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Polymer 48 (2007) 7291–7300

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

Wayne D. Cook*, Genhai G. Liang, Mangeng Lu, George P. Simon, Eudora Yeo

Department of Materials Engineering, Monash University, Melbourne, Victoria 3800, Australia

Received 9 July 2007; received in revised form 12 October 2007; accepted 19 October 2007
Available online 23 October 2007

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.

Keywords: DAOP; PVC; Polymerization kinetics

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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* Corresponding author. Tel.: +61 3 99054926; fax: +61 3 99054940.
E-mail address: wayne.cook@eng.monash.edu.au (W.D. Cook).

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doi:10.1016/j.polymer.2007.10.027

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-ethylhexanonate (TBPEH, Interox), cumyl hydroperoxide (CHP, Interox), 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

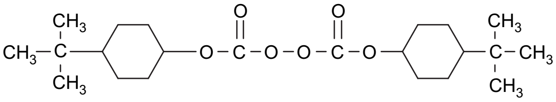
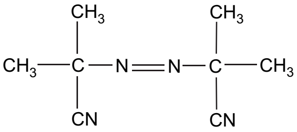
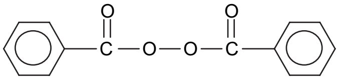
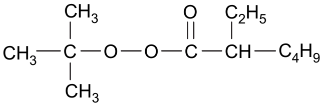
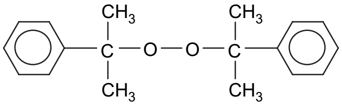
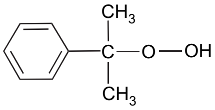
Differential scanning calorimetry (DSC) curing studies were performed on *ca.* 10 mg samples sealed in aluminum pans using a Perkin Elmer DSC7 and nitrogen as the purge gas. Usually heating scans were performed at 10 °C per min, although the curing of DAOP was also performed at 2, 5, 10, and 20 °C per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

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

Table 1
Initiators used

Initiator	Structure	Temp (°C) at 1 h half life
BCHPC		64*
AIBN	 $CH_3-C(CH_3)(CN)-N{=}N-C(CH_3)(CN)-CH_3$	82*
BPO		91*
TBPEH	 $CH_3-C(CH_3)_2-O-O-C({=}O)-CH(C_2H_5)-C_4H_9$	91*
DCP		136*
CHP		166*
AB	$(CH_3)_3CN{=}NC(CH_3)_3$	185[a]

*http://www.akzonobel-polymerchemicals.com/NR/rdonlyres/C2D64A96-B539-4769-A688-2447258D3DCA/0/InitiatorsforHighPolymersAkzoNobel2006.pdf.
[a] Calculated based on Ref. [47].

C=O stretching in DAOP [16], to that at 689 cm^{-1} due to C–Cl stretching in PVC [17]. The absorbance ratio of C=O to C–Cl in uncured blends versus the PVC content, gave a calibration curve over the entire range of composition and this was used to determine the fraction of PVC grafted onto the gel.

The T_g of DAOP monomer was measured with a TA DSC Q100 differential scanning calorimeter at 10 °C per min and was found to be −90 °C (with a heat capacity step of 0.55 J/g K) which compares favourably with T_gs of −85 °C, −82 °C and −72 °C for diethyl phthalate [18], dioctyl phthalate [18], and dibutyl phthalate [19], respectively.

3. Results and discussion

3.1. DAOP and PVC mixtures

As noted in Section 2, blends were formed by either melt or solvent blending with THF. During preparation of the samples by the melt blending method, it was found that DAOP very effectively decreases the processing temperature: for example, a transparent and homogeneous sample with 50 wt% PVC and 50 wt% DAOP was obtained at 100 °C without degradation of PVC. Fig. 1 shows the DMTA curves of uncured PVC/DAOP samples prepared by melt blending, from which it can be seen that the all mixtures exhibited a single glass transition, indicating miscibility at all of the compositions. Fig. 2 compares the variation in T_g with DAOP content with that predicted by the Fox equation [20]:

$$\frac{1}{T_g} = \frac{w_{DAOP}}{T_{g(DAOP)}} + \frac{w_{PVC}}{T_{g(PVC)}} \tag{1}$$

where w_{DAOP}, w_{PVC} are the weight fractions, and $T_{g(DAOP)}$, $T_{g(PVC)}$ are the glass transition temperatures of DAOP and PVC, respectively. Although the agreement between experiment and theory is good, it should be noted that DSC was used to determine the T_g of DAOP, in contrast to the use of DMTA for the other samples and it is known that the DSC T_g is approximately 10–30 °C lower than the T_g measured from the tan δ maximum [21,22]. The melt blended samples consistently have a T_g approximately 5 °C above the solvent-

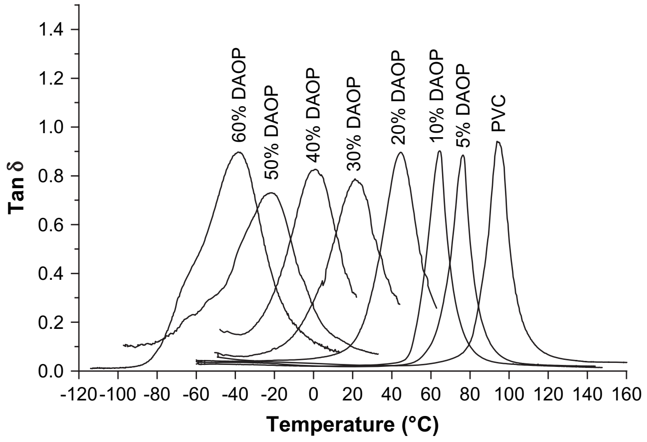


Fig. 1. The tan δ curves showing T_g of PVC/DAOP blends prepared by melt blending.

