**polymer**

# New transesterification between ester and alkoxysilane groups: application to ethylene-*co*-vinyl acetate copolymer crosslinking

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## Abstract

The transesterification between ester and alkoxysilane groups in the range of temperatures 100–250 °C takes place only in the presence of dibutyltin oxide (DBTO) as efficient catalyst. Without DBTO, no reaction is observed. This interchange reaction has been used to crosslink ethylene-*co*-vinylacetate copolymer. Kinetic and rheology data have shown that only two alkoxide groups from one tetrafunctional alkoxysilane molecule are involved in the crosslinking reaction. © 2002 Elsevier Science Ltd All rights reserved.

*Keywords:* Crosslinking; Ester–alkoxysilane exchange; Dibutyltin oxide

## 1. Introduction

The result of the reactive processing opens a wide field of potential applications such as the control and the stabilization of the morphology of immiscible polymer blends through the dynamic crosslinking of either the dispersed phase or of the major phase. The reactive processing was also used to promote the compatibility of immiscible polymer blends through the in situ synthesis of either grafted or block copolymers by chemical reactions between polymer chains in the interface during the processing operations [1–4]. At last, reactive blending was also a route to synthesize either grafted or block copolymers through interface reactions in the conditions of reactive extrusion [5, 6]. Whatever are the applications of the reactive processing, the kinetic of the chemical reactions must be compatible with the residence time of processes which is typically about 1 min for a continuous process such as extrusion and with the range of processing temperatures which depend upon chemical structure of the polymers. Furthermore, the chemical reactions must be selective to carry out the expected functionalization without formation of side reactions. At last, if the chemical modifications cause important changes in the rheological behavior and in consequence in the flowing of the polymers, the shaping step and the reactive step must be separated by using formulations temporally dormant. This is mainly the case of the crosslinking reactions when they are used on a line of elaboration of crosslinked articles. Because the radical reactions are not selective and give side reactions such as either chain scissions or crosslinking and because many polymers and copolymers contain ester groups in their backbone, our interest has concerned the ester interchange reactions.

Uncatalyzed ester–ester interchange reaction is not easy and occurs between 250 and 300 °C, but in this range of temperature many polymers undergo thermal decomposition [7–10]. Then to use these reactions to carry out chemical modification during processing operations, it is necessary to lower the temperature of interchange reaction. In previous works on the cocrosslinking of ethylene-*co*-vinyl acetate (EVA) and ethylene-*co*-methyl acrylate (EMA), we have shown that the temperature of acetic–acrylic esters interchange reaction may be lowered to 150 °C in the presence of dibutyltin oxide (DBTO) [11] with a greatest rate around 200 °C. Furthermore, the yield of ester–ester interchange reaction between methyl benzoate and EVA can reach about 40% in mole in 10 min at 180 °C in the presence of DBTO whereas it is about 10% in the presence of butyl titanate in the same experimental conditions that shows the higher efficiency of DBTO as catalyst of ester–ester interchange reaction [12]. Moreover our works with either aliphatic and aromatic model esters [2, 13,14] and with polymers bearing either pendant ester groups (EVA) [11] or ester groups in the backbone (polyethylene terephthalate) [2] have shown that DBTO

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$$CH_3-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-CH_3 \quad + \quad CH_3-O-\underset{\displaystyle \underset{CH_3}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{Si}}-O-CH_3$$

$$\downarrow$$

$$CH_3-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_3 \quad + \quad CH_3-O-\underset{\displaystyle \underset{CH_3}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{Si}}-O-CH_2-CH_3$$
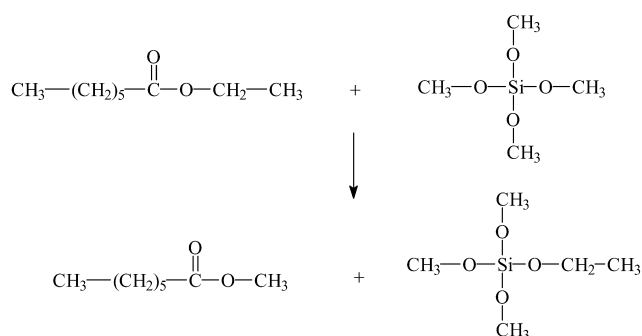
Fig. 1. Reactional scheme of the exchange reaction between ethyl heptanoate and TMOS.

