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Polymer 42 (2001) 5207–5213

polymer

www.elsevier.nl/locate/polymer

Random crosslinking of an ethylene vinyl acetate copolymer and a metallocene polyolefin elastomer in the presence of polyfunctional monomers

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Received 25 August 2000; received in revised form 14 December 2000; accepted 22 December 2000

Abstract

A combination of Monte Carlo simulation and gel content experiments was used to study the molecular structural evolution of two randomly crosslinked systems: ethylene vinyl acetate copolymer and metallocene polyolefin elastomer in the presence of a triallyl cyanurate polyfunctional monomer (PFM). The molecular weight distributions, crosslinking density and PFM density evolutions are simulated. There exist gaps in the crosslinking density and the bonded PFM density, between the gel and the sol fractions. The density gaps widen as the crosslinking reaction proceeds. Towards the end of the reaction, the gel crosslinking density increases at a rate higher than that for the gel PFM density. The crosslinking level for the PFM molecules in the gel fraction is much higher than that in the sol fraction. The evolved structures for the two polymer systems during the reaction are also discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular weight distribution; Crosslinking; Polyfunctional monomer

1. Introduction

The modification of polymers using crosslinking and grafting methods is an important commercial process for the purpose of improving the physical and chemical properties of these materials. The use of polyfunctional monomers (PFMs) to promote crosslinking density is gaining more popularity in commercial practices. Many efforts have been made to the development of reactive modification of polymers during their molding processes. Many research projects have been conducted in this area for a better understanding of the structure–property relationships [1–3]. In a peroxide initiated polymer crosslinking reaction, peroxides decompose to produce highly reactive free radicals which in turn react with polymer molecules and produce free polymer radicals. These radicals randomly combine with one another to produce crosslinks. In these processes, the reaction rate as well as the molecular weight distribution (MWD) is most important. Polyfunctional monomers have been used to control the reaction rate or the molecular weight distribution effectively. Generally speaking, PFM coagents, which promote the crosslinking efficiency, will also accelerate the crosslinking behaviors [2]. The details of a crosslinking structure have far-reaching effects on the relaxation behaviors of a polymer [1]. For processes involving crosslinked polymers, such as foam molding and wire–cable coating, the control between process time and material relaxation time is most critical. It is thus, very helpful to have a working model that can be used to predict the molecular structural evolution under different processing conditions.

Many theories have been developed to describe the gel–sol partition phenomena in nonlinear polymerization. Recent developments include a combination of statistical theories, with kinetic models, to calculate the polymer properties such as MWD and crosslinking density distribution in the reaction path [4–8]. The use of Monte Carlo computer simulations is a powerful method for investigating the entire molecular constitution. Detailed structural informations, such as, the full molecular weight distribution profile, the distribution of the crosslink points among various polymer molecules, the sol–gel fraction and the spatial distribution of the crosslinked polymer chains can be revealed. The Monte Carlo simulation application for the properties of dense polymer networks range from rather rigid model systems, where the crosslinks cannot move, to highly complicated, fully mobile, randomly crosslinked polymer melts [9–12]. Tobita developed several Monte Carlo sampling techniques to investigate history-dependent crosslinking, branching reactions in free-radical polymerization,

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PII: S0032-3861(01)00003-9

and random crosslinking and degradation reactions of polymer chains [13–17]. For the random crosslinking of a homopolymer, Tobita rederived a series solution, which was solved by Kimura for Saito's integrodifferential equation, and verified with a computer simulation based on a Monte Carlo sampling technique [16–19]. Tobita's approach used a large number of polymer molecules as samples from the population, enabling one to determine the statistical properties effectively. With a modification of Tobita's Monte Carlo simulation algorithm, Tai was able to simulate the structural evolution in a random crosslinking reaction of a polymer in the presence of PFM molecules [2]. It was demonstrated that a multimodal distribution would be obtained for a very narrow initial MWD. As the Monte Carlo sampling technique can account for the residence time distribution effect of the reacting species, extension of this present method to various reactor types is straightforward, if the parameters for the related reaction kinetics are available.