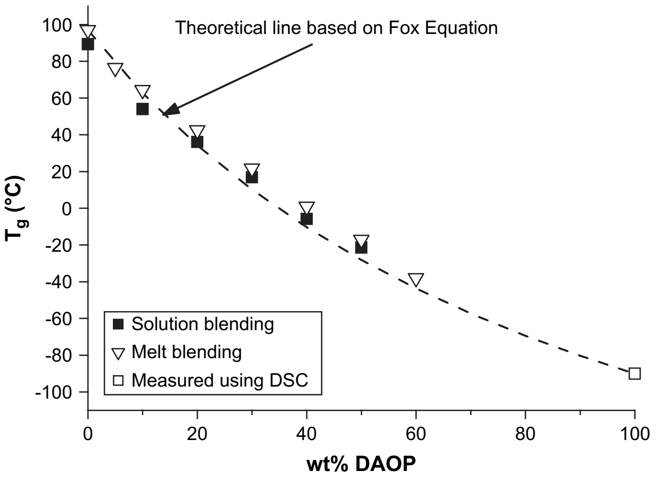


Fig. 2. Theoretical T_g (line) and measured T_g for PVC/DAOP mixtures. Note that the T_g of DAOP was determined by DSC while the others were measured by DMTA.

blended systems and this is probably due to the presence of residual THF trapped in the blend film when it vitrified at the drying temperature.

3.2. Curing of the diallyl monomers

The DSC curves of the curing of the four diallyl monomers with 2 pph of DCP are given in Fig. 3 and all show a single peak with similar peak temperatures exotherm shapes, indicating that the curing kinetics were similar. The heats of polymerization of DAPT, DAOP, DAIP and DEGDC were 516, 600, 566 and 540 J/g, respectively (or 63.5, 73.8, 69.5 and 74.0 J/mol of allylic groups) indicating that the curing energies were roughly the same for all monomers. Similarly, the curing behaviour of these monomers with TBPEH also showed very similar curves for each monomer, except that for this initiator the major curing peak was followed by a second smaller peak. Since there appeared to be little difference between the monomers, it was decided to use DAOP in the following work, as it is the most common of the phthalate monomers and is more similar in structure to common PVC plasticizers.

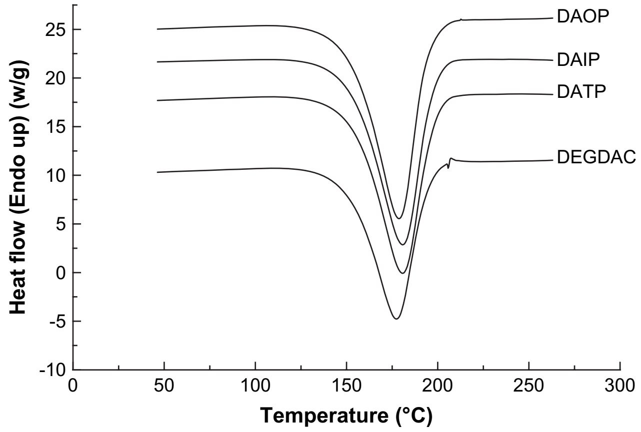


Fig. 3. Diallyl monomers cured with 2 pph of DCP and temperature ramped at 10 °C per min.

A range of initiators with varying half lives were investigated using DSC to determine the most suitable thermal initiator for the polymerization of DAOP monomer during the processing of PVC/monomer blends. As the neat PVC was processed at 180 °C, a reasonably high temperature initiator was required for the blends. It is important that an ideal monomer should not polymerize significantly during the melt blending process stage, since the curing will result in the increase in the molecular weight and possibly gelation, which raises the viscosity and processing torque. The temperature ramping DSC curves are shown in Fig. 4 and the curing parameters obtained from these data are given in Table 2. DAOP was polymerized in either an air or nitrogen atmosphere with AIBN and TBPEH but the curing behaviours were not very sensitive to the presence of oxygen existing in the air. Therefore for simplicity and because the FTIR and processing operations had to be performed in the presence of air, all of the other DSC experiments were also undertaken in the presence of air. A comparison of the onset temperature (Table 2) where polymerization has just commenced with the 1 h half life temperature (see Table 1) shows a reasonable correlation as the data reported elsewhere [23] for the cure of a dimethacrylate with a range of initiators. Such a correlation is expected because the 1 h half life temperature is an indication of how fast the radicals are being formed while the onset temperature indicates the point at which the polymerization by those radicals becomes noticeable. The peak cure temperature also shows a similar dependence on the half life temperature.

