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Diallyl orthophthalate as a reactive plasticizer for improving PVC processibility, Part II: Rheology during cure

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ABSTRACT

Rheological investigations of blends of PVC (polyvinyl chloride) and DAOP (diallyl orthophthalate) with and without free radical initiators have been conducted under steady and dynamic shearing modes. The results showed that the added DAOP acted as a reactive plasticizer for improving PVC processing, thus greatly decreasing the risk of the decomposition of PVC. The viscosity of the uncured blends was also significantly reduced and obeyed the log-additivity rule with the weight percentage of DAOP. Dynamic rheology of some of the uncured blends indicated the physical gel-like behaviour due to the presence of small crystallites acting as physical crosslinks. Blends with low levels of PVC obeyed the Winter–Chambon gelation criteria and the viscosity diverged at the gel point during the DAOP polymerization, but when the PVC level exceeded 20 wt% the tan δ did not exhibit a frequency independence and the viscosity remained finite up to the end of the reaction. This unusual behaviour is consistent with heterogeneous gelation due to either phase separation between DAOP and PVC components or the non-fractal nature of the gel structure.

1. Introduction

The processing of some intractable thermoplastics such as polyvinyl chloride (PVC) poses a dilemma: the polymer is too viscous to be processed at lower temperatures but too easily degraded at raised processing temperature [1,2]. Traditional methods for lowering the melt viscosity and/or the processing temperature include reducing their molecular weight, adding inert plasticizers such as dioctyl phthalate (DOP), and blending with more processable polymers [2–5] but these usually result in the impairment of the polymer's thermal-mechanical properties including lower strength and heat distortion temperature. Recently, it has been discovered that small amounts of cross-linkable monomer can be used as a reactive plasticizer [6–13]. After processing, this monomer can be polymerized, and this usually results in an entropically-driven phase separation of the components with the crosslinked component (a thermoset or elastomer) being a dispersed or co-continuous phase [6–12,14]. Using this strategy, thermoplastic processing can be more readily completed with reduced energy consumption and lower processing temperature, while the mechanical properties and high-temperature resistance of the original thermoplastic component can be retained.

The ultimate limit to the processability of a thermoset–thermoplastic blend is when the material can no longer flow, that is at the gel point, and so studies of the chemorheology and gelation are important to the application of this technology. Chemical gelation is the stage at which a branching process leads to the formation of an interconnected and infinite network. Since the gel point is located at the boundary line between the liquid state and the solid state, the steady shear viscosity approaches infinity and the equilibrium modulus becomes non-zero in the vicinity of the transition [15]. Dynamic rheology can also be employed to determine the gel point and it has an advantage of continuously monitoring the evolution of the structure from the liquid state, through the gel point, to the solid state. Early researchers [16] suggested that the gel point is located at the crossover point of G' and G'', or when tan δ is unity, however, this point is dependent on the measuring frequency and only a very limited number of systems undergoing gelation obey this criterion. Based on concepts of the self-similarity of the gel state, Winter and Chambon [15,17,18], proposed an universal rheological equation to identify the gel point in terms of the stress, $\tau(t)$ at a particular deformation time (t), in a critical gel when it is deformed at a rate $\dot{\gamma}$:

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$$\tau(t) = S\int_{-\infty}^{t}(t-t')^{-n}\dot{\gamma}(t')\mathrm{d}t' \quad 0<n<1 \tag{1}$$

where the stiffness of gel (S) and the relaxation exponent (n) are characteristic properties of the critical gel. Eq. (1) can be rewritten into Eq. (2) and Eq. (3) in terms of the dependence of the storage modulus G' and loss modulus G'' at the gel point:

$$G'(\omega) = S\Gamma(1-n)\cos\left(\frac{n\pi}{2}\right)\omega^n \tag{2}$$

$$G''(\omega) = S\Gamma(1-n)\sin\left(\frac{n\pi}{2}\right)\omega^n \tag{3}$$

where ω is the angular frequency, and Γ is the gamma function. Thus the tan δ can be expressed as:

$$\tan\delta(\omega) = \frac{G''(\omega)}{G'(\omega)} = \tan\left(\frac{n\pi}{2}\right) \tag{4}$$

From Eq. (4) it can be seen that tan δ is independent of frequency (ω) at the gel point, i.e., the gel point is located at the crossover point of curves of tan δ versus time at various frequencies, and the gel's relaxation exponent value, n, can be calculated from the tan δ value at the gel point – only when the relaxation exponent n is 0.5, then tan δ is unity. Typically, the relaxation exponent value ranges from 0.5 to 1 [17,19,20] for chemical gels, which lies within the range 0.33–1.0 predicted from various gelation theories [21]. Physical gels such as hydrogen-bonded proteins, polysaccharides, block copolymer solutions and crystallizing polymer solutions [22,23] have also found to obey the scaling behaviour of Eqs. (2)–(4). In these physical gels, the relaxation exponent can be of similar value as chemically crosslinked gels, for example 0.69 for 10 wt% gelatin in water [24], 0.79 for 2 wt% solution of Tamarind seed's polysaccharide [25], 0.8 in crystallizing PVC–DOP plastisols [26], but the relaxation exponent has been occasionally observed to be less than 0.5 such as a value of 0.3 for styrene–ethylene–butylene–styrene block copolymer [27], and 0.13 in the crystallization-induced gelation of elastomeric polypropylene [28] so that in these cases G'' is less than G' at the gel pint.

In the past, step-growth polymerized epoxy resin has been primarily used as a reactive plasticizer for processing intractable thermoplastics [6–12]. In this paper, we use chain growth polymerized diallyl orthophthalate (DAOP) as a reactive plasticizer for improving PVC processing. DAOP was chosen due to its free radically curable allylic functional groups, its low reactivity at the elevated temperatures required for processing of the blend [29], the high gel point conversion of this monomer [30,31] (which extends the processibility of the blend), and its similarity in chemical structure to a traditional plasticizer, DOP, which should make DAOP miscible with PVC. The polymerization mechanism of DAOP in the presence of PVC has been previously investigated [29]. In this paper, the rheological properties of the PVC plasticized by DAOP and in the absence or presence of initiator are further investigated to explore processability of PVC/DAOP blends and to investigate the applicability of the Winter–Chambon criteria [15,17] for gelation in thermoset–thermoplastic blends.

