Application of the rubber elasticity theory to the co-crosslinking of ethylene vinyl acetate and ethylene methyl acrylate copolymers by transesterification

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The molten state transesterification reaction of ester groups of ethylene vinyl acetate copolymers and ethylene acrylic ester copolymers leads to a tetrafunctional network. The time and temperature dependence on the network formation is assessed. From the statistical theory developed by Flory on tetrafunctional crosslinking networks, and assuming a log normal distribution of the crosslinkable sites, the theoretical gel network formation is compared with the experimental data assessment of the gel fraction. A good agreement is then obtained between experimental and theoretical values.

(Keywords: crosslinking; network; gel fraction; rubber elasticity)

Introduction

The phenomenon of rubber elasticity has been under investigation for over a century. A statistical theory of tetrafunctional crosslinking networks was presented by Flory[1] and Stockmayer[2] in the 1940s. An expression for the sol fraction, w_s, was derived using a method due to Flory. This method was used extensively for the elasticity of rubber networks and was extended to the structure of multifunctional networks with non-uniform primary polymer chains[3,4].

This method has also been used to characterize the network formation by co-crosslinking of miscible blends of ethylene vinyl acetate (EVA) and ethylene methyl acrylate (EMA) copolymers. Such a network forms through an exchange reaction of ester groups borne by the two copolymers, and contains tetrafunctional links only. However, these copolymers have a broad molecular weight distribution (polymolecularity $p_m \simeq 3.6$) and consequently a broad distribution of reactive sites. Assuming a log normal weight distribution, time and temperature dependence of the gel fraction formation calculated from Flory's theory has been compared with the experimental assessment of the gel fraction.

EVA/EMA network

Materials and methods. The amount of acetate and acrylate groups contained in these copolymers is about 28 wt% for each.

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). Molecular weights of EVA and EMA copolymer samples are, respectively: $M_{w1} = 53.5$ kg mol^{-1}, $M_{n1} = 19$ kg mol^{-1} and $M_{w2} = 94.3$ kg mol^{-1}, $M_{n2} = 22$ kg mol^{-1}.

The microstructure of these copolymers was determined by ^{13}C n.m.r. spectroscopy and 95% of vinyl acetate units are isolated. Therefore this copolymer can be assumed to be a statistical copolymer bearing 66 reactive sites (vinyl acetate units) per chain according to the number average molecular weight of the copolymer.

The miscible blend EVA/EMA/catalyst was fixed at 48/48/4 by weight. This blend was mixed in a twin-screw extruder. The temperature was regulated from 130°C at the feed zone to 165°C at the die. At these temperatures and for the residence times inside the extruder ($t \simeq 200$ s), no crosslinking occurs. The samples were then crosslinked at different temperatures ($T = 175$, 200 and 230°C) between two plates of a heating press. The accuracy of the reaction temperature was about ± 1°C.

The apparent gel content, g_{ap}, was determined by extraction with *p*-xylene at 70°C. Approximately 0.5 g of each sample was placed in 250 ml of *p*-xylene. Two days later ($\simeq 50$ h) the swollen network was dried under vacuum and weighed until a constant weight was reached. Then the calculation of the real gel content, g, was determined by assuming the non-solubility of the catalyst in the solvent. The catalyst may also be assumed to be trapped by the network. Then:

$$g = \frac{g_{ap} - C}{1 - C} \tag{1}$$

where C is the weight concentration of catalyst ($C = 0.04$).

Network formation. The chemical reaction of transesterification in the presence of dibutyl tin oxide (Bu_2SnO) as catalyst has been used to crosslink miscible blends of EVA and EMA copolymers. This reaction has been well characterized[5] in a molten state from titration of the volatile product of reaction (methyl acetate). This exchange reaction of ester groups creates a covalent chemical link through an ester bridge between the copolymer chains, as shown in *Figure 1* (reaction scheme). Then, such a network contains tetrafunctional links only.

