Co-crosslinking of ethylene vinyl acetate and ethylene acrylic ester copolymers by transesterification: chemical and rheological studies of kinetics

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The transesterification reaction in the molten state of ester groups of ethylene vinyl acetate copolymers and ethylene acrylic ester copolymers, in the presence of dibutyltin oxide as a catalyst, leads to crosslinking of the copolymer chains. The kinetics of this crosslinking reaction has been assessed by two different experimental methods: viscoelastic measurements of the dynamic storage modulus and thermogravimetric analysis coupled with gas chromatography which allows measurement of the evolved methyl acetate which is a volatile product of the crosslinking reaction. The equilibrium storage modulus calculated from theories of elastic modulus has shown that the kinetics of the crosslinking reaction may be determined through variations of the dynamic storage modulus.

(Keywords: crosslinking; transesterification; kinetics; melt viscoelasticity)

INTRODUCTION

Transesterification is a useful reaction for the chemical modifcation of polymers or copolymers bearing ester groups. Two types of catalyst are used, basic catalyst and organometallic compounds[1]. Studies of the mechanism of the exchange reaction of ester group in the presence of some organometallic compounds such as dibutyltin oxide has shown[2,3] that this kind of catalyst seems to be the most efficient. The chemical reaction of transesterification can be used to crosslink blends of copolymers such as ethylene vinyl acetate (EVA) and ethylene methyl acrylate (EMA) ester copolymers[3].

On the other hand, rheology has been used as a tool for analysis of polymer blends[4–6] and viscoelastic properties provide a useful method for following the chemical reaction of crosslinking[7–9]. This paper is devoted to a viscoelastic study of the crosslinking reaction between EVA and EMA copolymers. The kinetics of the crosslinking reaction may be determined by studying the time and temperature dependence on the dynamic storage modulus $G'(t)_{T,\omega}$. This rheological kinetics of the crosslinking reaction was compared with the kinetics of methyl acetate formation.

TRANSESTERIFICATION MECHANISM

A temporary complex between acetate groups of copolymers and organometallic compounds has been isolated as the true catalyst of the transesterification reactions, as indicated in *Figure 1a*. This complex has been characterized by Mössbauer and n.m.r. spectroscopy and it has been shown that an organometallic bridge forms between the polymer chains through a metal–oxygen bond. This complex, which forms at about 200°C, allows crosslinking of acetate groups of copolymers, as shown in *Figure 1a*. In the presence of ester groups generated from polyacids, such as either dimethyl phthalate or acrylic ester copolymers, this organometallic bridge is destroyed and crosslinking occurs through the ester bridge and methyl acetate formation as shown in *Figure 1b*.

EXPERIMENTAL

Materials

EVA and EMA copolymers were kindly supplied by Atochem. The respective amount of acetate and acrylate groups contained in these copolymers is about 28 wt%.

Molecular weights were measured by g.p.c. in trichlorobenzene at 135°C using a linear polyethylene NBS calibration with a series of μ styragel columns (10^4, 10^3, 10^2 and 50 nm). The respective molecular weights for the EVA and EMA copolymers are as follows: $M_{w1} = 53.5\,\text{kg mol}^{-1}$, $M_{n1} = 19\,\text{kg mol}^{-1}$ and $M_{w2} = 94.3\,\text{kg mol}^{-1}$, $M_{n2} = 22\,\text{kg mol}^{-1}$.

On the other hand, these copolymers are compatible and the molecular weights of the sample EVA/EMA (50/50 by weight) can be calculated from relations: $M_w = (M_{w1} + M_{w2})/2 = 74\,\text{kg}$ and $M_n = 2M_{n1}M_{n2}/(M_{n1} + M_{n2}) = 20.4\,\text{kg}$.

The microstructure of these copolymers was determined by ^{13}C n.m.r. spectroscopy. The experimental conditions were as follows: a.c. 250 (62.9 MHz) spectrometer, temperature 90°C, solvent tetrachloroethylene/C_6H_6,

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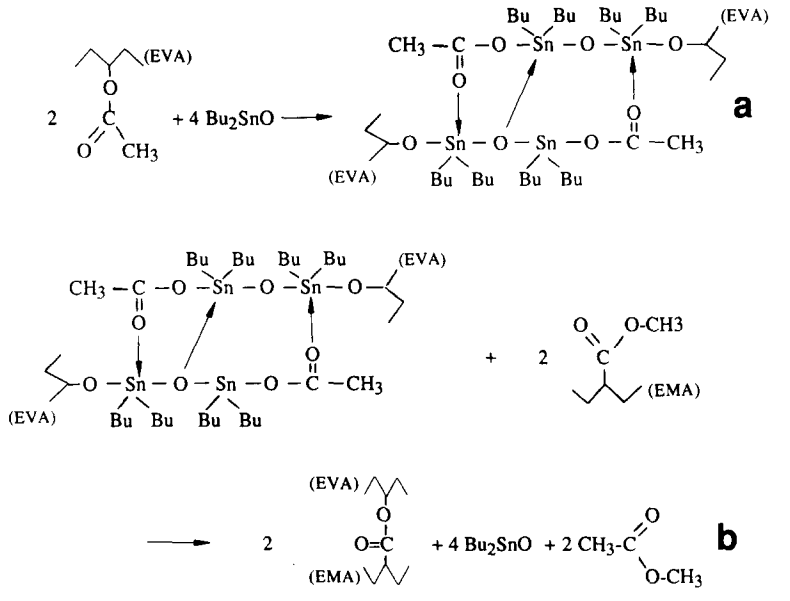