2. Experimental

2.1. Materials

The poly(vinyl chloride) 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 initiator, dicumyl peroxide (DCP), and the tetrahydrofuran (THF), were supplied by the Sigma–Aldrich. All materials were used without further treatment, and their chemical structures are listed in Table 1.

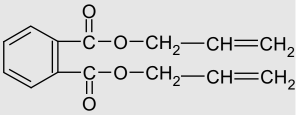
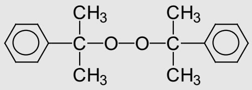
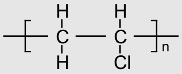
2.2. Sample preparation

The stabilized PVC powders were manually pre-mixed with DAOP on a particular weight to weight (w/w) basis. In some studies, no initiator was present in the DAOP and these PVC/DAOP blend samples were used to determine the steady shear and dynamic viscosities of the uncured blends. The plasticized PVC was loaded to the hopper of a MiniLab micro-extruder (Haake, Thermo Electron, Germany) and was 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 of the die ranged from 220 °C for neat PVC, down to 180 °C for PVC/DAOP (80/20, w/w), 160 °C for PVC/DAOP (60/40, w/w), and 140 °C for PVC/DAOP (40/60, 20/80, w/w) blends. The blend extrudate was rapidly transferred into a micro-injection moulding machine (DSM Research, The Netherlands), pre-set to the same operating temperature as the extruder, and was injected into a rectangular (2 mm × 5–10 mm × 80 mm) steel mould set at room temperature. All injection-moulded specimens were transparent. The unplasticized PVC injection moulded specimen had a brown colour, suggesting the decomposition of PVC, however the PVC/DAOP (80/20, w/w) specimen was only slightly yellowish, while the specimens of PVC/DAOP (60/40, 40/60, and 20/80, w/w) were almost perfectly colourless and transparent, suggesting these blends had undergone no obvious decomposition.

For the chemorheology studies where the curing of the blends was intended, the DAOP contained 3 wt% DCP based on the DAOP mass. To avoid partial polymerization of the DAOP in the PVC/DAOP/DCP blends which might affect the reliability of the data, DAOP and DCP were mixed with a concentrated solution of PVC (with stabilizers) in THF before evaporation of the THF from the 1–2 mm thick PVC/DAOP film under vacuum for 2 days at room temperature at which time the specimen weight showed no noticeable change. A disc was cut from the film and was transferred to the rheometer where it was compressed (sometimes at slightly elevated temperature) to the standard 0.5 mm thickness.

The blends are described by the notation: wt% PVC/wt% DAOP/wt% DCP where the wt% DCP refers to the amount of DCP added to the DAOP – this coding differs from that used in an earlier paper

Table 1
Materials used.

Material code	Name	Structure
DAOP	Diallyl phthalate	
DCP	Dicumyl peroxide	
PVC	Polyvinyl chloride	 $-\!\!\left[\mathrm{CH_2}-\mathrm{CHCl}\right]_n\!\!-$

[29] where the initiator concentration was expressed in parts per hundred of the PVC/DAOP blend. Thus, in the current paper, the code of 80/20/3 identifies the sample containing 80 wt% PVC, 20 wt% DAOP and with 3 wt% of DCP added to DAOP, so that the blend contained a total of 0.60 wt% initiator.

2.3. *Instruments*

The steady shear rheological properties of DAOP and the blends were measured using a stress-controlled Physica MCR 501 rheometer (Anton Paar, Germany) in parallel plate mode. The shear rates were 0.004–7 s^{-1} for uncured blends and 0.01 s^{-1} for curing samples by means of the rapid stress-feedback loop of the instrument. Samples of the blend 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. The chosen plate diameter ranged from 15 mm for PVC/DAOP blends with 80–100 wt% PVC, to 25 mm for 60 wt% PVC blend, 40 mm for the 40% PVC blend, and 50 mm for the 0 and 20 wt% PVC systems. For dynamic oscillation shear mode with uncured blends, the average strain was set at between 2.5% (15 mm plate) and 7.5% (50 mm plate), and for steady shear experiments the shear rate was 0.1 s^{-1}.

The dynamic rheology of curing systems was measured at various temperatures under dynamic oscillation mode with frequency ranging from 0.1 to 10 Hz using an ARES strain-controlled rheometer (Rheometric Scientific, USA) with a pair of parallel circular plates (8 mm diameter) with 0.5 mm gap. To maximize the dynamic range of the torque measurement, the applied strains were changed depending on the storage modulus value, ranging from 100% for $G' < 10^2$ Pa, to 0.1% for $G' > 10^7$ Pa.

3. Results and discussion

As mentioned above, the presence of DAOP in the PVC/DAOP blends significantly decreased the processing temperature and torque required and thus increased the processing window compared with neat PVC. In addition, the low colouration of the blends suggest that thermal decomposition of the PVC was greatly reduced or eliminated.