Fig. 4 shows that all of the initiators have two curing peaks, except for DCP. One interpretation may be that the first peak is due to the polymerization of the first allyl group in the DAOP to form a linear prepolymer with pendant allyl groups, and the second peak may be caused by polymerization of both the first and second allyl groups [24], however, this does not explain why the DAOP/DCP system has only one peak. Alternatively, for the low temperature initiators, this behaviour may be partly explained by the combination of the effects of premature initiator decomposition and the low propagation rate of allylic

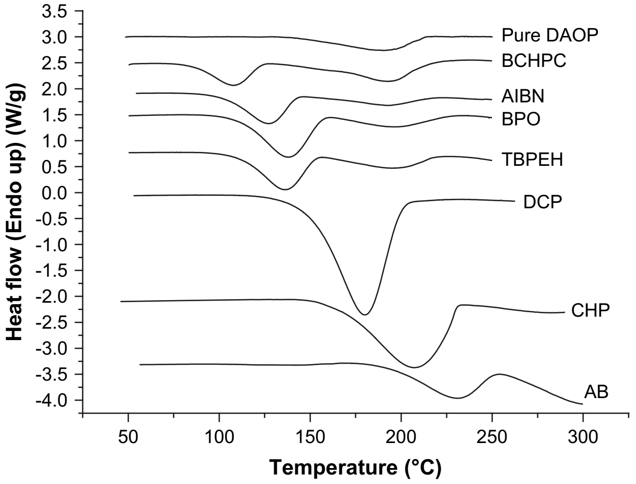


Fig. 4. DSC curing curves of pure DAOP and of DAOP using different initiators at the 1 pph level.

Table 2
DSC results of the polymerization of DAOP using different initiators

Initiator	Initiator concentration (pph)	Onset (°C)[a]	Temperature of first peak (°C)	ΔH (J/g)
None	0	126	188	51
BCHPC	1	83	108	173
	2	85	106	233
	3	85	106	293
AIBN	1	103	127	122
TBPEH	1	113	136	168
	2	109	132	255
	3	108	132	320
	5	110	134	388
	7	109	134	439
BPO	1	103	138	193
	2	111	137	259
	4	110	136	376
	5	111	134	340
DCP	1	151	180	438
	2	153	177	620
	3	152	175	648
	5	152	170	657
	7	152	169	671
CHP	1	168	207	359*
	2	173	194	388*
	5	167	197	495*
AB	1	192	230	*ca.* 100*
	2	197	226	*ca.* 230*

*By integration of the first peak only.

[a] Defined by the intersection of the initial base-line with the tangent to the peak.

monomers. Thus the first peak can be interpreted as being due to partial DAOP polymerization by the rapidly decomposing initiator. At the end of this stage, full cure is not attained because the initiator is depleted prematurely via dead-end polymerization [25,26] or because some of the radicals are converted into peroxy radicals. As the temperature is further raised in the DSC experiment, additional cure may occur as a result of radical formation from peroxy radicals or other unknown processes. This is consistent with the observation of a small peak with a maximum at 188 °C for pure DAOP in air and without added initiator as shown in Fig. 4. In the case of initiation by the higher temperature initiator, CHP, there is evidence of a higher temperature shoulder, while for the DAOP/AB system, the first exotherm with a peak at 230 °C appears to be followed by a second curing peak at even higher temperatures. This may be interpreted as being caused by ''initiator-less'' polymerization at lower temperatures and by CHP or AB-initiated cure at higher temperatures. Alternatively the lower-temperature peak may be due to initiation by CHP or AB and the second peak may be DAOP degradation. In contrast, the polymerization of DAOP using DCP exhibits a single, well defined curing peak (see Fig. 4). It appears that in this case, the rate of decomposition of the initiator is relatively slow compared with the rate of DAOP polymerization, so that the only polymerization process was that initiated by the DCP resulting in a single DSC peak. Furthermore, DCP was the only initiator that produced a nearly fully cured sample at a concentration of 1 pph (see Table 2 and Fig. 4) and it appears that this was due to the compatible rates of initiation and polymerization which meant that ''dead-end'' polymerization was less important for this system and so higher conversion could be attained.

The heat of polymerization of allylic groups has been variously reported to be 78.5 [11], 68.6 [27] and 71 kJ/mol [28] of allyl groups for DAOP, and 72 kJ/mol of allyl groups in DEGDAC [29]. Using a rounded value of 70 kJ/mol of allylic groups gives a theoretical heat of polymerization for DAOP of 570 J/g, however, it is not certain that the reported values were for complete polymerization of the allylic groups and so should be considered as a lower bound. Comparison of the values listed in Table 2 shows that for 1 pph of initiator, all of the systems are under-cured, but that DCP gives the highest level of reaction.

The influence of varying concentrations of initiator on the DSC rate can also be seen in Table 2. As the initiator level is raised, the heat of polymerization is found to rise. This is consistent with the argument that the dead-end polymerization [25,26] was occurring in most of the systems with relatively low initiator levels, because the initiator was exhausted before all of the allylic groups could react. For DCP, the heat of polymerization approached a plateau at 3 pph of initiator and the DAOP/DCP had the highest heat of polymerization with a maximum of 670 J/g which is somewhat higher than the value of 570 J/g predicted from the literature. The effect of initiator level on the onset temperature and peak cure temperature is less clear. The onset temperature does not show a systematic trend with initiator concentration for any of the systems, but this may be due to the lower accuracy in measuring these small changes. Most of the systems show a decrease in the peak temperature with increased initiator concentration, which is consistent with an increase in the polymerization rate. However, for the BCHPC and TBPEH initiated systems which have the lowest conversions, this trend is not clear. This may be partly due to the competition of the effect of initiator concentration on the rate and its effect on the final extent of reaction. If the final conversion is low for small initiator concentrations, then the peak will also occur at low conversions and thus at low temperatures, but when the conversion rises with higher levels of initiator, the conversion at the peak will rise and the temperature at the peak will tend to be higher. Thus this effect may counterbalance the expected decrease in peak temperature with increased initiator concentration for the BCHPC and TBPEH systems.