Figure 1 Mechanism of transesterification: (a) crosslinking of EVA; (b) co-crosslinking of EVA and EMA ester copolymers

weight concentration 10%. This study has shown that the EVA copolymer was composed of 95% of EVE triads (E, ethylene unit; V, vinyl acetate unit) and 5% of EVV triads. This copolymer can, therefore, be assumed to be a statistical copolymer bearing 66 reactive sites (vinyl acetate unit) per chain according to the number average molecular weight of the copolymer.

The blend EVA/EMA/Bu_2SnO was fixed at 48/48/4 by weight. This blend was mixed in a twin screw extruder (Leistritz, LSM 30–34). The main characteristics of the screws are: diameter, $D_s = 3.4 \times 10^{-2}$ m; length/diameter ratio, $L/D_s = 33.5$. The temperatures were regulated from 130°C at the feed zone to 165°C at the die. As described later, at these temperatures and for the residence times inside the extruder ($t \simeq 200$s), no crosslinking occurs.

Rheology

The rheological assessment was carried out on a rheometrics mechanical spectrometer (RMS 800) using a parallel-plate geometry ($R = 3.95 \times 10^{-3}$ m). In all cases, sample response linearity with respect to strain amplitude was verified and nitrogen gas was used to prevent thermal oxidation. The parallel-plate system was pre-heated at the temperature of the experiment. Then, the sample was put in between the plates once the temperature of regulation was reached. The sample was then heated by conduction through the plates as shown in *Figure 2a*. An approximate solution of the evolution of the temperature with time of the sample may be given[10] from the relation:

$$\frac{T_s - T_c}{T_s - T_0} \simeq \frac{4}{\Pi} \exp\left(-\frac{\Pi^2}{4}\frac{at}{e^2}\right) \simeq \exp\left(-\frac{1.28 \times 10^{-3}}{e} t\right) \quad (1)$$

where a is thermal diffusivity (1.3×10^{7} m^2 s^{-1}); t is time (s); $2e$ is thickness of sample (1.2×10^{-3} m); and T_s, T_c and T_0 are temperatures defined in *Figure 2a*. A simple calculation showed that the sample had reached the check temperature within 10 s.

Thermogravimetry coupled with gas chromatography

Analysis of methyl acetate and control of thermal degradation were carried out under nitrogen (1 ml s^{-1})

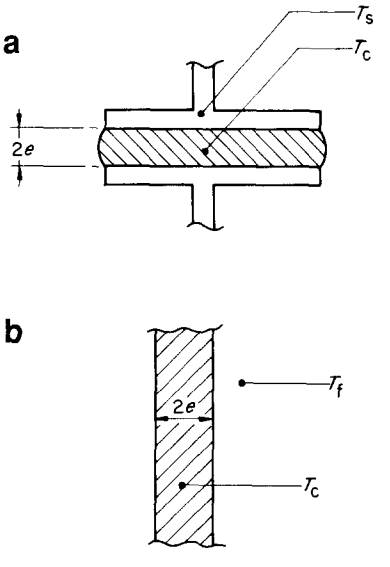

Figure 2 Conduction and convection heating: T_0, sample temperature before positioning ($T_0 \simeq 25$°C). (a) Rheometer, plane/plane geometry, conduction; (b) thermobalance, convection

in a Ugine-Eyraud B60 thermobalance. Samples of the gas stream from the balance were injected into a Intersmat IGC15 gas chromatograph by means of a slider-type gas sampling valve. The gas product was injected every 3 min through a pneumatically driven lever automatically operated by a timer. The gaseous products trapped in the sample loop (2 cm^3) were swept by the carrier gas into the column of the gas chromatograph.

The weight of samples (150 mg) and the temperature, monitored by a thermocouple placed near the sample boat, were recorded as a function of time in isothermal or programmed heating experiments. This technique was previously described as a thermal degradation technique[11].

The glass column of the chromatograph was filled with a chromosorb 101 phase and the chromatograph signal was recorded (10 mm min^{-1}).