The dynamic rheology data in Figs. 1 and 2 show that the neat PVC was extremely viscous (with a viscosity of *ca.* 1 MPa s) and exhibited solid-like behaviour [32] even at 220 °C, because $G' >> G''$ and G' was frequency-independent. Using the complex viscosity of PVC measured at 220 °C and the literature activation energy for flow (102 kJ/mol or 24.4 kcal/mol [1]), a predicted viscosity of 7×10^6 Pa s at 0.1 rad^{-1} at 180 °C was determined and this is well beyond the capabilities of ordinary extruders. However, the addition of DAOP significantly altered the rheological behaviour at 180 °C, so that all of the blends showed liquid-like characteristics as indicated by $G' \leq G''$ and a frequency dependency of both G' and G''. The complex viscosity (see Fig. 2) calculated from the storage and loss moduli at various frequencies shows a considerable reduction with the addition of DAOP in the blends, and as depicted in Fig. 3 it can be expressed using the log-additivity rule derivable from free volume considerations [33]:

$$\log \eta = w_{PVC} \log \eta_{PVC} + w_{DAOP} \log \eta_{DAOP} \tag{5}$$

where η, $\eta_{PVC,}$ and η_{DAOP} are the viscosities (Pa s) of the blend, the PVC, and the DAOP, respectively, and w_{PVC} and w_{DAOP} are the weight fractions of PVC and DAOP respectively in the blend. Thus an increase of *ca.* 20% DAOP in the blend reduced the viscosity by a more than a decade. The Fig. 3 also includes the steady shear viscosity of the blends. The reasonable agreement of the steady shear viscosity ($\eta(\dot{\gamma})$) and dynamic complex viscosity (η^*) suggests that the Cox–Merz [34] relationship is applicable for these simple blends:

$$\eta\left(\dot{\gamma}\right) = \left|\eta^*(\omega)\right|_{\omega=\dot{\gamma}} \tag{6}$$

where $\dot{\gamma}$ is the shear rate and ω is the angular frequency, holds for these simple blends.

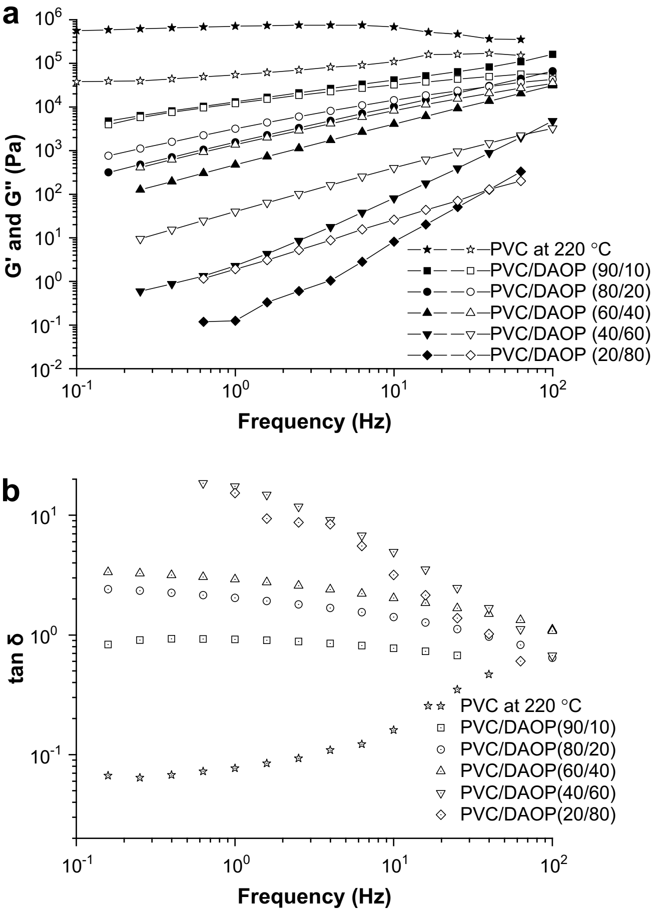


Fig. 1. Storage moduli (filled symbols) and loss moduli (unfilled symbols) in (a), as well as tan δ (unfilled symbols) in (b) of various PVC/DAOP blends without initiator at 180 °C along with the corresponding data of neat PVC at 220 °C.

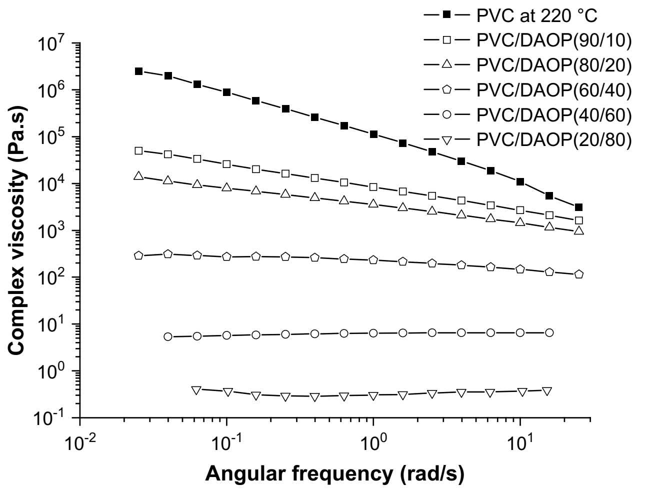


Fig. 2. Complex viscosities as a function of angular frequencies of various PVC/DAOP blends at 180 °C compared with the complex viscosity for neat PVC at 220 °C.

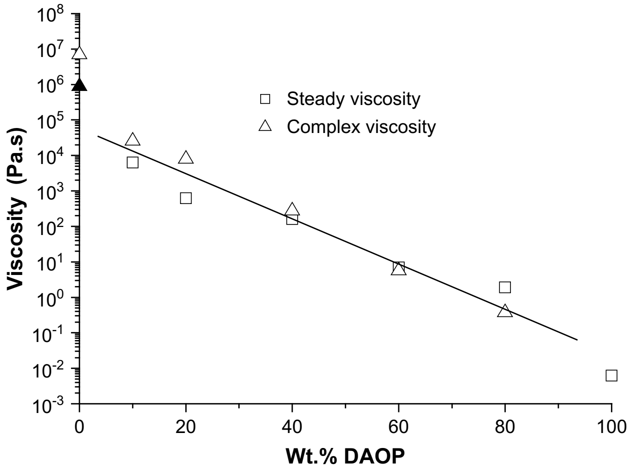


Fig. 3. Complex viscosities at 0.1 rad^{-1} of neat PVC at 220 °C (▲) and of various PVC/DAOP blends at 180 °C (△). The value of PVC at 180 °C was calculated using the Arrhenius equation. The steady shear viscosities at 0.1 s^{-1} (□) at 180 °C are also included.

