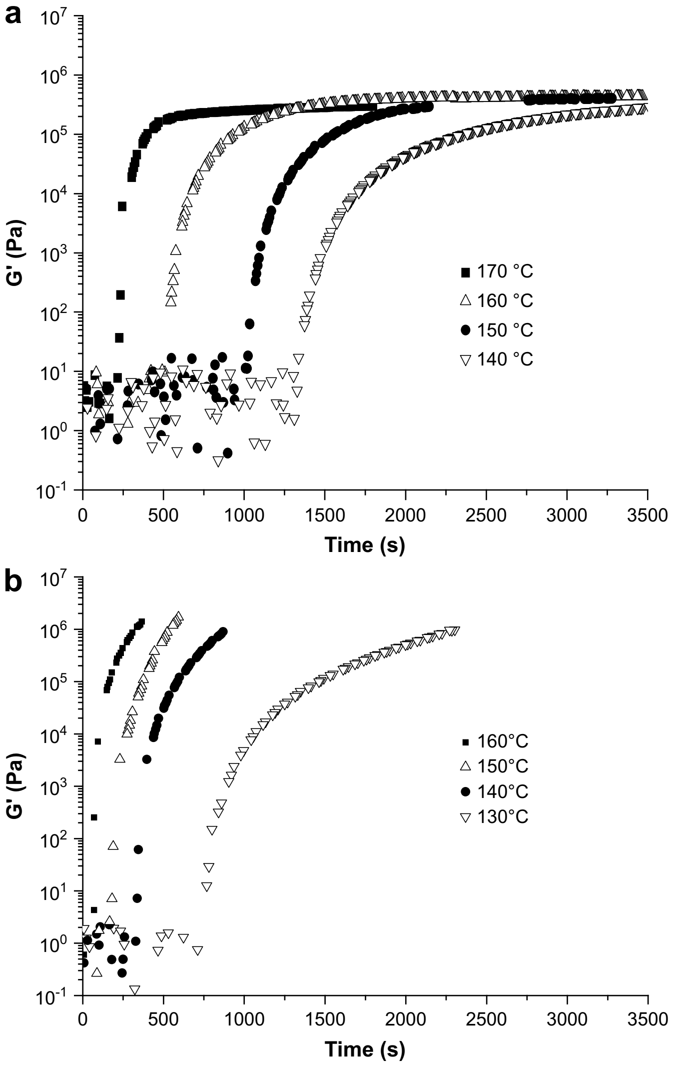


Fig. 4. Variation in dynamic modulus (G′) measured at frequencies of 0.1–10 Hz as a function of cure time for DAOP using 3 wt% CHP (a) and 3 wt% DCP; (b) at various curing temperatures.

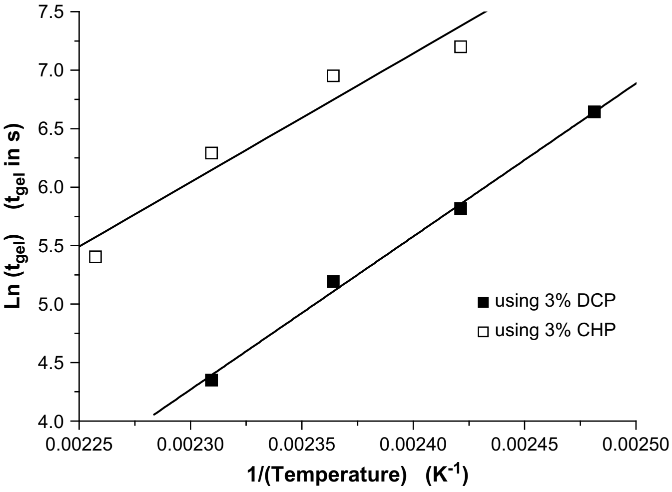


Fig. 6. Linear plot of natural logarithm of gel time and when G′ = 10 Pa (squares) versus reciprocal of temperature for DAOP with DCP or CHP. The tanδ gelation data overlaps with the G′ gelation data.