reacts with ester groups to give tetraorganodistannoxanes which are well known as efficient catalysts for ester–alcohol interchange reaction [15,16]. Then DBTO is not a catalyst in the common sense. It is the precursor of 1-alcoxy-3-acyloxytetrabutyldistannoxanes which are the true catalysts in the ester–ester interchange reaction through ligand exchanges between free ester and distannoxane [13, 14]. The previous distannoxanes are also the catalysts of the ester–amide interchange reactions [17]. From chemical engineering point of view, the main advantage of DBTO as precursor of distannoxane synthesized in situ is to enable the catalyst dispersion on a molecular level during processing operations and to control the starting of the ester–ester interchange reaction. Because of its high efficiency for transesterification, DBTO can promote the reaction during processing operations with a kinetic compatible with the residence time typically about 1 min for a continuous process such as extrusion [18]. The main applications that we have developed are cocrosslinking of miscible EVA and EMA blends either in bulk [19] or dispersed in a polypropylene matrix [18]. DBTO has offered also the possibility to synthesize EVA grafted aromatic polyester copolymers in situ during blending of non-miscible polymer blends such as EVA–polyethylene terephthalate [3] and EVA–polybutylene terephthalate [6].

This paper is devoted to the study of the new interchange reaction ester–alkoxysilane in presence of DBTO as catalyst and its application to EVA crosslinking. In a first part, the evidence of this new reaction has been shown with the help of model esters and tetramethoxysilane (TMOS). In a second part, this reaction has been applied to the crosslinking of EVA by the tetrapropoxysilane (TPOS).

## 2. Experimental part

### 2.1. Reagents

For model studies, ethyl heptanoate ($C_6COOEt$), methyl heptanoate ($C_6COOMe$), TMOS, tetraethoxysilane (TEOS), propyl acetate (PA) and DBTO are commercial products

from Aldrich. TPOS is obtained from Roth Sochiel. All these products are used without further purification.

For studies in the melt conditions, EVA was supplied by ATO-FINA under the reference Evatane® 2803. It contains 28 wt% of vinyl acetate units (VA) which corresponds to a molar composition of 10.6% of VA units [14]. Average molecular weights in number ($M_n = 19$ kg mol$^{-1}$) and in weight ($M_w = 53.5$ kg mol$^{-1}$) were measured by size exclusion chromatography in trichlorobenzene at 135 °C. The microstructure of this copolymer was determined by $^{13}C$ NMR. 95% of VA units are isolated and 5% are in diads and triads.

### 2.2. Reactions with model esters

The model ester–alkoxysilane interchange reactions (Fig. 1) were carried out in closed flasks and analyzed by gas chromatography. Different conditions have been tested, with or without the presence of the catalyst DBTO. TMOS and ethyl heptanoate are introduced in equimolar quantity and diluted in pentadecane and the reactional medium is heated at different temperature. Two concentration of catalyst were used (0.5 and 1% molar of DBTO relatively to ester function) at different temperatures (110, 120, 140, 150 and 180 °C).

### 2.3. Reactions of EVA crosslinking

For the reaction between EVA and tetraalkoxysilane, EVA, TPOS and DBTO were mixed in the melt with a Haake plasticorder equipped with an internal mixer (Rheomix 600). The mixer chamber temperature was set at 100 °C and the rotation speed was 50 rpm. The time of mixing was limited to 3 min to avoid the beginning of the crosslinking. Then the crosslinking reaction was carried out in the oven of the thermobalance coupled with a gas chromatography analysis to follow the evolution of PA as by product of the interchange reaction.

VA/OR is the molar ratio VA units/alkoxide groups from TPOS. PA/VA is the molar fraction of PA as a result of the interchange reaction.

### 2.4. Analytical technics

A Hewlett-Packard gas chromatography (model 5890) equipped with a flame ionization detector (flow rate ratio $H_2/air = 0.1$) was used. The column of the chromatograph was filled with chromosorb 101.