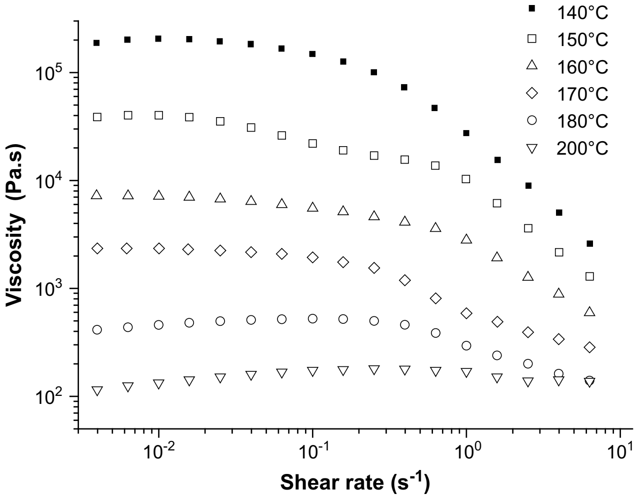


Fig. 4. Steady shear viscosities of identical PVC/DAOP (60/40) blends at various temperatures as a function of shear rate.

Figs. 1 and 2 also show that at 180 °C, only uncured blends with 40 wt% PVC or less showed typical liquid-like dynamic rheology behaviour including a non-identical frequency power law dependency of G' and G'' and a reduction in tan δ with frequency (see Fig. 1 (b)). The unplasticized PVC (at 220 °C) exhibited solid-like behaviour (see Fig. 1) and at 180 °C, several of the uncured PVC/DAOP blends (90/10, 80/20 and 60/40) showed characteristics of the gel state, having near-identical power law dependencies of G' and G'' on frequency and a tan δ which was virtually independent of frequency. This gel state is considered to result from the formation of PVC crystals from the melt which act as pseudocrosslinks and are interconnected by tie molecules [26,35–39]. Although there have been numerous rheological studies of physical gelation of PVC solutions, these appear to be either at low PVC concentrations [26,37,38,40,41] or at much lower temperatures than those used here [26,37,40]. The research which is closest to the conditions in the present work showed gelation behaviour for PVC in phthalate plasticizers at concentrations of *ca.* 37 wt% (444 g/L) and *ca.* 57 wt% (714 g/L) at 162 °C and 181 °C, respectively [40] or for PVC contents of 45.5 and 70.4 wt% at 190 and 210 °C, respectively [39]. These results appear to be consistent with the present work at 180 °C where the PVC/DAOP system with 40 wt% PVC did not show gel-like behaviour, but at a concentration of 60, 80 and 90 wt% PVC, the system was quite gel-like as indicated by the frequency independence of tan δ. Table 2 shows the relaxation exponent obtained for the near-critical gels. The systems with 60 and 80 wt% PVC have indexes which are close to the typical value of 0.75 observed by several workers [26,37–39], however the system with 90 wt% PVC has a lower index.

Fig. 4 shows the shear rate dependence of steady shear viscosity for the PVC/DAOP (60/40) blend at different temperatures. In most cases, the material exhibits Newtonian behaviour at low shear rates where the shearing is slow enough to not disturb the coil structure [32,42]. However at higher shear rates, pseudoplastic behaviour (shear rate thinning) is observed because the shearing process orients the polymer chains and decreases the chain overlap time thus reducing the chain entanglement density [42]. The viscosity of the 60/40 blend is also very temperature dependent – its viscosity at 140 °C was very close to that of PVC/DAOP (90/10) at 180 °C, and so the processing temperature can be decreased by 40 °C by adding extra 30% DAOP. At such low processing temperatures the PVC was relatively free from rapid decomposition.

Table 2
The relaxation exponents of various uncured PVC/DAOP blends at 180 °C.

PVC/DAOP	90/10	80/20	60/40
n	0.47	0.74	0.81

The most commonly used expressions for the temperature dependence of the viscosity of a polymer melt are the WLF [43] and the Arrhenius [44] equations. The former is based on the change in the free volume with temperature and is usually applied from T_g to $T_g + 100$ °C. It was also found that this viscosity data did not fit the WLF equation well, which is expected because the T_g for the PVC/DAOP (60/40) blend was *ca.* 0 °C [6] thus the temperatures used were all above $T_g + 100$ °C. The Arrhenius equation [44] is commonly used above $T_g + 100$ °C, where the energy required for a segment to jump into an unoccupied space is more important than the probability of locating an unoccupied hole [44]. This equation can be expressed as [44]:

$$\eta = Ae^{\frac{E_a}{RT}} \tag{7}$$

where η is the viscosity (in this case chosen in the Newtonian region at 0.1 s^{-1}), A is the pre-exponential factor, and E_a is the activation energy for flow, and R is the gas constant. It was found that within the temperature range of 140–200 °C, the viscosity of the PVC/DAOP (60/40) blend fitted the Arrhenius model very well, yielding an activation energy of 212 ± 10 kJ/mol ($r^2 = 0.994$), and a pre-exponential factor of $(1.9 \pm 0.1) \times 10^{-22}$ Pa s. Interestingly, in comparison with PVC (which has a reported activation energy of 102 kJ/mol [1]), it indicates that the viscosity of the PVC/DAOP blend was much more sensitive to temperature change. As discussed above, this material forms a physical gel at temperatures near 180 °C and so under the temperatures that the rheology was measured (from 140 to 200 °C as shown in Fig. 5), the material would have been in a physical gel state. In agreement with this, Utracki [45] found that the activation energy of PVC/DOP blends increased as the temperature of the gel was lowered.