A kinetic law has been proposed[5] for the description of the crosslinking reaction. The extent of the crosslinking reaction, p, 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:

$$p = \frac{ak_1t}{1 + ak_1t} p_\infty[1 - \exp(-t/\tau)] \tag{2}$$

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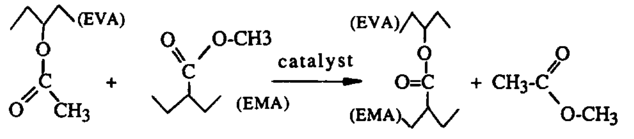

Figure 1 Chemical network formation by exchange reaction of ester groups of EVA and EMA copolymers: tetrafunctional links

where a is the initial molar concentration of acetate and acrylate groups in the molten state ($a = 1.48\,\mathrm{mol\,l^{-1}}$), k_1 is the rate constant:

$$k_1 = 2.11 \times 10^4 \exp(-58 \times 10^3/RT) \quad (3)$$

and τ and p are damping parameters of the network:

$$1/\tau = 8.35 \times 10^3 \exp(-44 \times 10^3/RT)$$
$$p_\infty = 0.23 \quad (4)$$

Assumptions. As the EVA/EMA sample contains EVA and EMA miscible chains with an identical concentration of crosslinkable sites (vinyl acetate site for EVA and methyl acrylate site for EMA), the EVA/EMA sample is assumed to be composed of identical linear polymer chains. The molecular weight distribution $W(M)$ of this 'EVA/EMA polymer' is assumed to be:

$$W(M) = \frac{W_1(M) + W_2(M)}{2} \quad (5)$$

with

$$\int_{-\infty}^{+\infty} W(M)\,\mathrm{d}\ln(M) = 1$$

$W_1(M)$ and $W_2(M)$ are the molecular weights of EVA and EMA samples, respectively. Therefore, the transitions of the EVA/EMA sample can be calculated from the relations:

$$M_w = (M_{w1} + M_{w2})/2 = 74\,\mathrm{kg\,mol^{-1}} \quad (6)$$
$$M_n = 2M_{n1}M_{n2}/(M_{n1} + M_{n2}) = 20.4\,\mathrm{kg\,mol^{-1}}$$

On the other hand a log normal form of the molecular weight distribution may be assumed, as shown in *Figure 2*:

$$W(M) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\ln^2\left(\frac{M}{M_0}\right)\Big/2\sigma^2\right] \quad (7)$$

with

$$M_w = M_0 \exp(\sigma^2/2) \text{ and } M_n = M_0 \exp(-\sigma^2/2)$$

therefore

$$p_m = M_w/M_n = \exp(\sigma^2)$$

As explained previously, the distribution of the vinyl reactive sites may be assumed to be statistical along the chains. Then the distribution $W(X)$ of the reactive sites will obey a log normal form, where X is the number of crosslinkable reactive sites per chain of molecular weight M. X_n and X_w are the number and weight average of crosslinkable sites, respectively.

Theoretical gel fraction

From definition, the relationship between gel fraction and sol fraction is:

$$g = 1 - w_s \quad (8)$$

For the calculation of the sol fraction, the following parameters were defined by Flory: p = fraction of reactive sites involved in crosslink, therefore p is the extent of the reaction; ϕ_s = probability that a randomly chosen non-crosslinked reactive site is part of the sol fraction; ϕ_s^2 = probability that a randomly chosen tetrafunctional crosslink belongs to the sol fraction.

The sol fraction, w_s, contains crosslinked reactive sites not belonging to the network ($p\phi_s^2$), and non-crosslinked reactive sites $(1-p)\phi_s$. Then:

$$w_s = p\phi_s^2 + (1-p)\phi_s \quad (9)$$

Generally $p \ll 1$ and the expression of ϕ_s is immediate, but in this case, where $0 < p < p_\infty (= 0.23)$, we have to resolve equation (9). Then:

$$\phi_s = \frac{p - 1 + \sqrt{(1-p)^2 + 4pw_s}}{2p} \quad (10)$$

Flory also introduced the probability, S_X, that a random primary polymer chain with X reactive sites is part of the sol fraction. This probability may be expressed as:

$$S_X = [1 - p(1 - \phi_s)]^X \quad (11)$$

So w_s can be calculated as follows:

$$w_s = \sum_X W_X S_X \quad (12)$$

or writing this equation in integral form:

$$w_s = \int_{-\infty}^{+\infty} W(X)[1 - p(1 - \phi_s)]^X\,\mathrm{d}\ln(X) \quad (13)$$