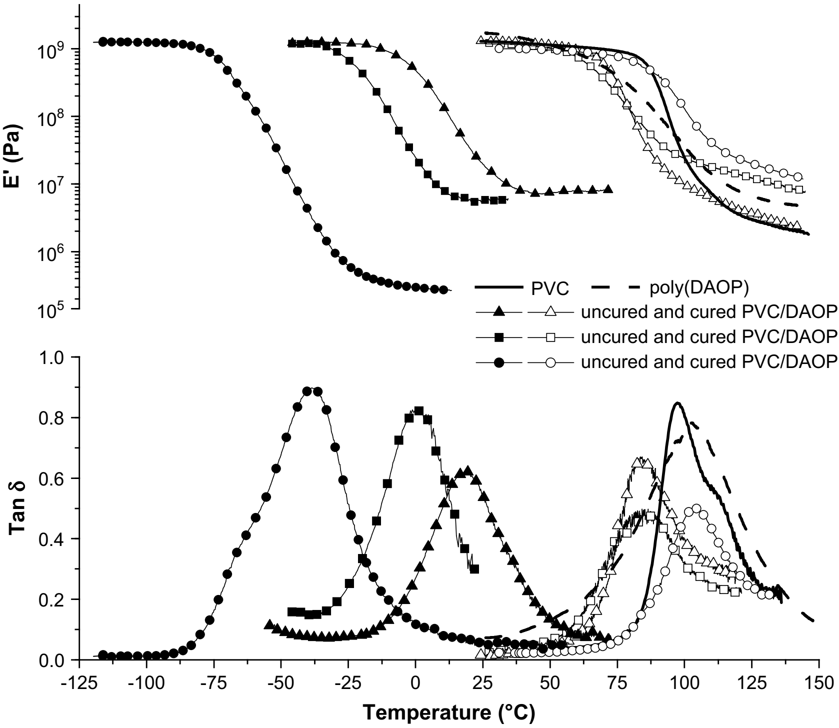


Fig. 7. DMTA results (E′ and tanδ) of poly(DAOP), PVC, PVC/DAOP(70/30), PVC/DAOP(60/40) and PVC/DAOP(40/60) blends without initiator (closed symbols), and their corresponding cured blends containing 3 wt% CHP (open symbols).

The DSC studies of the polymerization of the PVC/DAOP blends show (Table 1) that the peak curing temperature does not show a systematic variation with PVC content. The simplest analysis of radical polymerization, the rate of cure is given by [27]:

$$\frac{d(\alpha)}{dt} = k_p(k_d f[I]/k_t)^{1/2}(1-\alpha) \quad (1)$$

where α is the conversion, $[I]$ is initiator concentration, f is initiator efficiency, k_d is the dissociation constant of initiator, and k_p and k_t

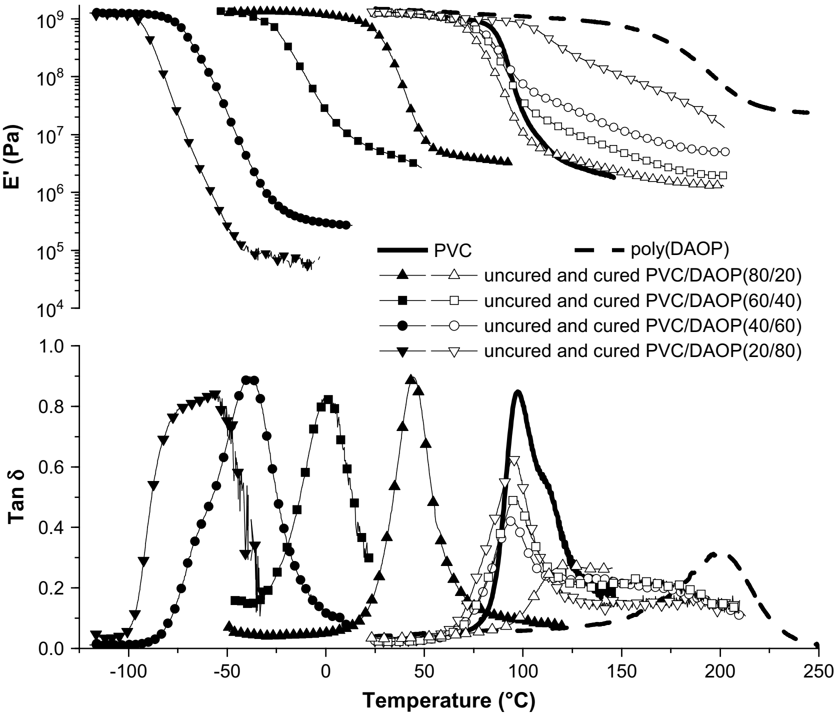


Fig. 8. DMTA results (E′ and tanδ) of poly(DAOP), PVC, various PVC/DAOP blends without initiator (closed symbols), and their corresponding cured blends containing 3 wt% DCP (open symbols).