Ethylene vinyl acetate copolymers (EVA) and metallocene polyolefin elastomers (m-POE) are popular in polymeric foam applications. Similar to processing of low density polyethylene (LDPE) foams, EVA and m-POE are modified using crosslinking methods to obtain a high melt strength [4,5,20,21]. Metallocene polyolefins are relatively new and EVA has received less research attention than LDPE. Trially cyanurate (TAC) is an effective PFM for polyolefins. The molecular structural evolution in a crosslinking LDPE–TAC system, simulated using a previously presented Monte-Carlo algorithm, has been explored thoroughly [2]. In this study, the molecular structural development of EVA–TAC and m-POE–TAC, such as the crosslinking point distribution in the gel fraction, the MWD in the sol fraction, sol–gel partition phenomena, PFM distribution in each of the sol–gel fractions, were investigated. The research results will be helpful in gaining some insight into the reactive processing of these polymer–PFM systems.

2. Experimental

2.1. Materials

The EVA resin used in this study was UE 630 supplied by USI Far East Corporation. It has a vinyl acetate content of 16%, a melt index of 1.5 g/10 min and a density of 0.937 g/cm^3. Its weight average molecular weight, $\bar{M}_w$, is 110 000 g/mol and its number average molecular weight, $\bar{M}_n$, is 37 000 g/mol. The m-POE resin used in this study was Engage EG 8100 supplied by DuPont Dow Elastomers. It has an octene comonomer content of 24%, a melt index of 1 g/10 min and a density of 0.87 g/cm^3. Its $\bar{M}_w$ is 113 500 g/mol and its $\bar{M}_n$ is 57 600 g/mol. The organic peroxide used was dicumyl peroxide (DCP) with an assay higher than 99%, supplied by Coin Chemicals Corporation. Triallyl cyanurate, which served as a crosslinking coagent, was supplied by Aldrich Chemicals Inc. It was stored in a −40°C refrigerator. All materials were used as received.

2.2. Sample preparation and analysis

The EVA–TAC and m-POE–TAC compounds were prepared using a Brabender Plasti-Corder PL2000 at 110°C at a mixing speed of 30 rpm. Roller blade type rotors were chosen for mixing the three components. The amounts of DCP and TAC added to the compounds were the same, each at a weight fraction of 1%. The resin pellets were first placed into the mixing chamber and allowed to melt for one minute, followed by TAC for another minute. After complete mixing of the compounds, DCP was added and mixing was maintained for one more minute. The torque readings were closely watched to avoid any scorch of the compounds. The compounds were quickly taken out of the mixing chamber and pressed into a thin sheet using a compression molding machine at a temperature of 110°C. These sheet specimens were then placed in a vacuum oven and heated isothermally at 200°C for more than 2 h to ensure full DCP conversion. The gel contents were then measured using the reflux extraction method. A sample of about 0.3 g was placed in a pouch made of 120 mesh stainless steel cloth and immersed in boiling xylene for 12 h. The amount of remaining gel was calculated according to ASTM D2765 [22]. The initial molecular weight distribution of the EVA and m-POE resins used here was assumed to follow a Schulz-Zimm distribution, whose weight fraction distribution is given by:

$$W(r) = \frac{\sigma^{\sigma}}{u\Gamma(\sigma)}\left(\frac{r}{u}\right)^{\sigma}\exp\left(-\frac{\sigma r}{u}\right), \quad (1)$$

where r is the chain length, u the number average chain length and σ a measure of the distribution breadth, defined as:

$$\sigma = \frac{1}{(\bar{M}_w/\bar{M}_n) - 1} = \frac{\bar{M}_n}{\bar{M}_w - \bar{M}_n}. \quad (2)$$

$\Gamma(\sigma)$ is the gamma function of σ. Crosslinking densities ρ were then calculated using the following equation [17,23]:

$$w^{\mathrm{gel}} = 1 - \left(\frac{\sigma}{\sigma + \rho u w^{\mathrm{gel}}}\right)^{\sigma+1}, \quad (3)$$

where w^{gel} is the experimental gel weight fraction.