The temperature of the glass column was fixed at 145°C and the temperature of the injector and of the detector

Table 1 Chromatographic retention times of gaseous products

Gaseous product	Retention time (s)
Reaction product	
Methyl acetate	66
Degradation products	
Acetic acid	117
Other products	33
	94
	159

(FID) was fixed at 250°C. With these experimental conditions, the retention times of different gaseous products (product of reaction and products of degradation) are given in *Table 1*. The products of thermal degradation of copolymers (acetic acid) appear for temperatures higher than 290°C whereas the product of thermal degradation of the catalyst appears for temperatures higher than 160°C. However, the amount of degradation of the catalyst remains low throughout the experiments. On the other hand, dibutyltin oxide was added into the blend in a catalytic amount and its thermal degradation may be assumed to be identical in both cases studied (rheology and t.g.–g.c.). Then, thermal degradation of copolymers was neglected for temperatures lower than 250°C.

The instantaneous rate of methyl acetate formation from the crosslinking reaction taking place in the thermobalance was assumed to be proportional to the peak height of the chromatographic signal. A calibration coefficient was determined by isothermally (T= 170°C) evaporating methyl acetate in the thermobalance at constant rates measured by weight loss. Then the total extent of the crosslinking reaction of copolymers was calculated from the area below the curve obtained by plotting the variations *versus* time of the instantaneous rate of methyl acetate.

In this technique, the sample is mainly heated by convection. The evolution of the temperature inside the sample at the beginning of the experiment may be described[10] by the relation:

$$\frac{T-T_f}{T_0-T_f} \simeq \exp\left(-\frac{h}{\rho c}\frac{t}{e}\right) \simeq \exp\left(-\frac{1.6\times10^{-5}}{e}t\right) \quad (2)$$

where ρc is the calorific capacity ($=2.51\times10^6\,J\,°C^{-1}\,m^{-3}$); h is the convection coefficient ($=20\,W\,m^{-2}\,°C^{-1}$); and temperatures T, T_0 and T_f are defined in *Figure 2b*.

This last expression is quite different from expression (1) through the value of the temporal coefficient. According to both systems of heating (conduction and convection), the thickness of the sample must be low in the case of convection, in order to obtain rapid heating comparable to the heating in the case of conduction. Therefore, the thickness of the sample placed in the thermobalance was about 1×10^{-4} m. But in spite of this extreme condition, the sample reached the check temperature after about 100 s.

RESULTS AND DISCUSSION

Thermogravimetric and gas chromatographic experiments

Figure 3 shows the variations of instantaneous rate of methyl acetate formation *versus* temperature obtained from crosslinking reaction in programmed heating (1°C min^{-1}). This curve indicates three domains of different activation energies of the chemical reaction. These domains may be characterized by the range of temperatures: I, 150°C < T < 230°C; II, 230°C < T < 290°C; III, T > 290°C.

When the crosslinking reaction occurs with increase in temperature, the density of the network increases. The mobility of the molecular segments and the accessibility of the reactive sites decrease and the reaction tends to slow down. But, when the programmed heating oversteps about 230°C, the mobility of the segment molecules between crosslinking bonds becomes most dominant compared with the densification of the crosslinking network, and the crosslinking reaction starts again with a high activation energy. An identical process may be described in the third region of heating but analysis in this region of heating is more tricky owing to the thermal degradation of copolymers.

Consequently, determination of the extent p of the chemical reaction through titration of methyl acetate in isothermal experiments has been made in the range of temperatures defined by the first domain (150°C < T < 230°C).

Figure 4 shows variations of the extent p of the reaction obtained for temperatures 170, 190, 210 and 230°C. At longer times, the instantaneous rate of methyl acetate formation was low and could not be recorded with good accuracy. Therefore, as shown in *Figure 4*, the total extent

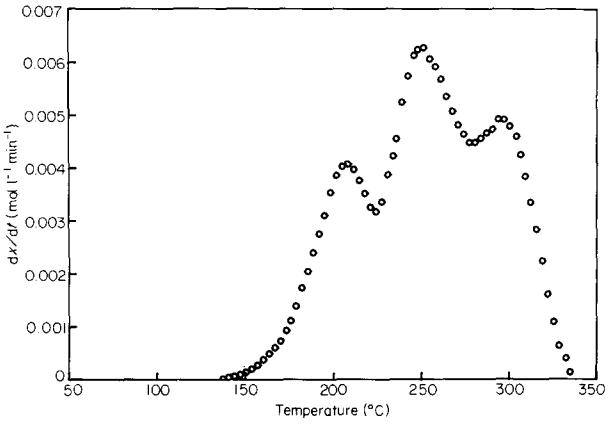

Figure 3 Variation of instantaneous rate of methyl acetate formation *versus* temperature (programmed heating, 1°C min^{-1})

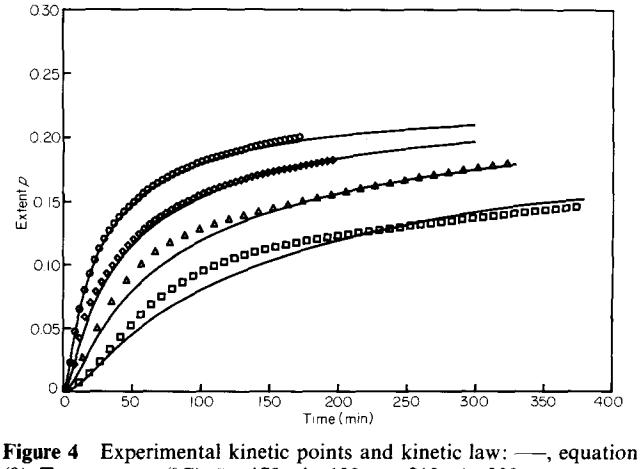

Figure 4 Experimental kinetic points and kinetic law: —, equation (9). Temperature (°C): □, 170; △, 190; ◇, 210; ○, 230