For model reactions, calibration curve of methyl heptanoate in the pentadecane was established and used to follow the conversion of the ethyl heptanoate into methyl heptanoate.

The interchange reaction VA–TPOS was carried out under nitrogen (1 ml s$^{-1}$) in an Ugine-Eyraud B60 thermo-balance in isothermal conditions. Samples of the gas stream from the oven were injected into the chromatograph every

Table 1
Chromatograph retention times of pure gaseous reagents and products

| Compound | TMOS | PA | TEOS | $C_6COOMe$ | $C_6COOEt$ | Pentadecane |
|---|---|---|---|---|---|---|
| Retention time (min) | 1.4 | 1.6 | 2.14 | 5.3 | 6.1 | 7 |

3 min. 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 experiments. The instantaneous rate of PA formation from the exchange reaction between ester group and alkoxysilane taking place in the thermobalance was assumed to be proportional to the peak area on the chromatogram. A calibration coefficient was determined by isothermally evaporating PA in the thermobalance at constant rates measured by weight loss. Then the total extent of the crosslinking reaction of EVA was calculated from the area below the curve obtained by plotting the variations of the instantaneous rate of PA versus time.

Such method was developed by Cassagnau et al. [11] for the study of the kinetic of EVA/EMA blends crosslinking by titration of the methyl acetate which is a subproduct of the transesterification reaction.

In these experimental conditions, the retention time of different pure gaseous reagents and products of reaction either with models or with EVA are given in Table 1.

## 2.5. Volume and mass swelling rate ($G_v$ and $G_p$)

Samples (50–80 mg) were put in toluene and heating during 2 days at 80 °C. Evaluation of the mass of swollen sample at the equilibrium is obtained by extrapolation at $t = 0$ of the mass loss in function of time. To measure the weight of dried sample, the previous one is put in an oven under vacuum at 40 °C during 2 days in order to evaporate solvent and then weight.

Following parameters are determined from these measurements:

$G_p$ = mass of the swollen crosslinked sample/mass of dried crosslinked sample

$$G_v = 1 + (G_p - 1)\rho_2/\rho_1$$

where $\rho_2$ and $\rho_1$ are, respectively, the dried polymer and solvent densities.

From $G_v$, the polymer volume fraction at equilibrium swelling in solvent $\nu_2$ can be calculated:

$$\nu_2 = 1/G_v$$

Finally $\nu_2$ parameter allows to have a relation between the elastic modulus at equilibrium and the swelling of a network in a good solvent and be the reflect of the density of crosslinking [20].

## 2.6. Viscoelastic studies

The evolution of the viscoelastic properties with respect to crosslinking reaction were measured with a Rheometrics mechanical spectrometer (RMS800). Nitrogen was used to prevent thermal oxidation. Rheological kinetics were carried out in real time with a parallel-plate geometry (diameter: $\phi = 13$ mm). Beyond 170 °C, the modulus of the EVA during crosslinking increases very quickly compared with the measured time. Furthermore, the domain of frequency used for following the chemical reaction must define the relaxation terminal zone as the viscoelastic response of the uncrosslinked polymer. In the region characterized by the longest relaxation times the introduction of chemical crosslinks significantly changes the shape of the storage modulus–frequency curves. However, the pulsation $\omega$ of the measure must not be too low because the time of measurement must be short compared with the time of the reaction. Therefore, only one pulsation (1 rad/s) was monitored. During crosslinking the modulus varies about over four decades. In order to adjust the sensitivity of the apparatus to the high variation of the moduli, it is necessary to adjust the applied deformation during the crosslinking time sweep.

The thickness of the sample (gap of the parallel plate) was about 1 mm. The parallel plate system was preheated at the temperature of the experiment. The sample was introduced between the plates through the observation hole of the oven. From this method, an approximate calculation of the evolution of the temperature of the sample between two plates showed that the sample had reached the check temperature within 10 s.

## 3. Results and discussion

### 3.1. Model esters: kinetics by gas chromatography

The exchange reaction between ethyl heptanoate and TMOS (retention time in Table 1) was expected to lead to the formation of methyl heptanoate (retention time in Table 1) according to the scheme in Fig. 1. In this chemical scheme it is supposed that only one ester group reacts with one alkoxide group from TMOS. Because TMOS is tetrafunctional, two, three and four exchanges can also take place and lead to a mixture of monoethoxy-, diethoxy-, triethoxy-methoxysilane and TEOS (retention time in Table 1).