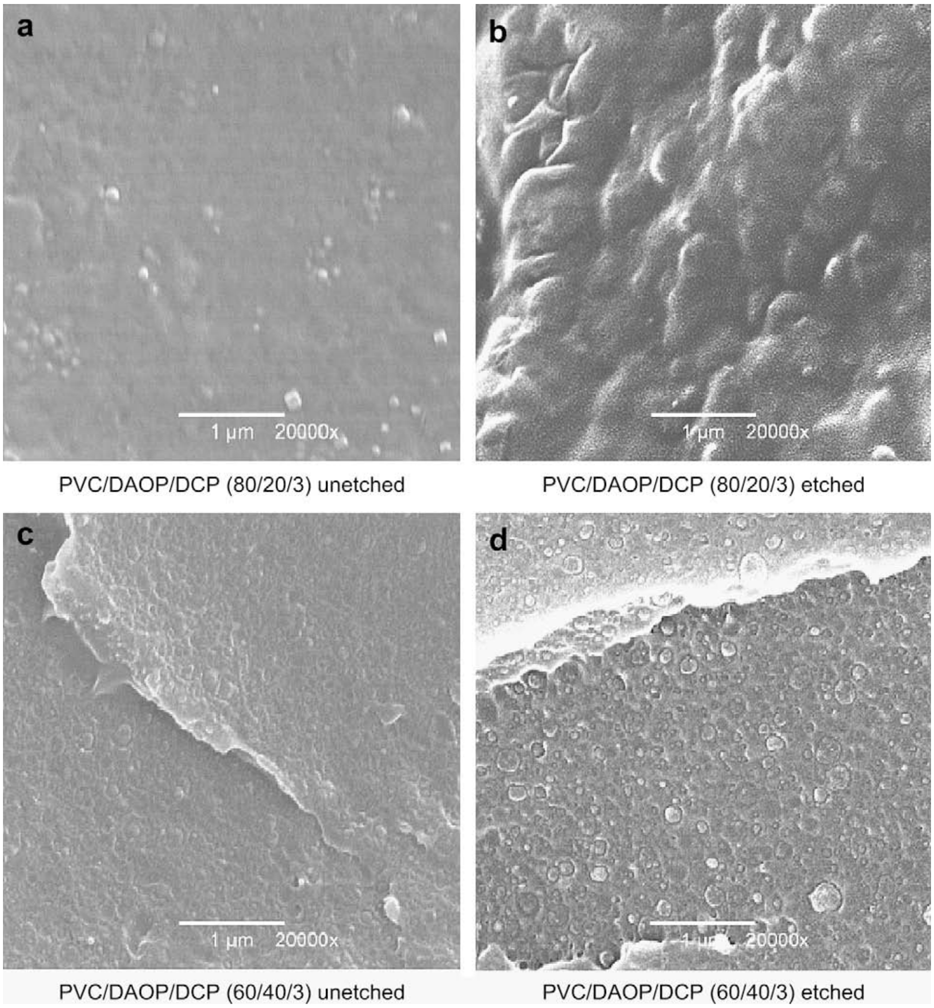
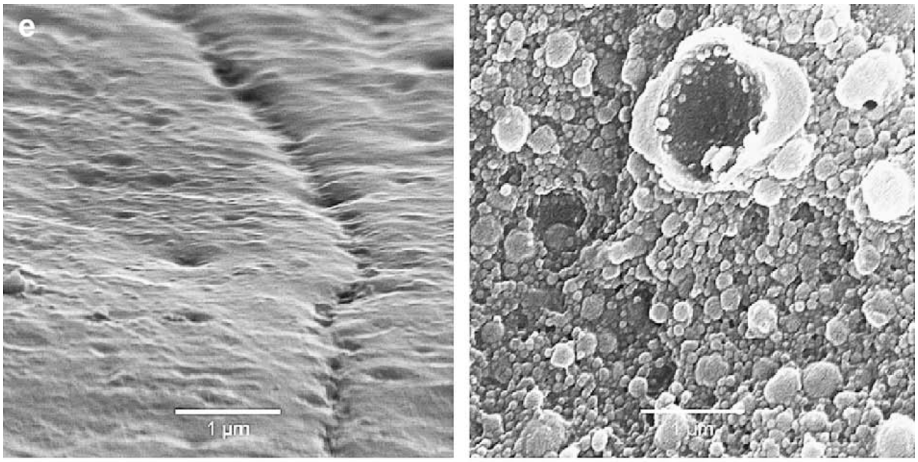


Fig. 9. SEM images of various cured PVC/DAOP/DCP blends of unetched and etched (3 min in THF) fracture surfaces.