3. Results and discussion

The algorithm for simulating the molecular structural evolution in a polymer–PFM system using the Monte Carlo method is presented in Appendix A. In our previous study on the LDPE–TAC system, various distributions, such as the fractional MWDs for polymers containing various numbers of crosslinkages or PFM molecules, the

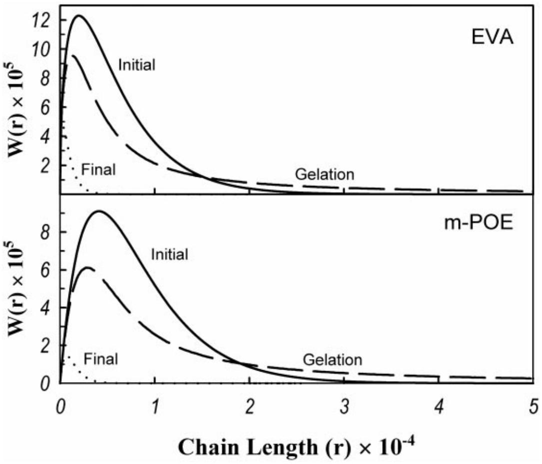

Fig. 1. Molecular weight distributions at various stages of crosslinking reaction for the EVA–TAC and m-POE–TAC systems.

crosslinking density and the PFM density as a function of the chain length were fully explored. In this article, the emphasis is on the overall distributions of crosslinking density and PFM density, within the gel and the sol fractions, in the path of the crosslinking reaction. The MWD curves for EVA and m-POE systems at 1 wt% of TAC at various crosslinking stages are shown in Fig. 1. In the beginning of a crosslinking reaction, polymer molecules combine with one another to form larger molecules. The polymer fractions with higher molecular weights (longer chains) increase at the expense of the fractions with lower molecular weights. The MWD curves at the gel point possess extremely long tails. Past the gel point, a gel network is formed. More and more large molecules join the gel network in the course of the crosslinking reaction. At the end of the reaction, only a small fraction of molecules exist in the residual sol fraction. Most of these molecules have low molecular weight. A polymer with a higher molecular weight has a higher chance to crosslink and enters the gel fraction. It is also interesting to note that each of the final MWD curves resembles its corresponding initial MWD curves.

Table 1 tabulates the crosslinking behaviors of various polymer systems, with or without TAC. To simulate the formation of a gel molecule with its molecular weight approaching infinity, the gel point in this table was located by increasing the crosslinking density to the point, where more than two out of 2000 000 samples had a molecular weight higher than 10^{12} g/mol. This criterion is in accordance with the divergence of the weight average molecular weight. This criterion had also been successfully implemented in an earlier article to predict correctly the gel points of a randomly crosslinking LDPE system and a randomly crosslinking sharp-MWD homopolymer system, whose gel points can be theoretically predicted by the Flory–Stockmayer theory [2]. The percolation approach is often capable of satisfactorily analyzing the properties of polymeric gels. However, to characterize the state of gelation within the percolation framework, both the functionality of percolation units and the concentration of crosslinks must be included. It is difficult to specify the functionality of percolation units in the polymer–PFM system. Experimental methods, such as the characterization of rheological or viscoelatic behaviors can also be used to locate the gel point; but they have to be combined with other methods (statistical models, numerical simulations or reaction kinetic models) to give a quantitative gel point. The addition of TAC is very effective in promoting the crosslinking density of polyolefin systems. The TAC fractions in the three polymer systems are the same, all at 1 wt%. An increase in crosslinking density ranging from 70 to 160% was observed. TAC is particularly effective for the polyolefin copolymers. The higher crosslinking efficiency for EVA could be attributed to the acetyl group on the copolymer, which stabilizes a radical on the attached carbon by resonance. While for m-POE, since there are more (compared with LDPE) evenly distributed long and short chain branches, more tertiary sites exist in the polymer. This provides more sites for efficient radical additions and results in higher crosslinking efficiency. It should be noted that the crosslinking yields in m-POE systems are actually higher than those in EVA systems. The higher crosslinking density values in EVA systems are due to the fact that the bulky acetyl side group in EVA is not accounted as a chain segment. It is also interesting to find that a polymer with a higher crosslinking yield in its homopolymer state will also have a higher crosslinking yield when a PFM is added. One can also see from Table 1 that gelation

Table 1
A comparison of crosslinking behaviors of various systems

	LDPE[a]	LDPE–TAC[b]	EVA	EVA–TAC	m-POE	m-POE–TAC
Gel content	0.705	0.841	0.837	0.937	0.860	0.971
Number of tie points/PFM		0.641		1.38		1.65
Fraction of reacted PFM functional groups		0.214		0.459		0.550
ρ	1.95×10^{-4}	3.35×10^{-4}	7.12×10^{-4}	1.44×10^{-3}	4.76×10^{-4}	1.22×10^{-3}
$\rho_{\text{gel point}}$	6.48×10^{-5}	6.43×10^{-5}	1.69×10^{-4}	1.67×10^{-4}	1.23×10^{-4}	1.22×10^{-4}
Degree of conversion at gel point	0.332	0.272	0.238	0.190	0.259	0.185

[a] Ref. [4].