RESULTS AND DISCUSSION

Substituting p by the expression of the kinetic law (equation (2)) in relation (13), the time dependence of the gel fraction, $g = F(t)$, can be expressed. However, the determination of the gel fraction requires a numerical resolution of the equation, for example using the Van

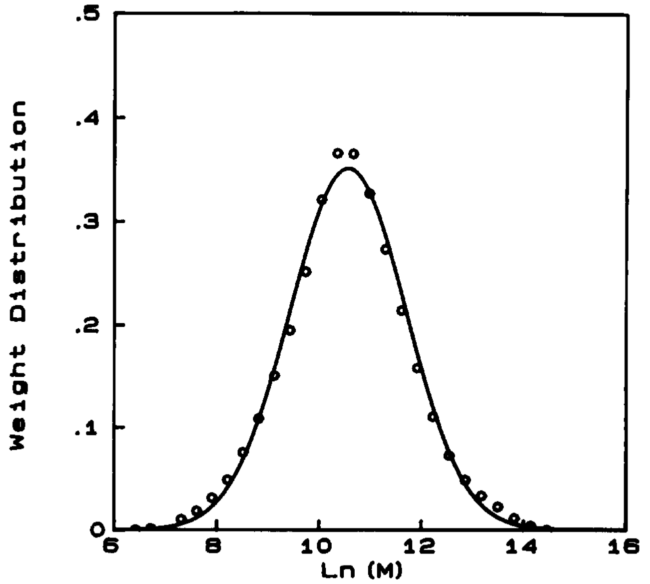

Figure 2 Molecular weight distribution of EVA/EMA sample: experimental data and log normal form

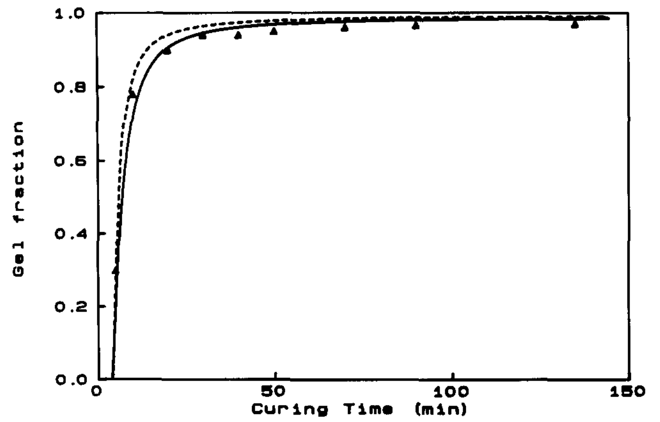

Figure 3 Gel fraction *versus* time: Schulz Zimm (- - -) and log normal (——) distribution of crosslinkable sites, $T=200°C$

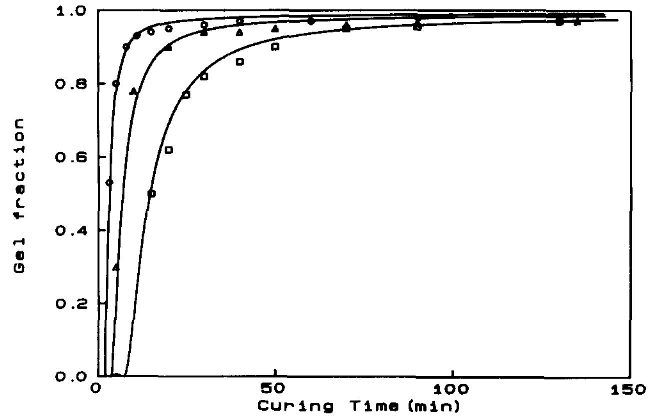

Figure 4 Gel fraction *versus* time at different temperatures: □, 175°C; △, 200°C; ○, 230°C. Log normal distribution