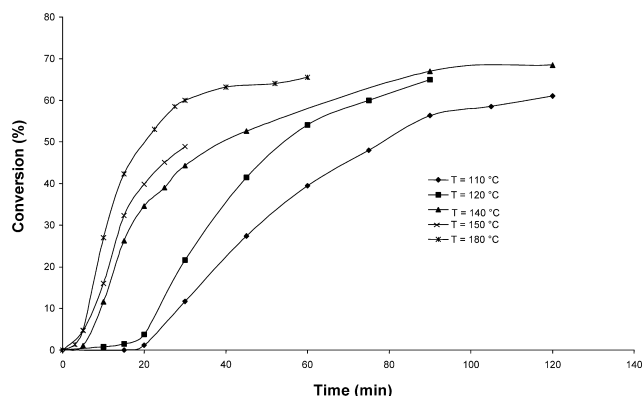As the reaction goes on with time, three non-identified

Fig. 2. Reaction kinetic ethyl heptanoate/TMOS in presence of 1% molar DBTO at different temperatures.



Fig. 3. Reaction kinetic ethyl heptanoate/TMOS in presence of 0.5% molar DBTO at different temperatures.

new peaks with retention times of 1.8, 1.93, and 2.19 min appear on the chromatogram with a predominance of the two last peaks. These peaks may correspond to the result of different degree of substitution of the tetraalkoxysilane.

The main purpose of this study being to show the efficiency of the ester–alkoxysilane exchange reaction, Figs. 2 and 3 show the evolution of methyl heptanoate with respect to the temperature and DBTO concentration. Without DBTO, no reaction is observed between ethyl heptanoate and TMOS until 235 °C. In the presence of DBTO, the interchange reaction takes place at about 100 °C and becomes faster at temperature higher than 140 °C. The kinetic of this exchange reaction is rapid at molar DBTO concentration as lower as 0.5% that shows its high efficiency. Below 140 °C, we observe an induction period which suggests the formation of alcoxy-acyloxytetrabutyl-distannoxane as the true catalyst of transesterification reaction as already explained in a previous study [13] concerning the interchange ester–ester reaction.

These results once more suggest that the rate of the transesterification at temperature below 150 °C is governed by the kinetic of distannoxanne formation.

These results show that all alkoxide groups of a tetraalkoxysilane can be exchanged with an ester. In consequence such reagents can be used to crosslink polymer and copolymer which contain pendant ester groups in its backbone and mainly in conditions of processing operations. This reaction has been used to crosslink EVA.

## 3.2. EVA crosslinking

### 3.2.1. Kinetics by gas chromatography

The influence of the concentration of TPOS assessed as VA/OR ratio has been studied from VA/OR = 10 to VA/OR = 1 with 0.5 phr (gram per hundred gram of EVA) of DBTO. Fig. 4 summarizes this study. The curves giving the evolution of PA formation with respect to the time are similar to those observed in the previous study with model esters (Figs. 2 and 3) and the kinetics are also comparable and compatible with reactive processing conditions. Whatever are the temperature and the TPOS concentrations, all the curves put in evidence a plateau which corresponds to an amount of PA always lower than the expected theoretical amount if all the alkoxide groups have reacted. Table 2 gather the experimental values of TPOS converted in PA at the plateau and the expected theoretical amount of PA by making the assumption that, respectively, only one, two, three and four alkoxide groups from the same TPOS molecule (Fig. 5) are involved in the exchange reaction. The comparison of these theoretical and

Table 2
Theoretical and experimental maximum VA conversion (%) with different VA/OR conditions