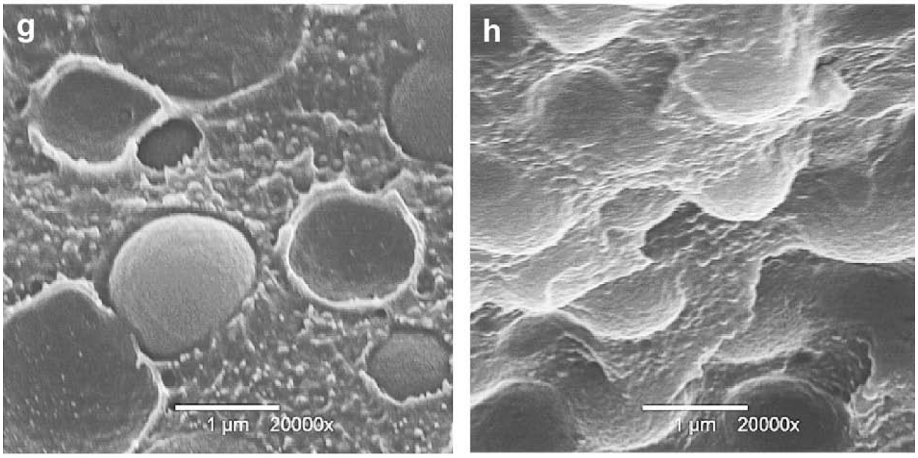
are rate constants of chain propagation and chain termination, respectively, and so one would expect that the rate should be reduced by addition of PVC to the blend because it reduces the concentration of both DAOP and initiator. However, it has previously been shown [12] that if the initiator concentration is kept constant an increase in PVC concentration actually increases the polymerization rate because PVC is grafted to the gel via a chain transfer reaction and this reduces the termination rate and therefore accelerates polymerization. Thus it appears that peak temperature passes through a minimum and so the cure rate passes through a maximum with increasing PVC concentration due to the competition of these two effects.

Isothermal FTIR was used to monitor the cure of DAOP using 3 wt% DCP and Fig. 3 (a) shows that consumption of the allylic groups is nearly complete after 4 h at 130 °C. Fig. 3 (b) shows the conversion data plotted versus time on the assumption that the polymerization kinetics can be approximately represented by a first order process. The rate constants obtained using this method were measured as a function of temperature and the activation energy for DAOP using 3 wt% DCP was found to be 123 ± 20 kJ/mol, which is similar to those obtained by DSC and near-FTIR in a previous study [12].

The evolution of the real modulus (G') of DAOP containing either CHP or DCP, respectively, during polymerization is shown in Fig. 4 (a) and (b). Initially, the real moduli is very low due to the liquid state of the material, however as the polymerization proceeded chain branching occurred followed by network formation and G' significantly increased at the gel point. With further curing, the shear modulus for the DAOP/CHP system approached a plateau region (see Fig. 4a) with a value of ca. 0.5 MPa. Within experimental error, this value is consistent with rubbery Young's modulus of 3 MPa obtained from the DMTA of the cured polymer (see Fig. 5) since the shear modulus is one third of the Young's modulus. It should be noted that 1 MPa is typical of a lightly crosslinked rubber [27] and so the observation that the modulus had reached a rubbery plateau but failed to vitrify suggests that the reaction had virtually ceased prior to complete cure which is in agreement with the DSC studies of CHP cured systems (see Table 2). The behaviour is somewhat different when DAOP is cured by DCP (see Fig. 4b). Even though the rise in shear modulus for the DAOP/DCP system was faster than that for the DAOP/CHP system at the same temperature due to the faster polymerization, the approach to a modulus plateau for the DAOP/DCP system was slower and the shear moduli measured at the end of the experiment was approximately 1 MPa and still rising. This suggests that the material was passing through the rubber region and entering the glass transition region due to continuing reaction. The DMTA behaviour of the cured polymer shown in Fig. 5 supports this interpretation because it shows that at the curing temperatures applied to the systems in Fig. 5, the storage modulus eventually attains values close to 1 GPa. These rheology results indicate that DCP was a more