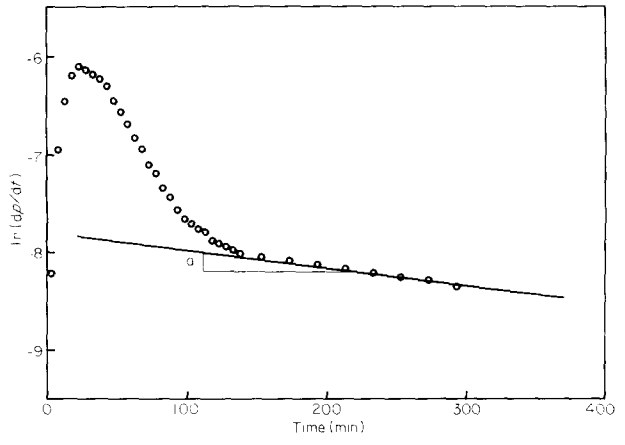

Figure 5 Semilogarithmic representation of dp/dt *versus* time, $T = 190°C$

Table 2 Extent of reaction: experimental determination of the extent of the reaction (pf) and extrapolated extent ($p_{e\infty}$)

Temperature (°C)	p_f	$p_{e\infty}$
170	0.15	0.22
190	0.20	0.24
210	0.18	0.21
230	0.20	0.23
250	0.27	0.28

of the crosslinking reaction is not reached. Nevertheless, the amount of methyl acetate still susceptible to be created at long times through the crosslinking reaction may be estimated from a plot on a semilogarithmic axis of the instantaneous extent of methyl acetate (dp/dt), as shown in *Figure 5* for a typical experiment ($T = 190°C$). The estimated truncation[12] of the reaction is simply the instantaneous extent of the last measure $(dp/dt)_f$ divided by the slope of the straight line portion (a) as shown in *Figure 5*:

$$R = \frac{(dp/dt)_f}{a} \tag{3}$$

For different temperatures, the values p_f of the extent of the reaction at the end of the experiment and the value $p_{e\infty}$ of the extrapolated extent ($p_{e\infty} = p_f + R$) at infinite times are reported in *Table 2*. These results may be related and are in agreement with the explanations given about *Figure 3*. Indeed, for the temperatures defined by domain I of *Figure 3*, $150°C < T < 230°C$, the extrapolated extent $p_{e\infty}$ of the reaction tends towards an identical value $p_{e\infty} = 0.22 \pm 0.02$, whereas for $T = 250°C$ defined by domain II, $230°C < T < 290°C$, the extent of the reaction tends to a higher value, $p_{e\infty} = 0.28 \pm 0.02$. On the whole, the extent of the reaction at the end ($t \to \infty$) of the crosslinking reaction is low ($p_{e\infty} \to 0.22$). Indeed, the crosslinking reaction involves a high number of reactive sites ($r_n = 66$) of two polymer chains. Consequently, as explained previously, the motions of polymer chains are slowed down by the chemical network and the relaxation times of the chains, which may be compared to a reptation process, tend to an infinite value with the degree of crosslinking. Then the probability of a reactive site accessing another reactive site vanishes.

Kinetic law

The reaction scheme of the transesterification reaction, given in *Figure 1*, may be written as follows:

$$\begin{array}{lcccc} & \text{EVA} + & \text{EMA} \rightarrow & \text{EVA/EMA} + & \text{methyl acetate} \quad (4) \\ t=0 & a & b & 0 & 0 \\ t>0 & (a-x) & (b-x) & x & x \end{array}$$

where a and b are the initial molar concentration of acetate and acrylate groups in the molten state. In this case $b = a = 1.48\ \text{mol l}^{-1}$.

If the transesterification reaction is second order, as generally assumed, the net rate of appearance of methyl acetate is:

$$dx/dt = k_1(a-x)^2 \tag{5}$$

where k_1 is a kinetic constant. From integration of this equation and from definition of the extent of the reaction ($p = x/a$) the extent of the reaction is given by:

$$p = \frac{ak_1t}{1+ak_1t} \tag{6}$$

However, as pointed out previously, the crosslinking reaction is slowed down by the chemical network and we assume that the equation of the extent of the reaction may be expressed as the product of two functions as follows:

$$p = \frac{ak_1t}{1+ak_1t} M(t) \tag{7}$$

where $M(t)$ is a 'damping function' which takes into account the effects of the crosslinking bonds over the mobility of copolymer chains. This function may be written as an exponential function:

$$M(t) = B[1 - \exp(-t/\tau)] \tag{8}$$

τ is a 'relaxation time' of the network. From boundary conditions, $t \to \infty \Rightarrow p \to p_\infty$, then $B = p_\infty$.
Finally:

$$p = \frac{ak_1t}{1+ak_1t} p_\infty[1 - \exp(-t/\tau)] \tag{9}$$

k_1, τ and p_∞ have been adjusted through a non-linear regression from experimental kinetic curves at different temperatures. The values of these constants are given in *Table 3*. For the temperature of 170°C, the non-linear regression does not lead to a solution.