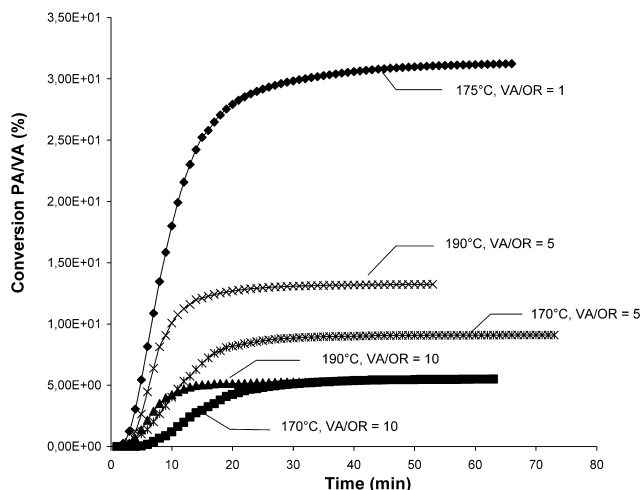| PA (% of VA) | VA/OR = 10 | VA/OR = 5 | VA/OR = 1 |
|---|---|---|---|
| Experimental | 5 | 10 | 35 |
| Theoretical $n = 1$ | 2.5 | 5 | 25 |
| Theoretical $n = 2$ | 5 | 10 | 50 |
| Theoretical $n = 3$ | 7.5 | 15 | 75 |
| Theoretical $n = 4$ | 10 | 20 | 100 |



Fig. 4. Reaction kinetic EVA/TPOS in presence of 0.5% molar DBTO at different temperatures and with different ratios between EVA and TPOS.
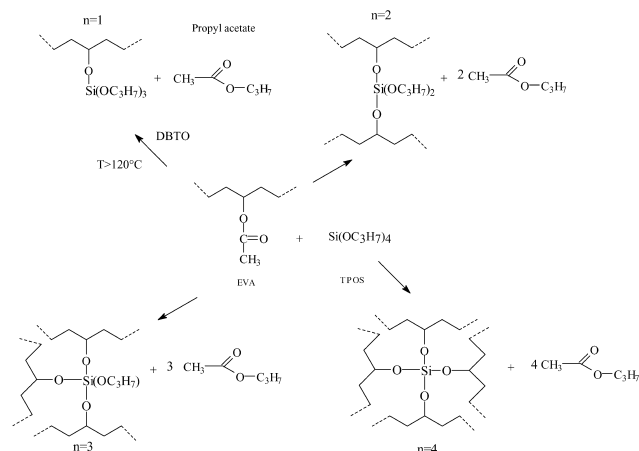
Fig. 5. Reactional scheme of the exchange reaction between ester group of EVA and alkoxide groups from TPOS: $n = 1–4$ for number of VA reacting with $n$ OR from the same TPOS molecule.

Table 3
Values of $t_{gel}$ (s) at different temperatures for different VA/OR ratios

| $T$ (°C) | $t_{gel}$ (s) | | |
|---|---|---|---|
| | VA/OR = 10 | VA/OR = 5 | VA/OR = 1 |
| 120 | | | 288 |
| 130 | | | 151 |
| 140 | | | 142 |
| 150 | | | 71 |
| 160 | | | 69 |
| 170 | 416 | 222 | 57 |
| 180 | | | 41 |
| 190 (195 for VA/OR = 1) | 240 | 129 | 18 |
| 210 | 139 | 77 | 13 |
| 230 | 100 | 58 | |

experimental value clearly shows that there is a good agreement between these values if two alkoxide groups of one TPOS molecule are involved in the exchange reaction with ester group of the EVA.

This observation suggests that the crosslinking can take place either in two steps (grafting and then crosslinking, Fig. 5) or through a simultaneous exchange between two alkoxide groups of one TPOS molecule with two pendant ester groups belonging to two different EVA chains (Fig. 5). The limitation of the collision probability between ester groups of the EVA and TPOS as the crosslinking density increases may contribute to decrease the speed of the reaction and so to reach the observed plateau.