Although the addition of DAOP to PVC can significantly improve the processibility, it also impairs the heat-resistance properties by reducing the glass transition temperature (T_g) [29] unless the DAOP can be successfully polymerized inside the PVC matrix. In our previous work [29] we have studied the curing behaviour of DAOP with different initiators, and found the DCP is a suitable initiator for polymerization of DAOP in PVC/DAOP blends, as indicated by curing rates and final monomer conversions which were consistent with the processing conditions required for the blends. Fig. 6 shows the

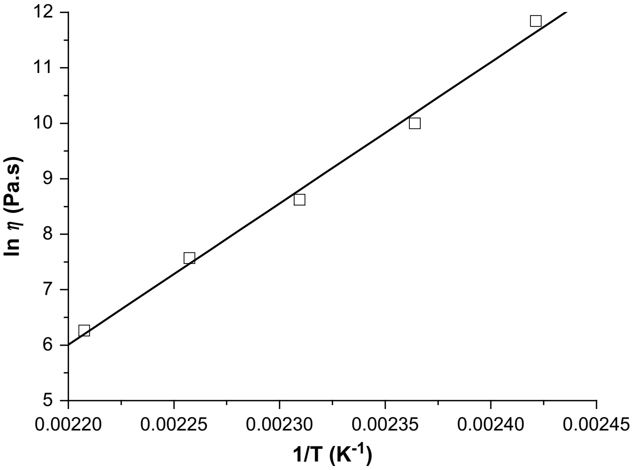


Fig. 5. The relationship between the logarithm of viscosity of the PVC/DAOP (60/40) blend at 0.1 s^{-1} and the reciprocal of temperature, based on the Arrhenius model.

dynamic rheological properties of neat DAOP containing 3% DCP at 140 °C during cure. At short polymerization times, the tan δ is high but decreasing whereas the real modulus is low but increasing. At *ca.* 430 s, tan δ becomes frequency-independent, suggesting the formation of an infinite DAOP gel. This time corresponds well with the value of *ca.* 400 s determined from an operational gel point definition [20] which uses the time for the real modulus to reach a certain but low value (here 10 Pa was used) as an indicator of the first development of the network. Due to the low value of the moduli and thus of the torque in the gelation region of DAOP, the frequency crossover point of tan δ could not be accurately determined and gave an anomalously low relaxation exponent of 0.05. After the gel point, G' rises to a plateau modulus of 1 MPa, suggesting rubber-like behaviour, and then rises to a second plateau with a modulus of *ca.* 0.1 GPa. The second plateau is due to vitrification of the matrix but the measured modulus is smaller than the typical glassy value of 1 GPa due to the limitation in the measuring system. At the same time tan δ decreases to a minimum in the rubber-like region and then rises to a maximum as a result of vitrification as has been observed by others [46].

The rheology during cure of the PVC/DAOP (20/80) blend is shown in Fig. 7, and the frequency independency of tan δ indicates a gel point at *ca.* 320–350 s, which is smaller than that in the neat DAOP, indicating that PVC accelerates DAOP gelation. This conclusion is consistent with previous studies of the polymerization of PVC/DAOP blends [29] which showed that PVC accelerated the curing reaction, apparently due to grafting with the PVC chain which enhanced the gel effect. In addition this grafting reaction would also reduce the conversion required for gelation in PVC/DAOP systems. Due to the higher moduli and therefore torque

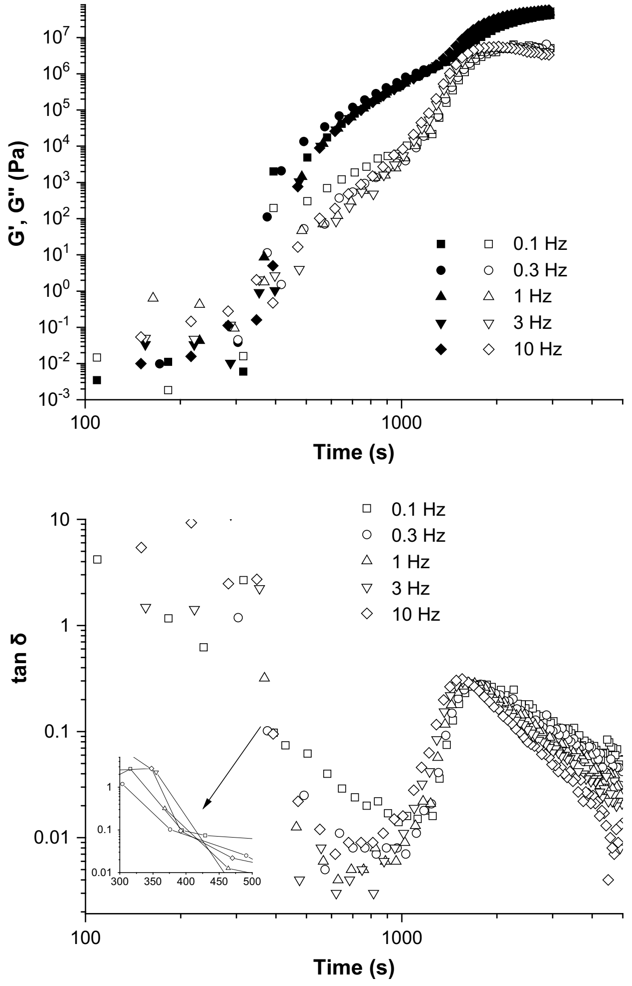


Fig. 6. G' (filled symbols), G'' (unfilled symbols) and tan δ (open symbols) of DAOP containing 3% DCP at 140 °C during the curing.