PVC/DAOP/DCP (40/60/3) unetched PVC/DAOP/DCP (40/60/3) etched



PVC/DAOP/DCP (20/80/3) unetched PVC/DAOP/DCP (20/80/3) etched

Fig. 9. (*continued*).

effective initiator in the curing of DAOP, which is consistent with the DSC results in Fig. 2 and Table 2.

A comparison of the rheology data (Fig. 4b) with the FTIR data (Fig. 3b) for DAOP/DCP shows that that the conversion of DAOP vinyl groups at the gel point was about 20%, which compares well with the result of 21% and 25% reported by Kircher [28] and Matsumoto et al. [29], respectively – note that the high level of agreement is probably fortuitous because the gel point of a chain growth system is very dependent on kinetic chain length and chain transfer which could vary considerably for different studies [27]. As expected, the gel points, determined from the frequency independence of tanδ or from the rapid rise in G' decreased with increased curing temperature. Assuming that the gel point conversion is independent of the cure temperature, the linear relations between the natural logarithm of gel point ($\ln t_{gel}$) and the reciprocal of the absolute temperatures, as shown in Fig. 5, gave polymerization activation energies of 92 ± 17 and 109 ± 5 kJ/mol for DAOP using 3 wt% CHP and 3 wt% DCP, respectively. Given the statistical uncertainty of these results, they agree reasonably well with the value of 123 ± 20 kJ/mol obtained by FTIR.

In agreement with the DSC results given in Fig. 2 and Table 2, DMTA of DAOP cured using either DCP or CHP as initiators (Fig. 5) also indicated that 3 wt% of DCP could cure DAOP at higher curing extent than 3% CHP, since the polymerized material, poly(DAOP), had much higher T_g (200 °C) compared with that for DAOP cured using CHP (with a T_g of 104 °C). In addition, poly(DAOP) cured with DCP had a higher storage modulus in the rubbery region – using the theory of rubber elasticity [27] this indicates that DCP produces a higher curing degree (Fig. 6).

Figs. 7 and 8 show the DMTA properties of the uncured and cured PVC/DAOP blends using either CHP or DCP as initiators. Since DAOP has a T_g of −90 °C [14], its presence substantially reduces the T_g to 44 °C, 0 °C, −38 °C and −60 °C for the 80/20, 60/40, 40/60 and 20/80 uncured blends, respectively. The rubbery moduli of the uncured 80/20 and 60/40 PVC/DAOP blends are significantly higher than for the 40/60 and 20/80 blends. This may be due to the ability of the PVC to form entanglements in blends with higher PVC contents or due to a small level of crystallization which acts as physical crosslinks as discussed in a sister paper [18].

After cure of the blends, Figs. 7 and 8 show that the T_gs of the blends rose to between 80 and 110 °C due to the combination of the effects of loss of plasticization by monomer and the influence of crosslinking. In addition, curing of each of the blends increases the modulus in the rubber-like region due to crosslinking.

The influence of the DAOP concentration on the T_gs of the cured blends is a little more complex. For the DCP-cured blends (Fig. 8), two glass transitions are observed indicating that two phases are present, as also suggested in a sister paper [18]. The temperature of the primary maximum in tanδ (ca. 94 °C) is very close to that of pure PVC (97 °C) and does not appear to change significantly as the

Table 3
Effect of THF solvent on the cured PVC/DAOP/DCP blends after storage at room temperature for 3 months.

PVC/DAOP/DCP	100/0/0	80/20/3	60/40/3	40/60/3	30/70/3	20/80/3	0/100/3
Effect of solvent	Dissolved	Disintegrated	Disintegrated	Disintegrated	No effect	No effect	No effect

level of DAOP is raised, suggesting that this phase is rich in PVC. However a second higher temperature tanδ maximum between 140 and 160 °C also appears (see particularly the 60/40/3 system in Fig. 8) and the modulus shows two inflections (see particularly the 80/20/3 and 60/40/3 system) suggesting an additional cured DAOP-rich phase is also present. It is not possible to determine how rich this phase is in poly(DAOP) because the reduction in T_g from 200 °C in pure poly(DAOP) to *ca* 150 °C in the blends could be either due to plasticization by unreacted monomer (see Table 2) or due to the effect of the PVC in reducing the T_g.