The constants k_1 and $1/\tau$ obey an Arrhenius law:

$$\begin{aligned} k_1 &= 2.11 \times 10^4 \exp(-58 \times 10^3/RT) \\ 1/\tau &= 8.35 \times 10^3 \exp(-44 \times 10^3/RT) \end{aligned} \tag{10}$$

The activation energy $E_{a1} = 58\ \text{kJ mol}^{-1}$ (from expression of k_1) is close to the value ($E_a = 70\ \text{kJ mol}^{-1}$) obtained in the case of chemical reaction using a transesterification

Table 3 Kinetic constant k_1, and constants τ and p_∞ with respect to temperature

Temperature (°C)	k_1 ($\text{l mol}^{-1}\ \text{min}^{-1}$)	τ (min)	p_∞
190	0.0073	12.5	0.235
210	0.015	6.25	0.22
230	0.024	5.0	0.23

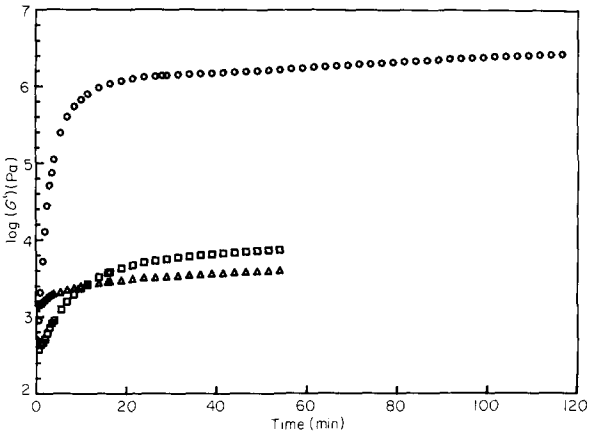

Figure 6 Storage modulus *versus* reaction time at 230°C. □, EVA + Bu_2SnO; △, EMA + Bu_2SnO; ○, EVA/EMA + Bu_2SnO

reaction to convert ester groups of an EVA copolymer to alcohol functions[13].

The second activation energy $E_{a2} = 44\,kJ\,mol^{-1}$ (from expression of $1/\tau$) may be correlated to the energy characterized by the range of temperatures defined by *Figure 3* ($150°C < T < 230°C$). This activation energy is a characteristic constant of the network in this range of temperatures.

The values of p_∞ (*Table 3*) are constant regardless of the temperatures: $p_\infty \simeq 0.23$. This value is very close to the value ($p_{e\infty} = 0.22$, *Table 2*) obtained from extrapolation of the end of the reaction as shown in *Figure 5*. This result confirms the method of extrapolation of the extent of the end of the crosslinking reaction. This characteristic constant, $p_\infty \simeq 0.22$, expresses the boundary density of the network which can be reached in this range of temperatures.

In *Figure 4* experimental kinetic points are compared to kinetic curves calculated from equation (9) with k_1, τ defined through the relations (10) and $p_\infty = 0.23$. On the whole, the kinetic law correctly describes the experimental kinetics.

Rheology experiments

The domain of frequency used for following the chemical reaction must define the relaxation terminal zone ($G' \sim \omega^2$) as the viscoelastic response of the uncrosslinked polymer. In the region characterized by the longest relaxation times[14] the introduction of chemical crosslinks significantly changes the shape of the storage modulus–frequency curves[15]. However, the pulsation ω of the measure must not be too low ($\omega > 0.1\,rad\,s^{-1}$) because the time of the measurement must be short compared with the kinetics of the reaction.

Figure 6 provides evidence of the transesterification process between ester groups of EVA and EMA chains through the variations of the storage modulus $G'(t)_{T=230°C,\omega=1\,rads^{-1}}$. However, samples are composed of two ester copolymers, EVA and EMA, which are susceptible to crosslinking through complexation of ester groups with dibutyltin oxide, as shown in *Figure 1a*. Indeed, the variations of the storage modulus could be attributed to the crosslinking of EVA[16] and the crosslinking of EMA copolymers without transesterification. When dibutyltin oxide was added in a catalytic amount, the magnitude of the evolution of the storage modulus for the EVA/Bu_2SnO and EMA/Bu_2SnO reactive samples (*Figure 6*, lower curves) is low whereas storage modulus of the EVA/EMA/Bu_2SnO reactive blends quickly tends to a high value, as shown in *Figure 6* (upper curve, $G'(t \to \infty) \to 2 \times 10^6$ Pa). This figure shows that the transesterification process between ester groups of the two copolymers can be characterized by variations of the storage modulus, and the respective crosslinking process of EVA and EMA chains can be neglected compared with the co-crosslinking process between the chains of these two copolymers.