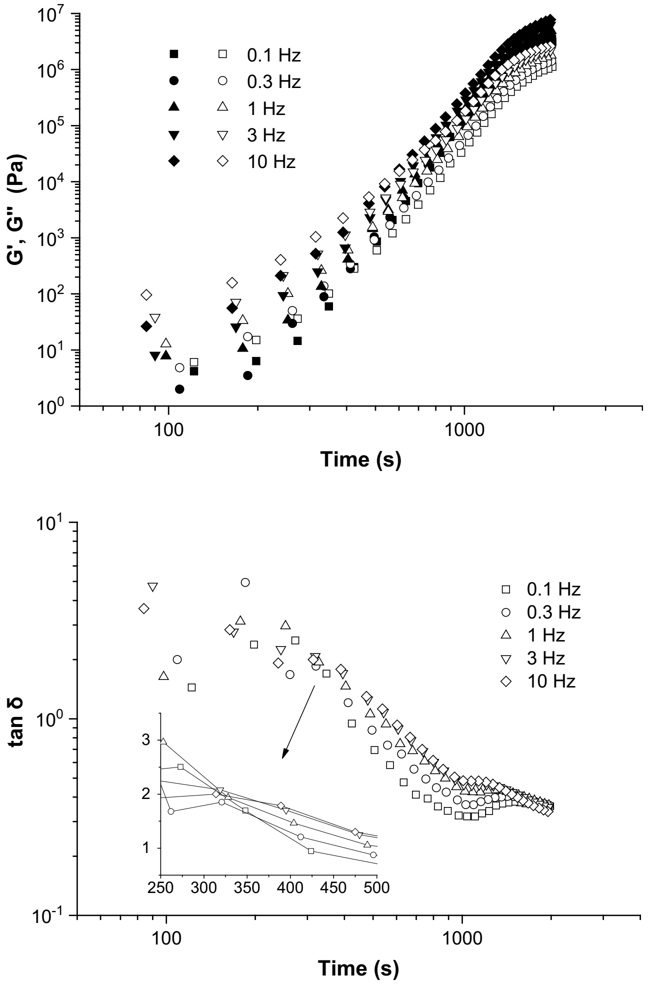


Fig. 7. G' (filled symbols), G'' (unfilled symbols), and tan δ (open symbols) of PVC/DAOP/DCP (20/80/3) blend at 140 °C during the curing.

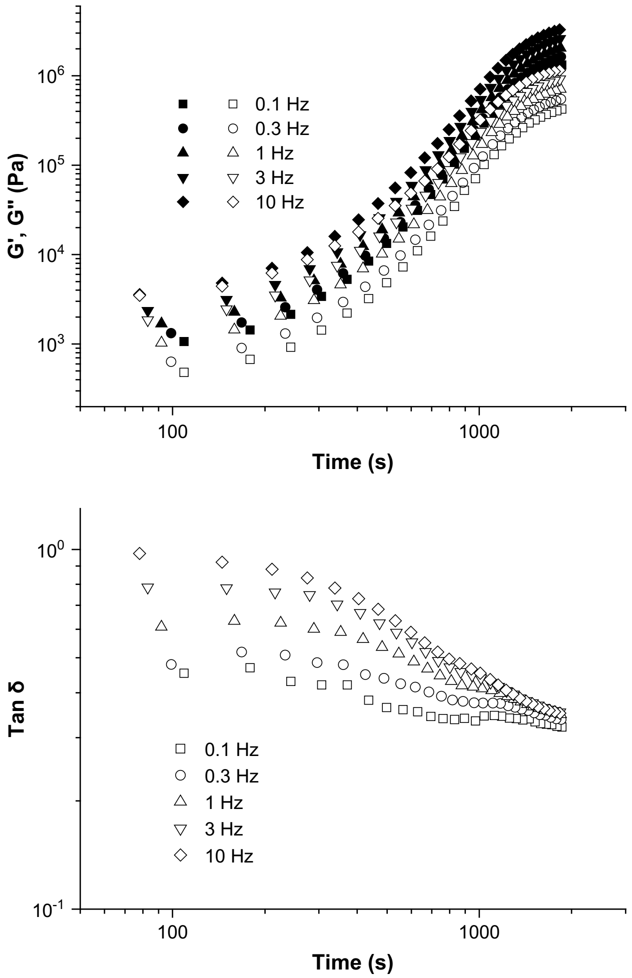


Fig. 8. G' (filled symbols), G'' (unfilled symbols), and tan δ (open symbols) of PVC/DAOP/DCP (40/60/3) blend at 140 °C during the curing.

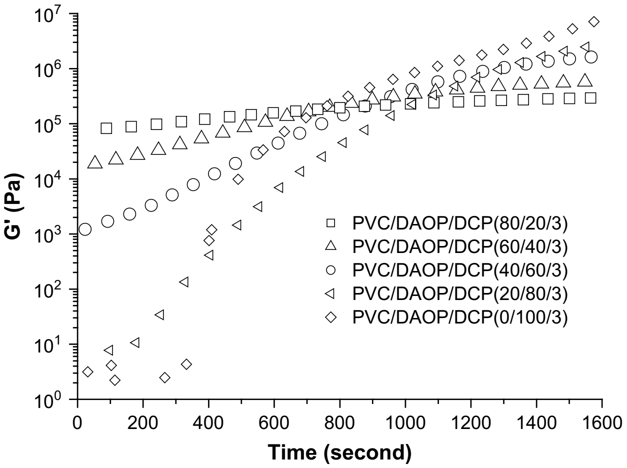


Fig. 9. Variation in dynamic storage modulus (G') at 1 Hz during the polymerization of DAOP in various PVC/DAOP blends using 3% DCP as initiator at 140 °C.

values during cure of this blend, the relaxation exponent (n) was more accurately determined and was found to be *ca.* 0.6.

As illustrated by the data for the PVC/DAOP (40/60) blend (Fig. 8), for PVC/DAOP blends with higher levels of PVC, the storage modulus rose from low to high values with cure time confirming that polymerization was occurring (as previously established by FTIR experiments [29]) however no clear frequency crossover of tan δ was observed. In addition, at this relatively low curing temperature (140 °C compared with 180 °C for the dynamic data in Fig. 1), G' exceeded G'' in all time ranges and so the material had solid-like characteristics. This unusual behaviour was also observed for the 60/40 and 80/20 blends and suggests that although gelation occurred in these blends, the Winter–Chambon [15,17] criterion is not applicable. Two possible reasons may be used to explain this unusual behaviour. One reason for this may be related to the basis of how the gel is normally considered to be a self-similar fractal structure [18] – such a structure develops from the random branching process however when the monomer is polymerized in the presence of a high molecular weight linear polymer (PVC), this self-similar requirement may no longer apply. A second explanation for the lack of a tan δ crossover is that in the PVC/DAOP system, gelation may be occurring in a non-homogeneous fashion due to phase separation of the crosslinked polymer from the PVC. This latter explanation is supported by swelling/dissolution and electron microscopy studies of the cured polymer blends [47]. Blends with 20 wt% PVC or less only swelled in the solvent suggesting a continuous network structure throughout the matrix. However, blends with higher levels of PVC disintegrated into micron-sized particles [47] indicating that either a poorly connected network structure throughout the bulk or a PVC matrix with dispersed crosslinked DAOP particles. Thus, for the latter systems, gelation does not occur throughout the whole volume of polymer and this may account for the inapplicability of the Winter–Chambon [15,17] criterion.