[b] Ref. [2].

occurs at a lower crosslinking density when TAC molecules are added, since the introduction of tri-functional crosslinking coagents increases the branching probability in the polymer–PFM system. As the TAC concentrations are low and only a small fraction of these PFMs are tri-connected (the fraction of PFMs whose three functional groups have all reacted is 1% for LDPE–TAC and 16% for m-POE–TAC), the crosslinking densities for the incipient network formation for systems with and without PFMs are not far apart. However, in terms of the degree of conversion at which gelation occurs, we see a more dramatic drop for all the three systems when a PFM is added. This implies that gelation actually occurs earlier and scorch can be an issue, so that precaution should be exercised during the processing of a polymer–PFM system. It can be concluded here that a PFM, which promotes the crosslinking level, will accelerate the gelation process even if it does not accelerate the crosslinking reaction.

Rheological properties are vital to the continuous reactive-processing of a polymer–PFM system. These properties are affected profoundly by the overall structural evolution of the system. Fig. 2 shows the growth of the average molecular weights for both systems at a low conversion degree. At a conversion degree of 10%, the increase in $\bar{M}_n$ is moderate, 8.5% for EVA–TAC and 13% for m-POE–TAC. In comparison, the increase in $\bar{M}_w$ is very dramatic, 92% for EVA–TAC and 88% for m-POE–TAC. The EVA system, with a higher polydispersity index, shows a higher growth rate in $\bar{M}_w$ and a lower growth rate in $\bar{M}_n$ (compared with the m-POE system). The m-POE system has a more uniform initial molecular weight distribution and thus shows more uniform molecular weight growth rates in $\bar{M}_n$ and $\bar{M}_w$. The higher growth rate in $\bar{M}_w$ over $\bar{M}_n$ indicates clearly that a crosslinking reaction will broaden the MWD. The $\bar{M}_w$s of the two polymers happen to be close to one another. At the same crosslinking density level, $\bar{M}_w$ grows faster for a polymer with a higher polydispersity index. The more dramatic increase of $\bar{M}_w$ also imposes a serious threat to a polymer–PFM reactive process. The relationship between the zero shear viscosity of a highly entangled polymer and the weight average molecular weight is given using [24]:

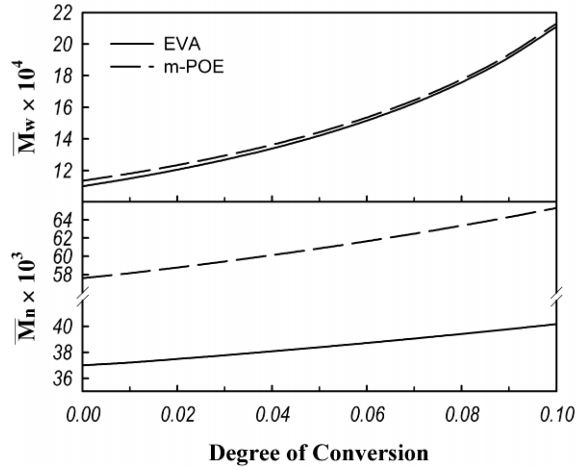

Fig. 2. Variation in $\bar{M}_w$ and $\bar{M}_n$ with the degree of conversion for the EVA–TAC and m-POE–TAC systems.