### 3.3. Viscoelastic characterization

When the reaction of crosslinking occurs, the storage and loss moduli increase with time as the network results. The crosslink reaction strongly affects the molecular mobility, which then leads to large change in rheology. At a critical point, named gel point the polymer chains forms a three-dimensional network. Consequently, the gel point, occurs during a random process of subunits into larger and larger molecules of macroscale. A complete review of the rheology near the liquid–solid transition has been published by Winter and Mours [21]. The gel point can be characterized by dynamic mechanical analysis by the measurement of the complex modulus $G^*$ at various extents of reaction. Therefore, the self-similar regions of the system were examined at different length scale, at varying frequencies. At the gel point, storage and loss moduli have the same power law frequency dependency

$$G'(\omega) \propto G''(\omega) \propto \omega^n \tag{1}$$

where $n$ is the relaxation exponent. Beyond the gel point, the material tends to behave as a Hookean solid (permanent elasticity) at low frequencies or large scale.

Winter and Mours [21] reported that for a high molecular weight precursor, $n$ varies as:

$$n \approx 0.4–0.5 \tag{2}$$

The EVA precursor chains can be considered to be high molecular weight as $M_w > M_e$. Furthermore, a previous study [19] based on the EVA crosslinking by exchange reaction showed that a such network at gel point exhibits congruent moduli varying with frequency as $n = 1/2$:

$$G'(\omega) = G''(\omega) \propto \omega^{1/2} \tag{3}$$

Then, the crossover between $G'(t)$ and $G''(t)$ defines the gel time only in the present particular case as $n = 1/2$. As shown in Fig. 6, the gel time was measured as the time of $G'$ and $G''$ crossover.

Values of $t_{gel}$ at different temperatures for different VA/OR ratio are reported in Table 3. As expected $t_{gel}$ decreases with increasing temperature. Furthermore, Fig. 7 shows that the variation of $t_{gel}$ obeys an Arrhenius law. The value of the activation energy, $E \approx 47$ kJ/mol was found to be independent of the catalyst amount and VA/OR ratio. This result means that the reaction mechanism governing the exchange reaction between VA and alkoxide group is the same in the temperature range investigated (170–210 °C) in the present work. Furthermore, from the knowledge of the kinetics formation of PA, we can define the extent of the reaction as the conversion of VA. Coupling these kinetic laws with the gel time measured from Fig. 6, we can calculate the extent of the reaction at the gel point, $p_{gel}$. However, at high temperature, $t_{gel}$ is in the same order of the retention time of PA in the column of the chromatograph. From the recursive method developed by Miller and Macoscko [22,23], $p_{gel}$ can be calculated in the present case for long chains crosslinked via copolymerization with small molecule

$$p_{gel} = \frac{1}{\sqrt{r(f_w - 1)(g - 1)}} \tag{4}$$

where $r$ is the stoichiometric ratio and from our notation $r = VA/OR$. $f_w$ is the weight functionality of the EVA

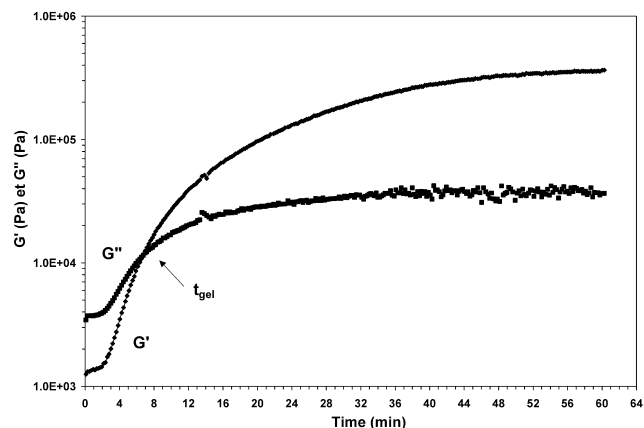Fig. 6. Variation of the shear complex modulus versus time for an EVA/alkoxysilane reaction system. VA/OR = 5, $\omega = 1$ rad/s, $T = 170\,°C$.