Fig. 9 compares the evolution of the storage modulus of DAOP/DCP and the PVC/DAOP/DCP blends during cure. The data for DAOP, and the blend with 20% PVC, show a reasonably abrupt rise in modulus during the gelation region, as expected for systems undergoing gelation. However, the blends containing more than 20 wt% PVC exhibit a more gradual modulus rise and the liquid-like to solid-like transition became less pronounced as the concentration of PVC was raised. This behaviour may be partly explained by the fact that the presence of the PVC in the blend raises the initial modulus and so makes the transition less abrupt. In addition, as discussed above, the systems with more than 20 wt% PVC do not form a homogeneously crosslinked polymer and so the dynamic properties are mainly determined by the matrix phase. This matrix phase is

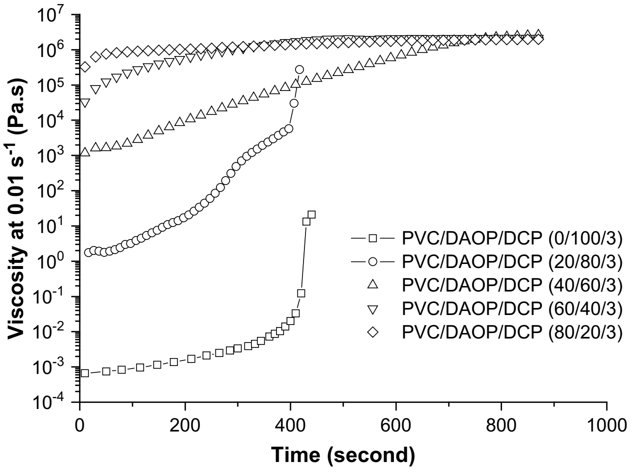
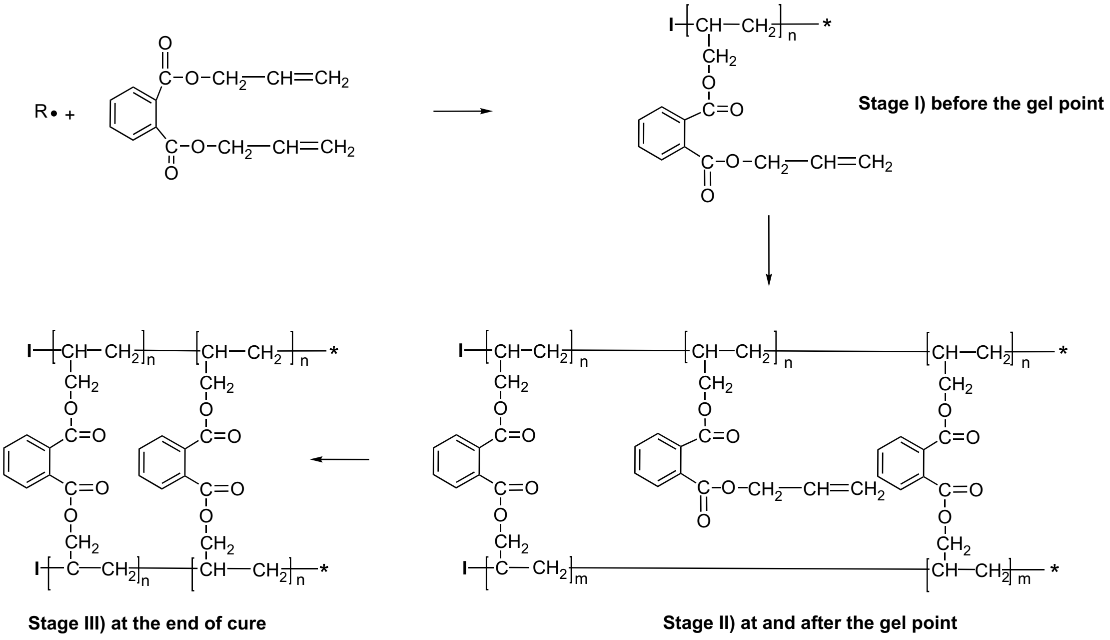


Fig. 10. Variation in steady shear viscosity at 0.01 s^{-1} during the polymerization of DAOP in various PVC/DAOP blends using 3% DCP as initiator at 140 °C.



Scheme 1. The stages of DAOP polymerization.

PVC with diminishing amounts of DAOP monomer as the polymerization proceeds which causes the slow rise in modulus.