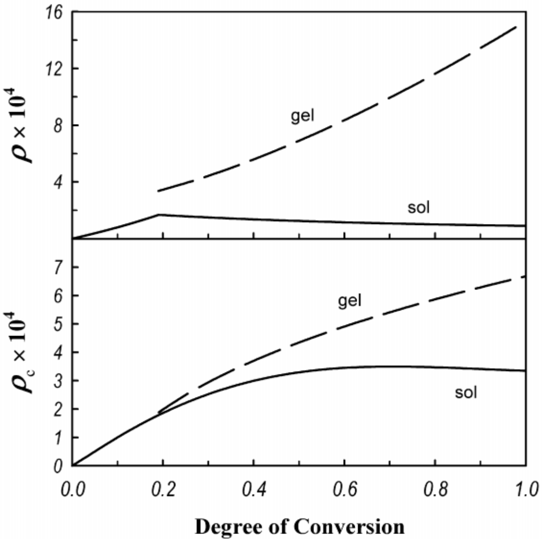

Fig. 3. Variation in the crosslinking density (ρ) and the PFM density (ρ_c) in the gel and the sol fractions, respectively, for the EVA–TAC system.

$$\eta_0 = K\bar{M}_w^{3.4}. \tag{4}$$

It is known that the melt viscosity is closely related to $\bar{M}_w$ than to $\bar{M}_n$. In assessing the processability for melt flow processes like mixing or forming, the growth rate of $\bar{M}_w$ becomes an important indicator. A run-away problem could occur in processing polymer–PFM melts if a premature crosslinking reaction triggers excessive shear heating. The Monte Carlo simulation provides us with detailed MWDs for these systems, which makes the evaluation of average molecular weight at various reaction extents possible if chemical kinetic data for the crosslinking reaction are available.

For a randomly crosslinked homopolymer system, the crosslinkage distribution within the gel fraction can be predicted using [25]:

$$\rho^{\mathrm{gel}} = \rho(2 - w^{\mathrm{gel}}), \tag{5}$$

where ρ^{gel} is the crosslinking density within the gel fraction. No such analytical equation exists for a polymer–PFM system. Meanwhile, it is very interesting to explore the gel–sol partition phenomenon in a crosslinking polymer–PFM system. In Figs. 3 and 4, we demonstrate the distributions of crosslinked units (ρ) and attached PFMs (ρ_c) within the gel and the sol fractions as the crosslinking reaction progresses. The distribution behaviors in the two systems, EVA–TAC and m-POE–TAC, are similar. There is a discontinuity at the gel point in the sol crosslinking density curve. Although, the overall crosslinking density increases

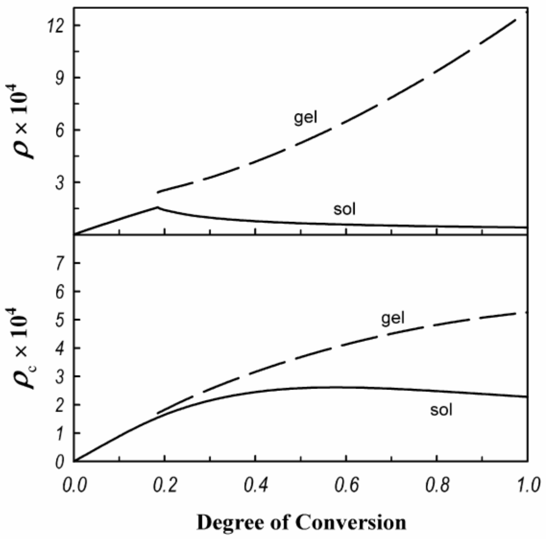

Fig. 4. Variation in the crosslinking density (ρ) and the PFM density (ρ_c) in the gel and the sol fractions, respectively, for the m-POE–TAC system.

as the crosslinking reaction proceeds, the sol crosslinking density decreases past the gel point. In our earlier study on the crosslinking LDPE–TAC system, we demonstrated that the crosslinking density in a chain increased initially with increasing chain length and then levelled off at a very high chain length (about 10^5 repeating units); also from the simulated MWD curves we knew that the molecular weight of the sol polymer molecules became lower and lower as the crosslinking reaction proceeded [2]. That is, most polymer molecules with a high chain length within the sol fraction have become attached to the gel network in the crosslinking path. These polymer molecules have a higher chain crosslinking density. As these molecules become attached to the gel network, the crosslinking density within the sol fraction decreases. The gel crosslinking density increases monotonically from gel point to the end of the reaction. At the gel point, the gel crosslinking density value is twice that of the overall crosslinking density. The gap between the crosslinking densities of the two fractions widens as the crosslinking reaction proceeds. At the end of reaction, the crosslinking density ratios between the two fractions are 17 for EVA–TAC and 31.5 for m-POE–TAC.