Fig. 7. Arrhenius plot of the inverse of $t_{gel}$. VA/OR = 1, 5, and 10.

chains. For the present EVA, $f_w \approx 265$. The functionality $g$ of the crosslinker agent is 4 assuming an equireactivity of the alkoxide group. However, as early discussed, chromatography analysis showed that the alkoxysilane behaves as a difunctional reagent. Consequently, it is very hazardous to calculate $p_{gel}$ with a good accuracy for the present crosslinking system. The order of magnitude of $p_{gel}$ is about:

$$p_{gel} \approx 0.01 \tag{5}$$

On the other hand Fig. 8 shows that the variation of the storage modulus considerably increase with increasing temperature. At the end of the crosslinking process, the storage modulus reaches a plateau. This plateau may be assumed to be the equilibrium shear elastic modulus defined by the theory of the rubber elasticity. It measures the density elasticity of the network, $\nu$. Several molecular models have been developed that predict the elastic and swelling behavior of polymer network. A review of various models that predict the extent of swelling that the network undergo when placed in good solvent and the relationships with the elastic modulus was made, as, for example, by Patel et al. [20]. In particular, they found that the Flory–Rhener model coupled with the phantom network predicts the experimental swelling results of imperfect network when the experimental value of the equilibrium elastic modulus $G_e$ is used

$$-\left[ \frac{\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2}{V_1 + \nu_2^{1/3}} \right] = \frac{G_e}{RT} = \nu \tag{6}$$

where $\chi$ is the polymer/solvent interaction parameter, $V_1$ the molar volume of solvent and $\nu_2$ is the polymer volume fraction at equilibrium swelling in solvent (toluene). In a previous study [19], we found that $\chi$ parameter is $\nu_2$ dependent on EVA/toluene system as:

$$\chi = 0.059 + 0.345\nu_2 \tag{7}$$

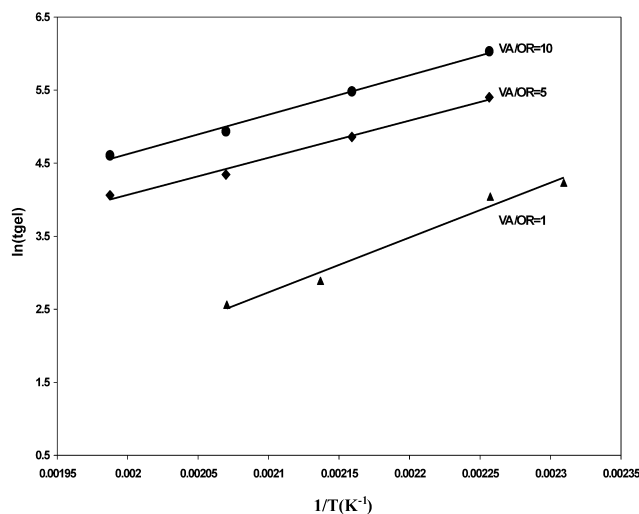Actually, Eq. (6) is a direct prediction of the original postulate of Flory and Rhener that swelling is determined by

balance between osmotic and elastic force. Furthermore, effects of trapped entanglements on swelling are include by this equation.

Fig. 9 shows that Eq. (6) agrees well with our experimental data whatever are the VA/OR ratio and the temperature used for the crosslinking process of the EVA network.

On the other hand, from the affine theory of the rubber elasticity, $G_e/RT$ is a measure of the concentration of elastically strands, $\nu$, if one assumes that only the network strands give rise to the rubber elasticity force. Gas chromatography allows us to measure the extent of the interchange reaction through the titration of PA, by-product of the reaction. However, the extent of the reaction is not directly a measure of the network junctions. Furthermore, as discussed in the chemical part, the four alkoxide groups are not equireactive as the conversion of the alkoxide group is only about 50% at the end of the crosslinking process. Starting from this analysis some assumptions can be made for comparing results obtained from chromatography
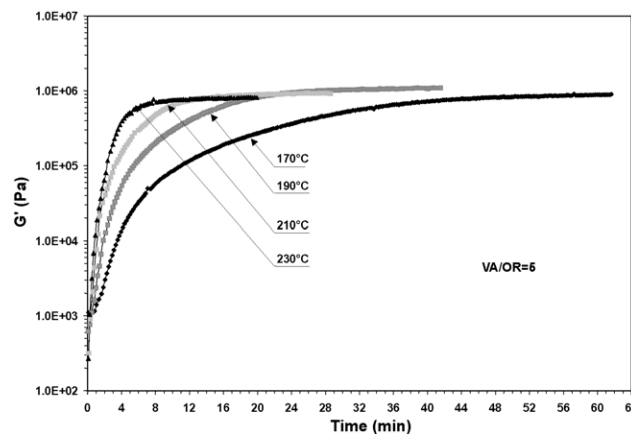


Fig. 8. Variation of the storage modulus versus time at different temperatures. Rheological kinetics, VA/OR = 5, $\omega = 1$ rad/s, $T = 170$, 190, 210 and 230 °C.