When the reaction occurs, the storage and loss moduli increase with time as the network results. At a particular point, the storage and loss moduli cross. This crossover between G' and G'' takes place at the same critical reaction time, within experimental error, independently of the frequency applied ($0.1\,rad\,s^{-1} < \omega < 5\,rad\,s^{-1}$), as shown in *Table 4*. This critical point may be defined as the gel point according to refs 17–21; at this time the chains form a three-dimensional network. At the gel point, the storage (G') and the loss (G'') moduli are equal over the whole spectrum of frequencies and proportional to the square of the frequency[19].

On the other hand, the variation of the inverse of the gel time (t_{gel}) obeys an Arrhenius law with an activation energy of $66 \pm 4\,kJ\,mol^{-1}$ as shown in *Figure 10*. Experimental values of t_{gel} are reported in *Table 5*. This value of the activation energy is close to the value of the activation energy ($E_{a1} = 58\,kJ\,mol^{-1}$) of the chemical reaction calculated from the kinetic law, relation (9).

Correlation between kinetics (t.g.–g.c.) and viscoelastic experiments

As defined by the range of frequencies $0.2\,rad\,s^{-1} < \omega < 1\,rad\,s^{-1}$, the storage modulus $G'(t)$ may be assumed to be the equilibrium shear elastic modulus $G_e(t)$ defined by the theory of rubber elasticity[22]. However, at times less than the t_{gel}, the EVA/EMA network is only constituted of few coupled chains which do not make a three-dimensional network. Furthermore, the rate of change of the linear viscoelastic properties follows a power law dependence of frequency in the vicinity of the gel point[23]. Then the assumption that the storage modulus $G'(t)$ is the equilibrium shear modulus G_e, is not valid in the vicinity of the gel point.

Table 4 Gel times ($G' = G''$) at $T = 190°C$ for different frequencies

Frequency, ω ($rad\,s^{-1}$)	t_{gel} (s)
0.2	450
0.5	430
1.0	430
5.0	400

Table 5 Gel times, at different temperatures, calculated from viscoelastic measurements ($G' = G''$, *Table 4*) and from the kinetic law (resolution plot of relation (21)). Extent of reaction at the gel point

Temperature (°C)	t_{gel} From $G' = G''$ (s)	t_{gel} From kinetic law (s)	p_{gel} ($\times 10^{-3}$)
170	1080	720	5.5
190	450	360	4.8
210	200	210	5.0
230	130	120	4.6

Theories for elastic modulus have been extensively treated in the literature. A review of the theoretical relations for the equilibrium shear modulus was made by Gottlieb *et al.*[24] and Pearson and Graessley[25]. The expression generally accepted is the following:

$$G_e = (\nu - \mu h)RT + G_e^{max} T_e \quad (11)$$

The first term is the chemical contribution due to crosslinking where ν and μ are the respective concentrations of elastically active strands and junctions per volume unit, and h is an empirical parameter $0 < h < 1$. The second term, where G_e^{max} is the maximum possible contribution of entangled chains to modulus and T_e is the contribution of the portion of topological interactions or entanglements between chains which are permanently trapped by the chemical network. T_e is equivalent to the probability that any pair of interacting units are each part of elastically effective chains.

Values of μ, ν and T_e from the random networks may be calculated from the sol fraction w_s using relations derived by Pearson and Graessley[25] assuming that a crosslinking bond is tetrafunctional (a bond joining two chains becoming a tetrafunctional branch point). In this case, these relations are:

$$\mu = \frac{\rho}{2M_o} p(2\psi_1\psi_2 + \psi_1^2) \quad (12)$$

$$\nu = \frac{\rho}{2M_o} p(3\psi_1\psi_2 + 2\psi_1^2) \quad (13)$$

$$T_e = \psi_2^2 \quad (14)$$

$$w_s = 1 - \psi_1 - \psi_2 \quad (15)$$

where ρ is density, p is the fraction of crosslinkable sites actually linked at the time t (extent of the reaction) and M_o is the molecular weight of the molecular segment between two consecutive reactive sites of the EVA/EMA chains (when $p=1$, $M_o = M_n/r_n$). ψ_1 is the probability that a randomly chosen uncrosslinked unit is connected to the gel by one path and ψ_2 is the probability that it is connected by two paths:

$$\psi_1 = 2(1 - \varepsilon - \psi_2) \quad (16)$$

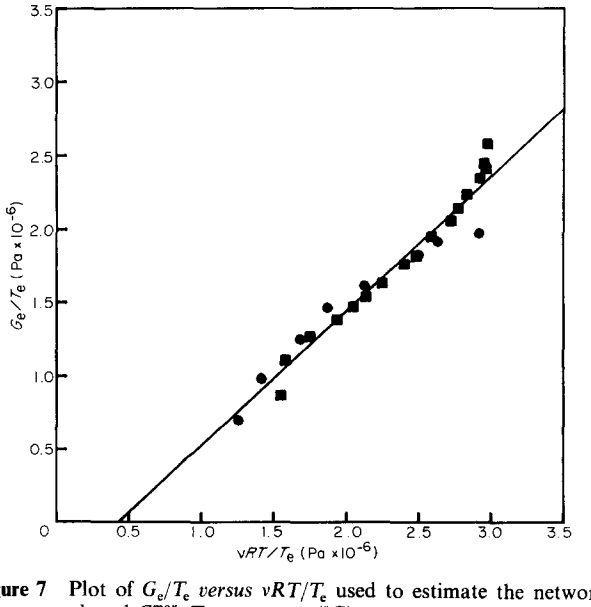

Figure 7 Plot of G_e/T_e *versus* $\nu RT/T_e$ used to estimate the network parameters h and G_e^{max}. Temperature (°C): ■, 190; ●, 230

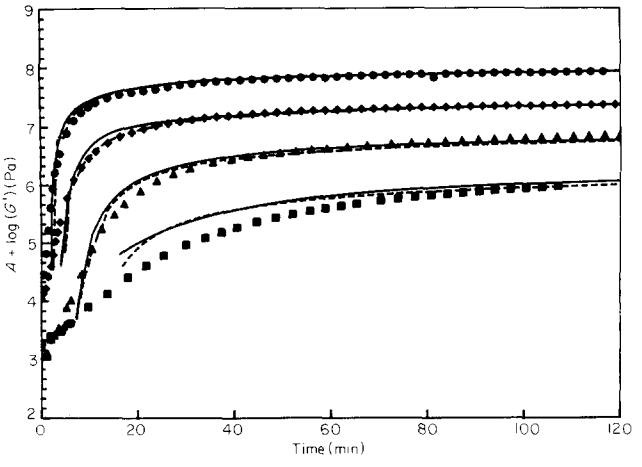

Figure 8 Correlation between viscoelastic experiments and storage modulus calculated from relation (20) and experimental kinetics (—) and kinetic law (-----). Semilogarithmic axis, $A + \log(G')$ *versus* time: ■, 170°C, $A = 0$; ▲, 190°C, $A = 0.5$; ◆, 210°C, $A = 1$; ●, 230°C, $A = 1.5$

$$\psi_2 = 1 - 2\varepsilon + (1 + pr_n\xi/b)^{-b-1} \quad (17)$$

A Schulz–Zimm form of the molecular weight distribution may be assumed with $b = r_n/(r_w - r_n)$, where r_n and r_w are the number average and weight average of crosslinkable reactive sites, respectively. The parameters ε and ξ are:

$$\varepsilon = [1 - (1 + pr_n\xi/b)^{-b}]/pr_n\xi \quad (18)$$

$$\xi = 1 - w_s$$

From equations (15), (16) and (17) the sol fraction can be calculated from the extent p of the reaction as follows:

$$p = b(w_s^{-1/(b+1)} - 1)/r_n(1 - w_s) \quad (19)$$

The determination of w_s requires a numerical resolution of equation (19) such as, for example, the Van Wijngaarden–Dekker–Brent method. Then, the extent of the reaction can be used to calculate ν, μ and T_e.

In *Figure 7* G_e/T_e *versus* $\nu RT/T_e$ is plotted, considering some data (some data have been omitted to clarify the figure) for temperatures of 190 and 210°C; from equation (11) the slope and the intercept of the straight line are, respectively, $1 - h\mu/\nu$ and G_e^{max}. The experimental slope of this line is 0.98 which, within experimental error, is equal to the value of $1 - h\mu/\nu$ obtained for the parameter $h = 0$. The intercept G_e^{max} of 5.5×10^5 Pa may be close to the average value of G_N^0 determined for the uncrosslinked polymer ($G_N^0 \simeq 6 \times 10^5$ Pa). These results, in agreement with those of Pearson and Graessley[25], show that entangling interactions can strongly influence the equilibrium elastic modulus through the network parameter T_e and suppression of junction fluctuations ($h = 0$).

Then, considering these previous results on the network parameters, the variation of the storage modulus *versus* time, for times higher than the t_{gel}, can be calculated from equation (11) as follows:

$$G'(t) = G_e(t) = \nu(t)RT + G_e^{max} T_e(t) \quad (20)$$

$$t > t_{gel}$$

Figure 8 shows that the storage modulus, $\log[G'(t)]$, calculated through relation (20) from experimental kinetics (full line) and kinetic law (dotted line) is in good agreement with the values of the storage modulus