For the CHP-cured systems, T_gs rise from 83 to 104 °C as the DAOP concentration is increased. Unlike the DCP-cured systems, the tanδ and modulus curves only indicate one transition however since the DAOP conversion in these systems is lower than for the DCP-cured blends (see Table 2), the plasticization by the monomer may cause and overlap of the transitions.

Figs. 7 and 8 also show that the modulus in the rubbery region increases with DAOP level. This may be due to an increase in the crosslink density of the matrix due to the presence of a small amount of poly(DAOP) co-continuous with the PVC matrix. Alternatively, the increase in modulus could be caused by a reinforcement effect of the solid cured DAOP particles on the modulus of the PVC matrix. The data shown in Figs. 7 and 8 indicate that the cured PVC/DAOP blends have a similar or higher thermal-resistance than PVC and illustrate that the strategy of using a reactive plasticizer to improve the processing, followed by its cure, can also sustain or even improve the intractable plastic's thermal properties.

Evidence of phase separation during cure is also confirmed by the change of the appearance of the blend from a transparent state before cure to an opaque state after cure. This phase separation can also be observed by SEM of the cured blends as shown in Fig. 9. The particulate nature of the phase separation in the unetched fracture surfaces is made more obvious when the surface was etched by THF which is a good solvent for PVC but which is unable to dissolve the poly(DAOP) network. In the cured PVC/DAOP/DCP blends with more than 60 wt% PVC (Fig. 9a–f), it appears that poly(DAOP) nanoparticles (*ca.* 100 nm in diameter) are dispersed in a PVC matrix, because the appearance of the particles just becomes more obvious on etching due to the removal of the PVC matrix which covers them. However, in the PVC/DAOP/DCP (20/80/3) blend (Fig. 9g and h), PVC appears to be the dispersed phase because the particles (diameters of *ca.* 1 μm) in the unetched surface are removed by dissolution in the etching process.

The phase morphology revealed in the SEM images of Fig. 9 is in agreement with dissolution studies of the cured PVC/DAOP blends in THF (see Table 3). On one extreme and as expected, neat PVC readily dissolved in THF. In contrast, blends with 70 wt% or more of DAOP were unaffected by THF, which indicates that at high levels of DAOP, poly(DAOP) either forms the matrix phase or is co-continuous with PVC in forming the matrix. For the intermediate blend ratios, blends with 20–60 wt% DAOP disintegrated into very fine particles with diameters of the order of μm (observed by optical microscopy). These particles could actually be composed of PVC and cured DAOP, because we have previously shown [12] that this grafting reaction is quite significant for blends with these compositions. Alternatively a small fraction of the poly(DAOP) network may be co-continuous with the PVC in the matrix and due to the swelling forces of the solvent the network may break into micron-sized particles.

4. Conclusions

The addition of DAOP to PVC was found to significantly improve the processability of the blend by reducing the melt viscosity and as a result the processing temperature can be reduced to such level that the decomposition of PVC during the processing can be effectively avoided.

Rheology studies of the polymerization of neat DAOP showed that gelation occurred at a relatively high conversion of approximately 20% which minimizes the likelihood of premature gelation prior to the finalization of product shaping. Upon polymerization of DAOP in the blends, the T_g rises and approaches that of the original polymer. Based on the higher conversions determined by dynamic DSC studies, the evolution of the modulus during cure and the higher thermal-resistance obtained in the blends, DCP was found to be a better initiator than CHP. In the case of DCP, the thermal-resistance of the cured PVC/poly(DAOP) blends is better than the neat PVC.

The curing of DAOP also induced phase separation of poly(DAOP) from the PVC – at low levels of PVC, the matrix is poly(DAOP), but at higher levels poly(DAOP) nano-particles are embedded into the matrix. On the basis of the present data, it can not be determined whether this matrix is a continuous PVC phase or a PVC-rich phase with a co-continuous poly(DAOP) network.

These studies indicate that the problem of using PVC in long cycle time processes may be readily solved by using a reactive plasticizer which can be subsequently polymerized, thus potentially restoring the original thermoplastic polymer's properties.

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