3.3. Curing of the DAOP/PVC blends

Typical temperature ramping DSC results for PVC/DAOP blends shown in Fig. 5 and listed in Table 3 reveal that the onset (T_{onset}) and peak temperatures (T_{p}) shifted to lower temperatures as PVC contents increased, implying that the polymerization of DAOP was accelerated in the blend. At first sight, this appears to be a surprising result because at higher concentrations of PVC, the concentration of DAOP actually

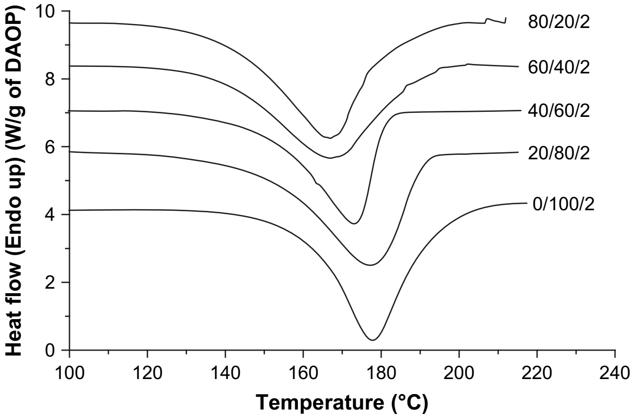


Fig. 5. DSC traces for different PVC levels.

decreases and so the rate of DAOP polymerization would be expected to slow down. Such acceleration might be interpreted as a Trommsdorff effect [13], in which the higher viscosity of the blend containing more PVC content reduces the translational diffusion rate of the polymer radical and the diffusion-controlled radical termination rate, thus accelerating the total reaction rate. However, the concept that the termination rate constant is controlled by the bulk viscosity rather than the micro-viscosity has been shown to be false [30]. The length of the polymer chain formed from diallyl monomers is normally quite short − the degree of polymerization has been determined to be approximately 20 [31] which is far less than that for the PVC (1400 based on the average of M_w). Therefore it appears that the high molecular weight of PVC relative to the growing poly-DAOP radicals would decrease the diffusion rate of the terminating radicals and so would increase the polymerization rate. An even greater acceleration of the polymerization would occur if the growing radical chains were grafted to the higher molecular weight PVC, and as discussed below, this does occur.

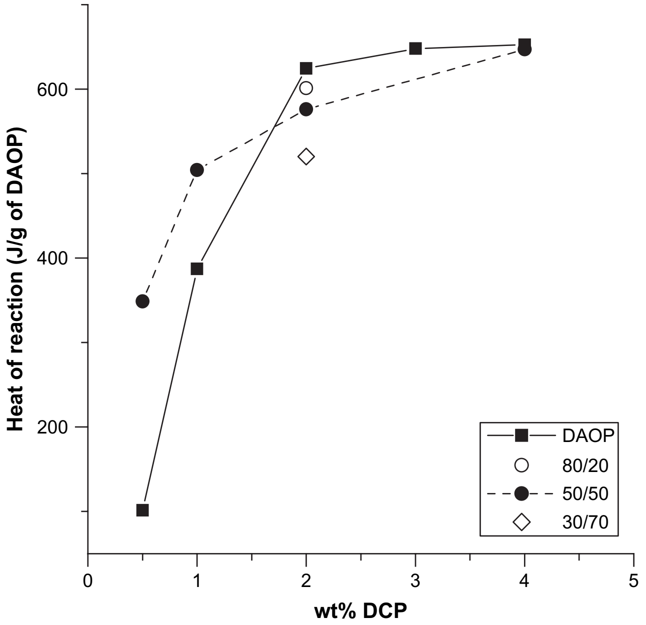


Fig. 6. Heat of the reaction of DAOP in pure DAOP and in various PVC/DAOP blends as a function of the DCP concentration (in pph).

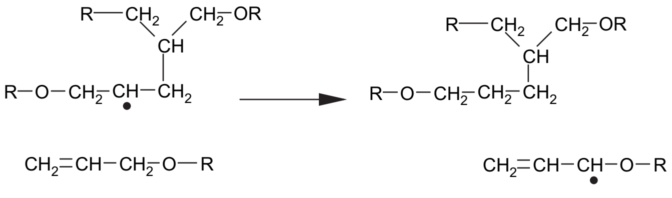
Fig. 6 shows that the heat of reaction rapidly rises to a plateau as the concentration of DCP approaches 2 pph in either neat DAOP or the 50 wt%PVC/50 wt%DAOP blend. A similar trend has been found for pure DAIP [32]. The incomplete polymerization of DAOP at lower initiator levels can be explained by premature loss of initiator as discussed above or by degradative chain transfer [33] (see Scheme 1) in which an allylic radical abstracts an α hydrogen, thus forming a resonance stabilized and unreactive radical. Therefore, for the remainder of this work 2 pph of DCP was used.