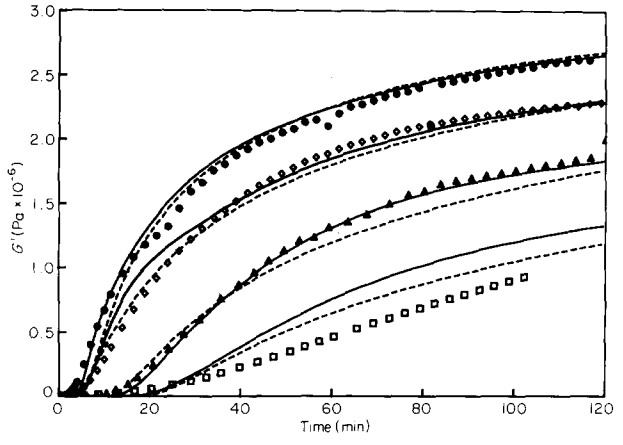

Figure 9 Correlation between viscoelastic experiments and storage modulus calculated from relation (20) and experimental kinetics (—) and kinetic law (-----). Temperature (°C): □, 170; ▲, 190; ◇, 210; ●, 230

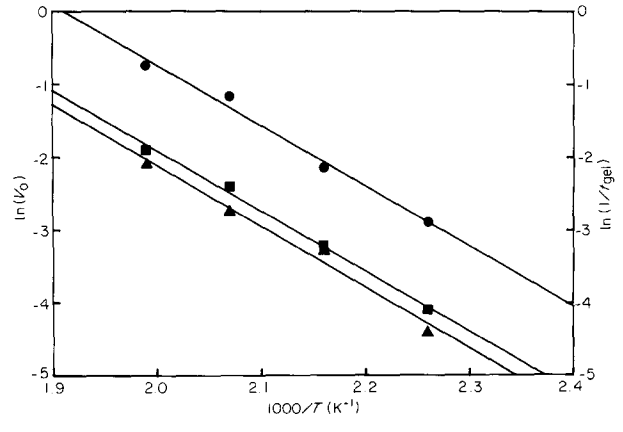

Figure 10 Arrhenius diagram: $\ln(V_0)$ *versus* $1/T$. ■, From curves of *Figure 9* (—), equation (20); ▲, from points of *Figure 9*, viscoelastic measurements; ●, $1/t_{gel}$ from $G'=G''$

measured from rheology experiments. However, for the temperature of 170°C, the calculated curves do not accurately fit the rheology experiment at the beginning of the crosslinking reaction. On the other hand, *Figure 9*, plotted without a semilogarithmic axis, shows that the kinetics of the crosslinking reaction determined either from titration of methyl acetate (full line) or from the kinetic law (dotted line) are in good agreement. *Figure 10* summarizes the Arrhenius diagram of the initial slopes V_0 ($V_0=dG'(t)/dt$, $t>0$), obtained from curves of *Figure 9* (full line, kinetic law through equation (20)) and from points of *Figure 9* (viscoelastic measurements). Then, the activation energy of this chemical reaction may be measured from the experimental extent of this reaction, the adjustment of a kinetic law, the inverse of t_{gel} and variations of the storage modulus $G'(t)_{\omega,T}$.

From relations (9) and (19) the sol fraction w_s can be expressed numerically as a function of time:

$$w_s = F(t) \tag{21}$$

From a resolution plot of this function we can deduce the gel time through a knowledge of the kinetic law from the following definition of the gel time: when $t \to t_{gel}$ then $w_s \to 1$ ($t > t_{gel}$, $w_s < 1$). The gel times for the different temperatures were compared in *Table 5* to the gel times determined from the time of crossover between G' and G''. Except for $T=170$°C, the results are in good agreement. On the other hand, from a knowledge of t_{gel} and the kinetic law (equation (9)) we can deduce the extent of the crosslinking reaction p_{gel} at the gel point. The values of p_{gel} are reported in *Table 5*. Whatever the temperatures, the extent of the reaction at the gel point is constant $p_{gel}=(5.0\pm0.5)\times10^{-3}$. This value is close to the theoretical value according to the theories of Stockmayer and Flory. At the gel point for tetrafunctional crosslinking:

$$p_{gel} = 1/r_w \tag{22}$$

$$p_{gel} = 4.2 \times 10^{-3}$$

This slight difference between the theoretical and the experimental value of p_{gel} may be mainly attributed to the determination of the molecular weights of copolymers by g.p.c.

CONCLUSIONS

The exchange reaction of ester groups in the presence of dibutyltin oxide as catalyst can be used in the molten state to cause the crosslinking of thermoplastic blends such as EVA copolymers and EMA copolymers. In the case of co-crosslinking of EVA/EMA blends, the crosslinking reaction can be assessed by classical chemical route through assessment of methyl acetate as a volatile product of the transesterification reaction and by dynamic rheological measurements.

The extent of the crosslinking reaction is well fitted by a kinetic law of second order coupled with a damping function which allows the densification of the network to be taken into account as the conversion rate increases. Dynamic rheology through storage modulus is also a useful method for following the extent of the crosslinking reaction of EVA/EMA blends. Knowledge of the extent of the crosslinking reaction permits calculation of the variations of the storage modulus *versus* time from theories for elastic modulus. There is a good agreement between these values and the experimental values of the storage modulus. In other words there is a good agreement between the kinetic data supplied by dynamic rheology and kinetic data supplied by chemical assessment.

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