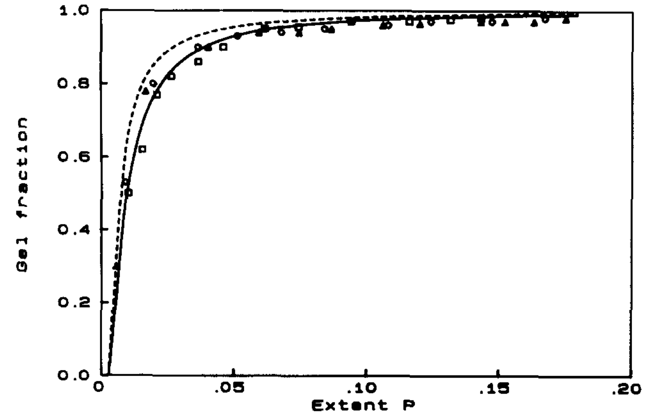

Figure 5 Gel fraction *versus* extent of the reaction. Experimental data for *T*: □, 175°C; △, 200°C; ○, 230°C. Schulz Zimm (- - -) and log normal (——) distribution of crosslinkable sites

Table 1 Values of the gel time, t_{gel}, from *Figure 3*, and extent of reaction at the gel point, p_{gel}, from equation (2)

Temperature (°C)	t_{gel} (min)	p_{gel} ($\times 10^{-3}$)
175	8.5	4.07
200	4.0	3.95
230	1.9	4.20

Wijngaarden–Dekker–Brent method. *Figure 3* shows the variation of the gel fraction *versus* curing time at 200°C. This figure compares the theoretical variations of the gel fraction from a Schulz Zimm distribution (dotted line) and a log normal distribution (solid line) of the reactive sites. As expected, the model is in good agreement with experimental data for the gel fraction when taking into account a log normal distribution.

On the other hand, as shown in *Figure 4*, such a model, with a log normal distribution of reactive sites, gives a very good description of the dependence on temperature ($T=170$, 200 and 230°C) of the gel fraction *versus* time. The intersection point between the curves and the curing time axis defines the gel time, t_{gel}. From definition, at this time the chains make a three-dimensional network and consequently the gel fraction appears. Values of t_{gel} are reported in *Table 1*.

From t_{gel}, the value of p_{gel}, the extent of the reaction at the gel point, can be obtained through relation (2); this value is constant, whatever the temperature:

$$p_{gel}=4.1\times10^{-3}$$

On the other hand the value of p_{gel} can be calculated by approximating relation (13):

at the gel point, $p \ll 1 \rightarrow \phi_s \simeq w_s$

$$w_s=\int_{-\infty}^{+\infty} W(X)[1-pX(1-\phi_s)]\,\mathrm{d}\ln(X)$$

$$w_s=1-(1-w_s)\int_{-\infty}^{+\infty} W(X)pX\,\mathrm{d}\ln(X) \qquad (14)$$

Then the extent of the reaction at the gel point ($w_s \rightarrow 1$) is:

$$p_{gel}=1/X_w=4.15\times10^{-3} \qquad (15)$$

This is the value of the intersection point between the curve and the axis representing extent of reaction, as shown in *Figure 5*. As expected, the curve obtained from a log normal distribution gives a very good fit with the experimental data of *Figure 5*. However, a slight difference is observed at $g\rightarrow1$. This difference may be attributed to a partial solubility, *s*, of the catalyst in the solvent. In fact, the relationship between the real gel content and the apparent gel content will be:

$$g=\frac{g_{ap}-C(1-s)}{1-C} \qquad (16)$$

Such an expression tends to give a higher value of experimental data and consequently a better agreement between experimental data and theoretical predictions.

Conclusions

The time and temperature dependence of the network formation by co-crosslinking of EVA/EMA miscible blends has been assessed. Such a network, which forms through an exchange reaction of ester groups of the two copolymers, contains tetrafunctional links only. From the statistical theory developed by Flory on tetrafunctional crosslinking networks, and assuming a log normal distribution of the crosslinkable sites, the theoretical gel network formation has been compared to the experimental data assessment of the gel fraction. Then, with such copolymers having a broad molecular weight distribution, a good agreement is obtained between experimental and theoretical values. On the other hand, knowledge of the kinetics of the crosslinking reaction allows the gel time at different temperatures to be obtained from the model, and consequently the extent of the reaction at the gel point.

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