Table 3
Onset and peak temperatures (from the DSC scan at 10 °C per min) and heat of reaction (averaged from the DSC scans at 2−20 °C per min) from temperature ramping DSC scans

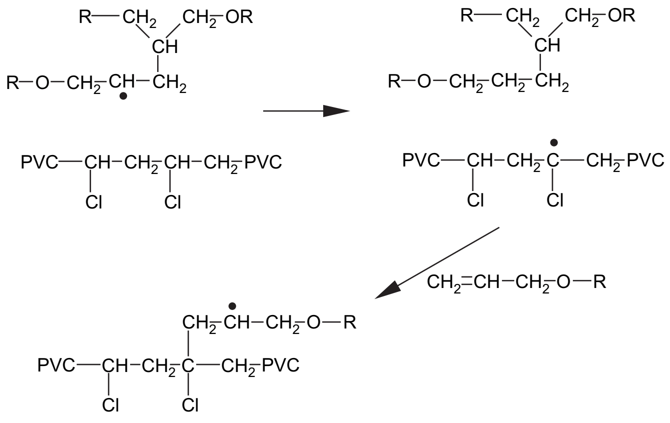
Sample code	T_{onset}, °C	T_p, °C	Heat of reaction, J/g of DAOP
DAOP	154	179	624
10/90/2	152	176	608
20/80/2	147	172	601
30/70/2	150	174	579
40/60/2	146	173	608
50/50/2	146	172	576
60/0/42	138	167	517
70/30/2	145	169	520
80/20/2	141	167	551
90/10/2	135	157	659

The heat of DAOP polymerization in PVC given in Table 3 appears to decrease with increasing PVC content. In the present system, radicals may abstract a tertiary hydrogen from the PVC, possibly producing a radical with low reactivity but as discussed below this is inconsistent with the occurrence of PVC−poly(DAOP) grafting. Another possible reason is that because the average monomer concentration in the matrix is lowered, it is more difficult to link the monomer units together into a poly-DAOP structure.

Previous studies of PVC−allyl plastisols have shown that the chain transfer to PVC can occur during radiolysis [7] or radical curing [34] of the system and this is probably due to abstraction of the tertiary PVC hydrogen [35] as shown in Scheme 2. To determine how extensive this was in the present systems, cured DAOP−PVC system samples (using 2 pph of DCP as initiator) were subjected to Soxhlet extraction and the dried residual material was analysed gravimetrically and by FTIR to determine the gel content and the PVC content in the gel. Fig. 7 shows that the wt% gel in the cured blend increases as the concentration of PVC is reduced. This is expected because it is the DAOP which forms the three



Scheme 1. Degradative chain transfer.



Scheme 2. Abstraction of the tertiary PVC hydrogen by the propagating DAOP radical producing a larger chain radical.

dimensional network. However, if the data are plotted as the mass of gel divided by the mass of DAOP in the blend it is seen that the data do not appear to extrapolate to 0 wt% gel for pure PVC, suggesting that PVC is grafted to the DAOP network. This was confirmed by the appearance of a 689 cm^{-1} peak in the gel, which can be attributed to the C−Cl stretching in PVC [17], thus supporting the grafting of the DAOP to the PVC via abstraction of the tertiary PVC hydrogen (see Scheme 2). Fig. 7 also shows the dependence of the wt% PVC in the gel on the wt% PVC in the blend. The fraction of PVC in the gel appears to pass through a maximum. This can be explained by two contrary effects − at low concentrations of PVC in the blend there is low probability of PVC being incorporated in the gel, while at high PVC concentrations the fraction of PVC in the gel decreases because there are fewer DAOP molecules linking the PVC chains to the gel [36].

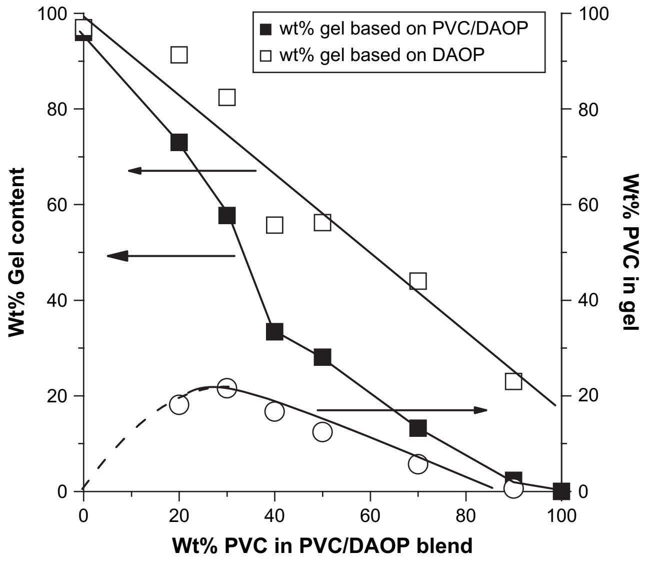


Fig. 7. Gel analysis of the cured PVC/DAOP blend as a function of the PVC content: wt% gel content expressed as a percentage of the total mass of the blend (■), or as a percentage of the mass of DAOP in the blend (□), and wt% PVC in the gel (○).