Table 4
Number of elastic strands, $\nu$, calculated from rheological data and from gas chromatography analysis

|  | VA/OR = 10 | VA/OR = 5 | VA/OR = 1 |
|---|---|---|---|
| $\nu$ from rheology (mol/m$^3$) | 20 | 130 | 600 |
| Propyl acetate from GC (mol/m$^3$) | 200 | 400 | 550 |

analysis and results obtained from rheology or swelling of the EVA network. Actually, a crosslink join is created when at least two PA come from the same Si(OR)$_4$ molecule. On the other hand, the functionality of the crosslink join is $f = 4$, 6 or 8 when two, three or four alkoxide groups have reacted to form a crosslink join, respectively, as shown in Fig. 5. Furthermore, assuming a perfect network, the relationship between the number $\nu$ of elastic strands and the number $\mu$ of crosslink joins is:

$$\mu = 2\nu/f$$

Consequently, the number of elastic strands is the number of alkoxide groups which have reacted whatever is the functionality of the crosslink join.

In Table 4, are reported the number of elastic strands calculated from rheological (or swelling) data and the number of elastic strands calculated from gas chromatography analysis as explained earlier. Considering the equimolar ratio (VA/OR = 1), a good agreement is obtained between rheological and gas chromatography data as the two technique measure the same amount of elastic strands. Furthermore, as the conversion of alkoxide is around 50%, we can assume that two alkoxide groups react by alkoxysilane compound to form a crosslink join so that the functionality of the network is 4.

A quite different trend is observed for higher VA/OR ratio. For example, for VA/OR = 10, gas chromatography predicts a number of elastic strands 10 times higher than those calculated from the elastic equilibrium modulus assuming that each alkoxide group which has reacted with an VA unit contributes to the elasticity of the network.

Actually these results mean for the lowest network density, the functionality of a crosslinking join cannot be considered to be equal to 4 as the network is an imperfect network.

## 4. Conclusion

The exchange reaction between ester and alkoxysilane groups takes place in the range of temperatures 100–250 °C only in presence of DBTO as efficient catalyst at concentration as lower as 0.5 wt%. Without DBTO no reaction is observed.

The kinetic studies have shown that this exchange reaction is compatible with the EVA processing conditions such as temperatures and residence times which are typically in order of 1 min for continuous process such as extrusion.

The transesterification ester–alkoxysilane has been applied to ethylene-*co*-vinylacetate copolymers crosslinking by a tetrafunctional alkoxysilane. The kinetic data of the acetic ester as by product of the exchange reaction and from rheology carried out in real time suggest that two alkoxy groups of the tetraalkoxysilane are concerned in the crosslinking reaction.
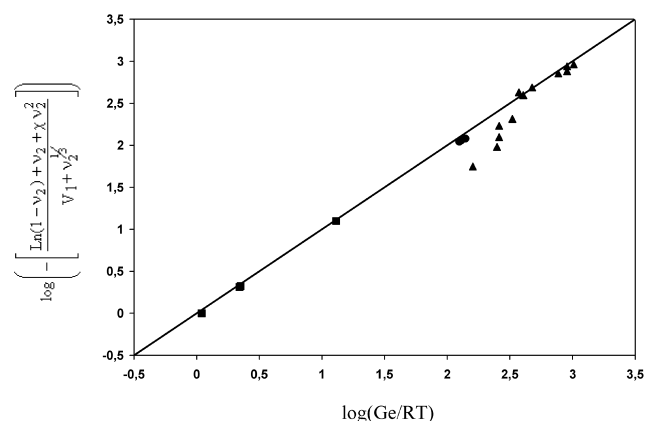


Fig. 9. Elastic strands concentration in the EVA network. Comparative results between swelling and rheological data (■ VA/OR = 10, ● VA/OR = 5 and ▲ VA/OR = 1).

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