The PFM density distribution behavior is quite different from that of the crosslinking density distribution. There is no obvious discontinuity point in the sol PFM density curves. A maximum exists in the sol PFM density curves. The gel PFM density curves, on the other hand, show a monotonically increasing trend. There also exists a gap between the PFM density curves of the two fractions. The difference between the PFM density values of the two fractions is small at the gel point. As we previously demonstrated for the LDPE–TAC system [2], the PFM density in a chain increases rapidly with increasing chain length and then levels off at a short chain length (about 500 repeating units). The fraction of molecules with low PFM density is relatively small and its contribution to the sol PFM density is consequently small (compared with the crosslinking density distribution). As the crosslinking reaction proceeds, polymer chains with a high PFM density join the gel fraction. The gap between the PFM densities of the two fractions widens. The PFM density ratio between the two fractions at the end of reaction is 2 for EVA–TAC and 2.3 for m-POE–TAC. These numbers are considerably smaller than those of the crosslinking density ratios. The gel crosslinking density curves in Figs. 3 and 4 are concave upward, while the gel TAC density curves are concave downward. The gel PFM density increases at a decreasing rate while the crosslinking density increases at an increasing rate. This implies that, toward the end of the reaction, a higher fraction of the pedant functional groups of the PFM molecules in the gel fraction have reacted and the crosslink points are generated. (Note that the junction point between a PFM, with two pedant functional groups, and a polymer chain is not counted as a crosslink point, see Appendix A.) While the number of the attached PFM increases at a low rate, the crosslinking density increases at a much higher rate through the assumption of the remaining double bonds of those attached PFMs. The difference between the number of PFM molecules in the two fractions is not great, but the difference in their contributions to the crosslinking density is much greater. The PFM molecules in the gel fraction are highly crosslinked, while a high proportion of the PFM molecules in the sol fraction may have two pendant functional groups.

4. Conclusions

TAC is a very effective PFM for promoting the crosslinking level in polyolefin copolymers. With the addition of 1 wt% of TAC, the increase in crosslinking density is 102% for EVA and 160% for m-POE. The increase in crosslinking level also accelerates the gelation process for the polymer–PFM system. In the pregelation period, the polymer polydispersity index increases as the crosslinking reaction proceeds. At the same initial $\bar{M}_w$, the polymer with a higher initial polydispersity index will have a higher $\bar{M}_w$ growth rate. In the course of the reaction, the sol crosslinking density increases up to the gel point and then begins to decrease, while the gel crosslinking density increases with an upward concave trend. The sol PFM density shows a different trend. The sol PFM density increases initially and then begins to decrease slowly in the middle of the reaction. The gel PFM density increases monotonically with a downward concave trend.

Acknowledgements

The author gratefully acknowledges funding from National Science Council of the Republic of China (Grant number 90-2216-E-214-004).

Appendix A. Simulation algorithm [2,16,17]

Suppose that there are polymer molecules and tri-functional TAC monomers in the system initially and the cross-linkages are introduced randomly among these molecules. The basic assumptions are:

1. crosslinking proceeds without any cycle formation;
2. only two types of linkages exist: the one formed by the combination of two polymer radicals and the other formed by the combination between a polymer radical and a TAC molecule;
3. all functional groups on the TAC are equally reactive; the principle of equal reactivity is assumed to hold throughout the crosslinking reaction so that the reactivity of a given functional group is independent of the size or structure of the molecule to which it is attached [26,27].

In the simulation, one unit was selected randomly from all primary molecules existing in the reaction system. The size of the molecule to which this particular unit belonged was determined by the Monte Carlo method. This molecule was designated as the zeroth generation polymer molecule. The chain length of the selected primary EVA or m-POE molecule was determined using Eq. (1). After choosing the zeroth generation polymer molecule, we then proceeded to determine the number of tie points that it possessed. Let P_0, P_1, P_2 and P_3 be the probabilities that a TAC molecule has connected to zero, one, two and three polymer molecules, respectively. Since the probability that any one of the functional groups in a TAC molecule has reacted, p, is the same for all functional groups, the probabilities, P_0, P_1, P_2 and P_3 are given by a binomial distribution:

$$P_j = \binom{3}{j} p^j (1-p)^{3-j}. \tag{A.1}$$

The probability for each unit of all primary polymer molecules to possess a tie point is the same and is equal to the overall tie point density. A tie point is defined here as either a polymer–polymer tribranching point or a polymer–PFM junction point. The combination of two polymer radicals forms a crosslinkage with two crosslinked units. When a polymer radical combines with a PFM molecule, a single tie point, but no crosslink, is formed. Only, when this particular PFM molecule reacts with one more polymer radical, two tie points and two crosslinked units are formed. If this particular PFM reacts with two more polymer radicals, i.e. all three functional groups have reacted; there are three tie points and three crosslinked units. The number of tie points, n, on a primary polymer molecule of chain length r can be determined from a binomial distribution:

$$p(n) = \binom{r}{n} \rho'^{\,n} (1-\rho')^{r-n}, \tag{A.2}$$

where ρ' is defined as the fraction of units that either bear tribranching polymer–polymer tie points or polymer–PFM tie points.

The next thing was to determine the type of each tie point. Assume that the overall tie point density for polymer with an initiator alone is ρ_1 and the overall tie point density of polymer with the presence of TAC is ρ'_2. Notice that, in the absence of TAC molecules, the overall tie point density is equal to the crosslinking density. With the presence of TAC molecules, the system consists of polymer–polymer crosslink points, polymer–TAC–polymer crosslink points and pedant polymer–TAC tie points. The increase in tie point density is due to the creation of polymer–TAC tie points. The fractions of polymer–polymer and polymer–TAC tie points are ρ_1/ρ'_2 and $1-(\rho_1/\rho'_2)$, respectively. If a polymer–polymer tie point is selected, the chain length of the connected primary EVA or m-POE molecules (next generation) can again be determined using Eq. (1). If, instead, a polymer–TAC tie point is selected, then the number of polymer molecules connected to this TAC molecule must be determined. The equation required to calculate the probabilities for the TAC molecule on the selected polymer–TAC tie point to be connected to one, two or three polymer molecules is

$$P_C(n) = \binom{2}{n-1} p^{n-1} (1-p)^{3-n}, \tag{A.3}$$

where n can be either 1, 2 or 3. If there are more than one polymer molecules connected to this TAC molecule, the chain length of the connected primary polymer molecules (next generation) can again be determined using Eq. (1). These procedures were reiterated until all primary polymer molecules fail to be connected to the next generation. Once the connection rule among the primary polymer molecules and the PFM molecules was made clear, the Monte Carlo computer simulation could be implemented to investigate the entire molecular constitution.

There are two parameters in the simulation: ρ' and p. The method for obtaining these simulation parameters is described as follows. Let there be N_P structural units in the polymer system. After the crosslinking reaction, there are X_P polymer–polymer tie points in the homopolymer system. The crosslinking density is then

$$\rho_1 = \frac{X_P}{N_P}. \tag{A.4}$$

When N_C TAC molecules are introduced into the system, additional X_T polymer–TAC tie points are created. Let, N_0, N_1, N_2, N_3 be the number of TAC molecules in the system that have connected to 0, 1, 2, 3 polymer molecules, respectively. It follows

$$N_C = N_0 + N_1 + N_2 + N_3 \tag{A.5}$$

and

$$X_T = X_P + N_1 + 2N_2 + 3N_3 \tag{A.6}$$

and the overall tie point density becomes

$$\rho_2' = \frac{X_T}{N_P}. \tag{A.7}$$

Only those units, bearing TAC molecules, which have connected to more than two polymer molecules can be counted as crosslinked units. The number of crosslinked units is then

$$X_C = 2N_2 + 3N_3. \tag{A.8}$$

The crosslinking density for the system with the presence of TAC molecules then becomes

$$\rho_2 = \frac{X_P + X_C}{N_P} \tag{A.9}$$

and

$$P_0 = \frac{N_0}{N_C}, \qquad P_1 = \frac{N_1}{N_C}, \qquad P_2 = \frac{N_2}{N_C}, \qquad P_3 = \frac{N_3}{N_C}. \tag{A.10}$$

Combining Eqs. (A.4), (A.8) and (A.9), we have

$$2P_2 + 3P_3 = (\rho_2 - \rho_1)(N_P/N_C). \tag{A.11}$$

N_P and N_C are known values for the system and ρ_1, ρ_2 can be obtained from gel content experiments, using Eq. (3). Then, p can be obtained by solving Eq. (A.11) and ρ' can be obtained using Eq. (A.7).

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