Table 4
Kinetic parameters calculated according to ASTM E 698-79

Sample	A, min^{-1}	E_a, kJ/mol
DAOP	5.77×10^{15}	137
10/90/2	1.96×10^{15}	131
20/80/2	8.63×10^{14}	125
30/70/2	2.71×10^{14}	124
40/60/2	3.69×10^{14}	124
50/50/2	3.12×10^{14}	124
60/40/2	1.58×10^{14}	122
70/30/2	0.80×10^{14}	120
80/20/2	1.81×10^{14}	122
90/10/2	1.32×10^{14}	117

3.4. Curing kinetics

3.4.1. Temperature ramping DSC curing

DSC studies of the cure of the blends were undertaken at several temperature ramping rates and the heats of reaction were found to be approximately independent of ramping rate, implying that the same structure was formed. The peak temperatures were analysed using the ASTM E 698-79 method by plotting the logarithm of scanning rate (ln β) versus the reciprocal of the absolute peak cure temperature ($1/T_p$). The obtained activation energies (E_a) are listed in Table 4 and the value for neat DAOP is 137 kJ/mol which is comparable to the results of 147, and 150 kJ/mol reported by Immelman [27] and Willard [28], respectively. Table 4 also shows that as the concentration of PVC rises, the activation energy decreases, which is consistent with the increase in cure rate as illustrated by Fig. 5. There are a number of factors affecting the overall activation energy − including initiation, propagation, chain transfer and termination − and so it is difficult to explain this trend in activation energy. If chain transfer is neglected, the overall activation energy (E_a) for free-radical polymerization is given by [37]:

$$E_a = E_{s(\text{propn})} + E_{a(\text{initn})}/2 - E_{a(\text{termn})}/2 \qquad (2)$$

where $E_{a(\text{propn})}$, $E_{a(\text{initn})}$, and $E_{a(\text{termn})}$ are the activation energies of propagation, initiation and termination, respectively. Since it is unlikely that either $E_{a(\text{propn})}$ or $E_{a(\text{initn})}$ would decrease with higher concentrations of PVC, perhaps $E_{a(\text{termn})}$ increases as the PVC content is raised because it becomes more difficult for the radicals to diffuse through the blend.

The average value of the pre-exponential factor or collisional frequency (A) was also determined from the variation in peak exotherm with DSC temperature ramping rate, calculated using the expression [ASTME 698-79]:

$$A = \frac{\beta E_a}{R T_p^2} \exp\left(\frac{E_a}{R T_p}\right) \qquad (3)$$

where T_p is the peak temperature at the scanning rate (β), E_a is the overall activation energy and R is the gas constant. Interestingly the pre-exponential factor also systematically decreases with increasing PVC content, which would normally suggest that the reaction rate was becoming slower. According to simple collision theory for solution reactions [38] this

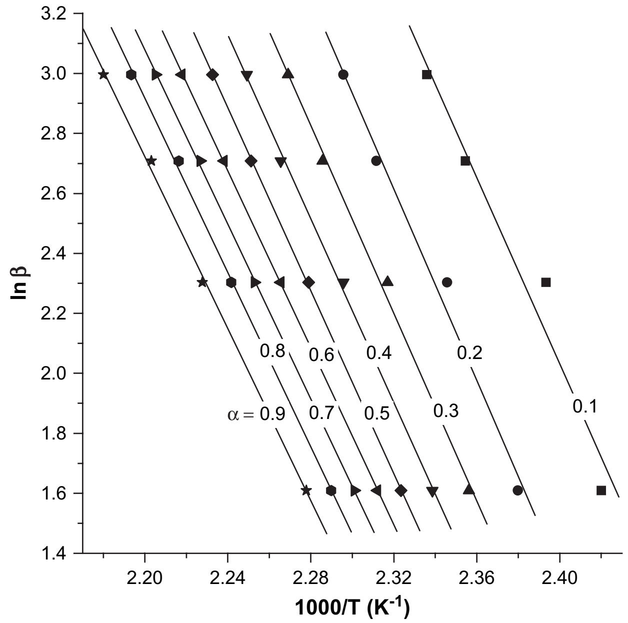


Fig. 8. Isoconversional plots from different heating rates for the sample 50/50/2.

implies that the interactions between the components are less favourable than between like molecules, so that the duration of the state of encounter between the reacting species is reduced – this appears reasonable since interactions between dissimilar compounds are usually less favourable than between themselves [39]. The result of the competition between the decrease in activation energy and pre-exponential factor with increased PVC content is that the activation energy dominates: for a reaction at 100 °C, the change in activation energy from 137 kJ/mol to 117 kJ/mol causes a rate increase of 560 but the change in the pre-exponential factor is only 44 (from 5.77×10^{15} to 1.32×10^{14} min^{-1}) so that overall addition of PVC raises the rate as discussed above.