The evolution of the steady shear viscosity of DAOP/DCP and the PVC/DAOP/DCP blends during polymerization at 140 °C (see Fig. 10) also show a very similar pattern to the dynamic rheology properties. At the commencement of the reaction, the viscosity of neat DAOP is very low. As the curing reaction in neat DAOP proceeds, the viscosity increases at a relatively low rate, suggesting that the DAOP primarily undergoes linear polymerization reaction with the formation of pendant non-reacted allyl group [30] as shown in Scheme 1, or via intermolecular cyclization reaction [48]. However, as the reaction further proceeds, some of the pendant allyl groups on the predominantly linear DAOP polymer chain react, causing an increase in chain branching as shown in Scheme 1, with the result that the viscosity rose at an increasing rate and then diverged towards infinity when the crosslinked network formed at *ca.* 410 s. This gel time is very close to that obtained using the dynamic rheology at 400 s, and by comparison with FTIR studies of the polymerization reported elsewhere [47], the conversion of reacted allyl groups at the gel point was about 20%, which is in agreement with the results of 21% and 25% obtained by Kircher [30] and Matsumoto et al. [31], respectively. The variation of the steady shear viscosity of PVC/DAOP/DCP (80/20/3) was similar to that of neat DAOP – the viscosity rise was slow initially but accelerated near the gel point at 400 s. However the viscosity did not increase as regularly as was found with neat DAOP. An inflection is observed in the logarithmic viscosity at *ca.* 200 s prior to the rapid rise as gelation approached. Possibly this behaviour is caused by phase separation of the PVC into a dispersed phase which reduces the concentration of polymer in the continuous phase and thus reduces the rate of increase in viscosity. Similar behaviour has been reported by Bonnet et al. [11,12,49] for the phase separation of polyetherimide from a diamine-cured epoxy. In contrast, the blends with higher levels of PVC – PVC/DAOP/DCP (40/60/3, 60/40/3, 80/20/3) – only show a gradual rise in viscosity with time and then reach a plateau but do not show evidence of gelation. This is consistent with the evidence discussed above that in blends with more than 20 wt% PVC, the DAOP polymer phase separates into a dispersed phase which is surrounded by PVC-rich matrix.

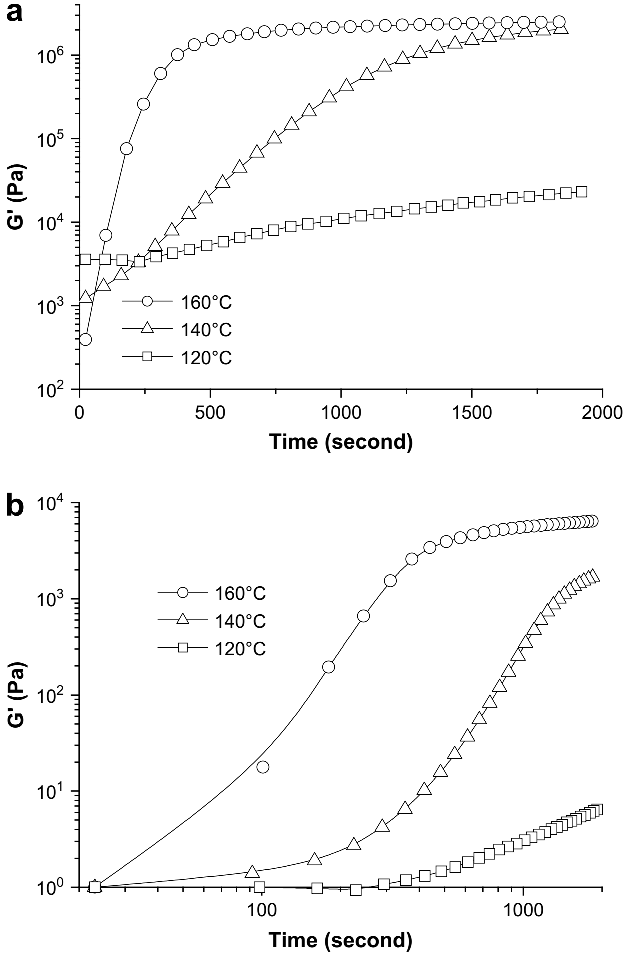


Fig. 11. a) Variation in G' of three identical PVC/DAOP/DCP (40/60/3) blends at 1 Hz during polymerization at various temperatures. b) Ibid with G' data normalized by the initial value and plotted versus the logarithm of time.

Consequently, in these blends the matrix appears to have a finite viscosity even after the DAOP component has gelled.

Fig. 11 compares the evolution of G' for the PVC/DAOP/DCP (40/60/3) blend during cure at 120, 140, and 160 °C. As expected, the modulus is initially lower when the cure temperature is higher because the material is in a state which is closer to the glass transition temperature of the uncured blend. However the polymerization proceeds at a faster rate at higher temperatures and so the G' curves crossover during the curing process. If as a rough approximation, the modulus data is scaled by its initial value, it can be seen that when plotted on a logarithmic time axis, the curves have a similar shape and are separated by a similar shift factor as indicated by the equal distances between the data at different cure temperatures – in fact, application of the Arrhenius equation yields an activation energy for cure of 90 ± 20 kJ/mol which is similar to the value of 126 ± 3 kJ/mol determined by isothermal FTIR studies of the same blend [29].

4. Conclusions

The addition of DAOP to PVC significantly reduced the viscosity and processing temperature of the blends thus greatly decreasing the risk of the decomposition of PVC. Thus these studies indicate that the problem of using PVC in long cycle time processes, such as rotational moulding, may be readily solved by using a reactive plasticizer.

The variation of viscosity with weight fraction of DAOP in the uncured blend obeyed the log-additivity rule. The dynamic rheology of the uncured blends indicated that some of them were in a physical gel state at 180 °C and the relaxation exponent was similar to that observed by other workers. The Arrhenius activation energy of the blend with 40 wt% DAOP was twice that of pure PVC, possibly due to physical gelation.

During cure, the dynamic rheology of pure DAOP and DAOP with 20 wt% PVC showed a frequency independence of $\tan\delta$ and an abrupt rise in storage modulus at the gel point. In contrast, blends with higher levels of PVC did not show such behaviour and so did not agree with the Winter–Chambon criterion [15,17]. Similarly, pure DAOP and PVC/DAOP (20/80) exhibited a rapid rise in real modulus near the gel point but this was not observed for blends with higher PVC levels. This difference in behaviour was interpreted in terms of either a non-fractal nature of the gel structure due to the presence of the pre-formed high molecular weight PVC or due to inhomogeneous gelation due to phase separation. These results were supported by steady shear viscosity studies during cure. The viscosity of samples with either 80 or 100 wt% DAOP tended to diverge at the gel point but samples with lower levels of DAOP exhibited a slow rise and then plateau in the steady shear viscosity, suggesting that in these samples the DAOP was not a continuous matrix.

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