As a comparison, the isoconversional activation energies were determined from the temperature ramping DSC data at a range of scanning rates. The basic assumption of isoconversional analysis is that the dependence of rate on conversion has the same functional form regardless of the temperature and that the reaction rate at a constant conversion depends only on the temperature. Therefore, for each scanning rate, the temperature at which the polymerization had resulted in a predetermined conversion (e.g. 10, 20, … , 90%, calculated using the ratio of the partial reaction heat to total reaction heat for that DSC scan) was measured and plots of the logarithm of scanning rate ($\ln \beta$) versus the reciprocal of the absolute temperature ($1/T$) at a constant extent of cure [40,41] was used to produce the data in Fig. 8. The activation energy E_α at a given conversion can be calculated from these curves using the method of Friedman [40], Ozawa [42], Flynn [43], and Doyle [44], i.e., by plotting $\ln \beta_i$ vs $T_{\alpha,i}^{-1}$ (here $T_{\alpha,i}$ is the temperature at which a certain conversion α_i is attained at heating rate β_i and i is ordinal number of the DSC run). In agreement with the data obtained from the peak curing temperature (Table 4), the activation energy listed in Table 5 decreases as the PVC level is raised but the dependence on conversion is less well defined and appears to show an increase with higher conversions at low PVC levels but a decrease with higher conversions at high PVC levels.

3.4.2. Isothermal curing

The isothermal curing reaction of the blend 40/60/2 at 130 °C for various times characterized using NIR is shown in Fig. 9 and the change in conversion with time for a specific temperature is given in Fig. 10. It is clear that reaction at low temperatures does not lead to full cure and this is most likely caused by the vitrification of the matrix [45] due to the increased crosslink density which raises T_g. This suggestion is confirmed in Fig. 10 for the 50/50/2 blend which had ceased curing after 900 min at 110 °C but which recommenced reaction with an increase in the cure temperature to 140 °C due to an increase in the mobility of the matrix.

The effect of PVC content on curing behaviour is given in Fig. 11. As can be seen, the blends with higher PVC contents have a higher curing rate in the early stages of reaction, indicating that the curing of DAOP was accelerated by PVC, which is consistent with the DSC results shown in Fig. 5 and Table 3. However, these blends have lower final conversions. It is not likely that this is due to vitrification caused by the higher levels of PVC because the T_g of PVC (*ca.* 95 °C) is much less than the curing temperature. It is more probable that at higher levels of PVC, the pendant allyl groups

Table 5
Activation energies calculated from the isoconversional analysis, using the Friedman method [40]

Fractional conversion	Activation energy, kJ/mol									
	DAOP	10/90/2	20/80/2	30/70/2	40/60/2	50/50/2	60/40/2	70/30/2	80/20/2	90/10/2
0.1	132	133	121	127	120	129	127	126	126	108
0.2	133	136	123	128	121	133	125	127	120	108
0.3	136	137	126	126	123	130	122	125	118	109
0.4	141	139	131	128	122	127	118	123	120	108
0.5	140	141	129	126	124	127	116	122	118	107
0.6	143	140	133	126	125	123	116	121	115	108
0.7	142	140	134	124	127	121	114	121	115	105
0.8	139	141	136	125	131	121	115	120	104	101
0.9	140	143	133	125	138	119	115	122	92	97
Average	138	139	129	126	126	125	120	123	101	106

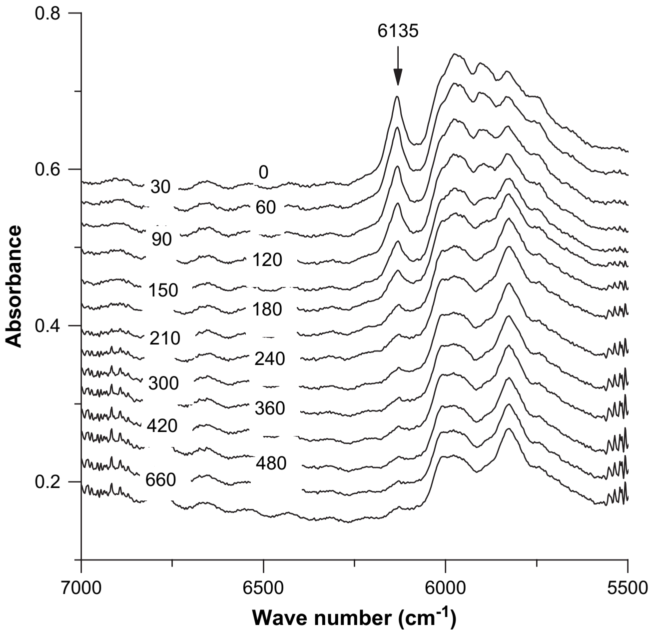


Fig. 9. The near FTIR spectra of sample 40/60/2 at 130 °C at different times (min) as indicated.

tend to be spatially isolated and cannot react with one another, thus causing the lower conversion, which is consistent with the temperature ramping DSC data (see Table 3).

According to the simplest analysis of radical polymerization, the rate of cure is given by [13]:

$$\frac{\mathrm{d}(\alpha)}{\mathrm{d}t} = k_\mathrm{p}(k_\mathrm{d} f[I]/k_\mathrm{t})^{1/2}(1-\alpha) \tag{4}$$

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 are rate constants of chain propagation and chain termination, respectively. On the assumption that these "constants" are invariant with the conversion, integration of Eq. (4), gives:

$$-\ln(1-\alpha) = k't \tag{5}$$

where k' is the lumped rate constant. As implied by the near-linear behaviour shown in Fig. 11, the kinetics approximated to first-order behaviour until relatively high conversions (30–50%, depending on PVC content and reaction temperature). Similar results have also been reported for pure DAOP [28] and DAOP/epoxy IPN systems [46]. Table 6 lists the rate constant k' at 140 °C and suggests that the presence of PVC in the blend accelerates the curing reaction of the DAOP in an agreement with the data given in Tables 4 and 5. In addition, the final allyl conversion obtained after curing at 140 °C decreases as the PVC concentration in the blend is raised as discussed above.

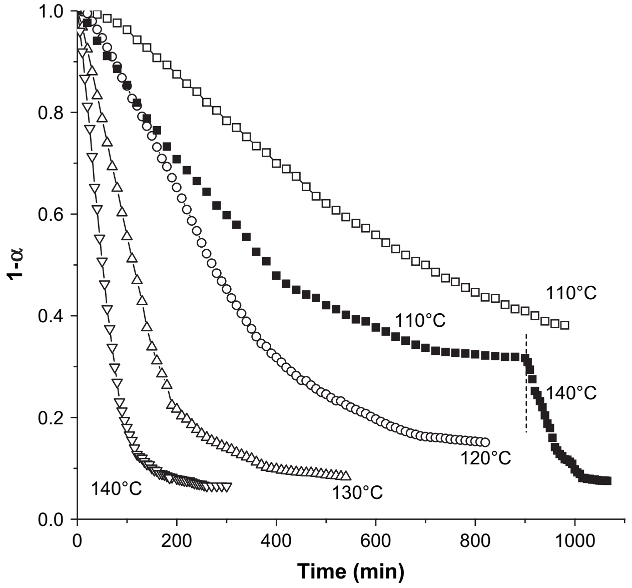


Fig. 10. Monomer fraction $(1-\alpha)$ versus time for the blend 40/60/2 at different temperatures (open symbols), and for the blend 50/50/2 at 110 °C for 900 min followed by the post-cured at 140 °C (closed squares).

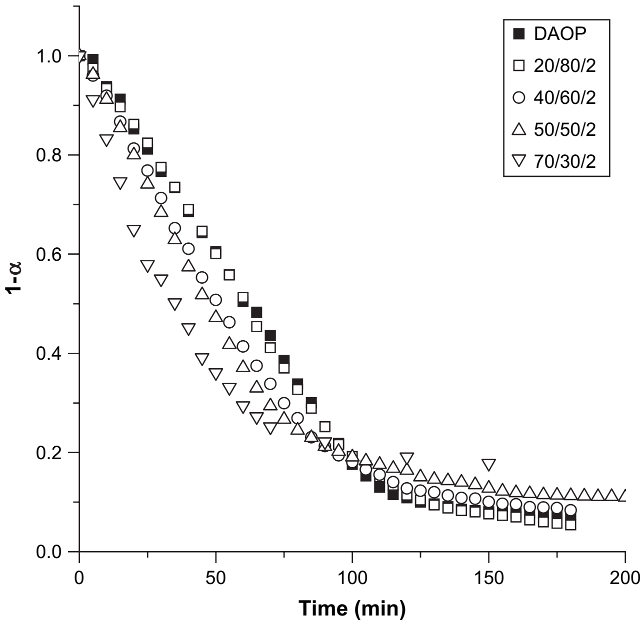


Fig. 11. DAOP conversion with time in the PVC blends at 140 °C.

Table 6
Kinetic parameters obtained from NIR studies of the cure of PVC/DAOP blends

Sample	$\alpha_{\max}$ at 140 °C	$k' \times 10^4$ (s^{-1}) at 140 °C
DAOP	0.93	1.88
10/90/2	0.96	1.92
20/80/2	0.94	2.08
30/70/2	0.91	2.83
40/60/2	0.92	3.32
50/50/2	0.89	3.63
70/30/2	0.82	4.13

4. Conclusions

The temperature ramping DSC cure of four diallyl monomers were studied and was found to be very similar. DSC cure studies of DAOP with a range of initiator systems revealed either single or double exotherms, depending on the initiators' activity. For all initiators, the heat of reaction decreased with lower initiator concentration apparently due to premature loss of initiator (similar to dead-end polymerization) but for DCP at high concentrations, the heat of polymerization approached a plateau of ca. 660 J/g (81 kJ/mol of allyl groups).

Blends of DAOP and PVC were completely miscible and the dependence of T_g on composition was in approximate agreement with the Fox equation. From temperature ramping DSC, the polymerization of DAOP in various PVC/DAOP blends was found to be accelerated by the PVC and appeared to result from a gel effect caused by the grafting of the poly-DAOP to the PVC which slowed down the termination rate. Analysis of the DSC data suggested that this rate acceleration was caused by a decrease in the overall activation energy which dominated over the conflicting decrease in the pre-exponential factor with increased PVC levels. This behaviour may be due to an increase in the activation energy for termination resulting from the increased difficulty for the polymer radicals to diffuse in the PVC/DAOP medium. The final conversion of allyl groups decreased with higher PVC levels, due to topological effects.

Isothermal curing studies using NIR indicated that the early stages of the reaction were pseudo first order. The cure kinetics was accelerated by the presence of PVC in agreement with the DSC data. The final allylic conversion decreased with higher PVC levels in agreement with the DSC data.

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