

Kinetic Study on Cross-Linking and Blowing Behavior of EVA/EPDM/CPE High Elasticity Material

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ABSTRACT: Blend of ethylene-vinyl acetate copolymer (EVA), ethylene-propylene-diene terpolymer rubber (EPDM), and chlorinated polyethylene (CPE) filled with talc was cross-linked with dicumyl peroxide and blown simultaneously with azodicarbonamide for preparation of high elasticity material by injecting, cross-linking, and blowing process. It had excellent mechanical properties and elasticity. It was found that mechanical properties were a function of cross-linking and blowing temperature and time and formula. A good cross-linking and blowing temperature was in the range of 440–450 K and the optimum temperature and time were 448 K and 360 s, respectively. Kinetics of both cross-linking and blowing reactions were investigated by closed nonrotor torque rheometer. The results showed

that both cross-linking and blowing reactions were first order. The activation energy of the cross-linking reaction was higher than that of the blowing reaction. With increasing of EPDM content, the activation energy of the cross-linking reaction reduced whereas it increased for the blowing reaction. The gas cell morphology was characterized by scanning electron microscopy (SEM). The results of SEM and mechanical property analyses showed that the morphology and mechanical properties were improved by incorporating CPE. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 897–908, 2007

Key words: kinetic; activation energy; cross-linking; injection molding; blending

INTRODUCTION

Cross-linking and blowing process of ethylene-vinyl acetate copolymer (EVA) is still active research area. EVA and ethylene-propylene-diene terpolymer rubber (EPDM) could be melt mixed because the breakdown of EVA and EPDM was minimum at 110–120°C and 150–160°C.¹ Blend (EVA/EPDM) had partial miscibility in the amorphous region.² Dicumyl peroxide (DCP) was used as an initiator in cross-linking EVA/EPDM over the entire range of composition.³ Consequently, miscibility and mechanical properties of EVA/EPDM were improved. Mishra et al.⁴ studied the cross-linking characteristics of EVA/EPDM by differential scanning calorimetry and torque rheometer. They concluded that the activation energy decreased with an increase of EVA content in the blend and the cure rate increased as well.

The viscosity of EVA/EPDM increased with EPDM content, but low vinyl acetate (VA) content of EVA also rendered high viscosity.⁵ To ensure that the extruding and injecting processes were favorably and successfully, the blend ratio of EVA/EPDM

must be controlled to obtain an optimum viscosity for extruding and injecting.⁶

Chlorinated polyethylene (CPE) used at a level of 20 parts in the natural rubber–polyethylene blend could make the heterogeneous phases compatible.⁷ CPE not only improved the room temperature impact resistance of polyvinyl chloride (PVC), but served as a compatibilizer⁸ of the blend of PVC/EPDM. CPE also played the role of a compatibilizer^{9,10} in poly(styrene-*co*-acrylonitrile) (SAN)/EVA blend because of its respective moderate interactions with SAN and EVA. Mechanical properties of these blends could substantially be improved by incorporating CPE.

It was expected that CPE could serve as a compatibilizer and improve the polarity of EVA/EPDM for blowing agent of azodicarbonamide (AC) to disperse perfectly in the blend of EVA/EPDM/CPE; as a result, the gas cell morphology of this blowing material would be finer and homogeneous so that mechanical properties would be improved.

DCP and AC had been practiced for a long time in producing cross-linking and blowing materials. However, they still influenced mechanical properties. In fact, the cross-linking and blowing technology processes were a function of temperature and time. It indicated that we should pay more attention to the cross-linking reaction and should choose a blowing agent that its decomposition temperature suited for the technology processes.

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TABLE I
Formulation of the Blend

Formula	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#	11#	12#	13#	14#	15#	16#	17#	18#
EVA	100	90	80	70	60	70	70	70	70	70	70	70	70	70	70	70	70	70
EPDM	0	10	20	30	40	30	30	30	30	30	30	30	30	30	30	30	30	30
CPE	0	5	5	5	5	0	5	5	0	5	5	5	5	5	5	5	5	0
TA	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
ST	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
ZnST	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
ZnO	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
DCP	0.80	0.80	0.80	0.80	0.80	0.80	0	0.80	0	0.40	0.60	1.00	1.20	0.80	0.80	0.80	0.80	0
AC	2.50	2.50	2.50	2.50	2.50	2.50	2.50	0	2.50	2.50	2.50	2.50	2.50	1.50	2.00	3.00	3.50	0

In our work, under certain pressure and temperature, EVA/EPDM/CPE filled with talc (TA) was cross-linked with DCP and blown simultaneously with AC for preparation of high elasticity material by injecting, cross-linking, and blowing process. This material was used as a protective material for counteracting outside impact and strike energy, for example, as athletic footwear material to have high elastic power during sport. The kinetics on cross-linking and blowing reactions of EVA/EPDM/CPE were investigated using a torque rheometer by determining simultaneously the cross-linking torque and blowing pressure versus time, and then the apparent activation energy and frequency factor were calculated. The gas cell morphology was characterized by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Materials used for this study were all commercial products. EVA (Elvax 462) with 21 wt % VA and 1.5 g/10 min of melt-flow index was supplied by Du Pont (USA). EPDM (Nordel IP 3745P) and CPE (FWP 0580) with 36 wt % of chlorine content and density of 1.16 were supplied by Du Pont Dow Elastomers (USA). TA, stearic acid (ST), zinc stearate (ZnST), and zinc oxide (ZnO) were supplied by Rongjiang (China). DCP (99%, Gaoqiao, China) was used as cross-linking agent. AC (Liuhe, Taiwan) was used as blowing agent, which gave 215–225 mL/g of gases and decomposition temperature was 178–185°C.

Mixing, pelletizing, injecting, cross-linking, and blowing

EVA, EPDM, CPE, TA, ST, ZnST, and ZnO were melt mixed for 10 min in a mixer that was set at 80°C. When material temperature reached 120°C, DCP and AC were together put in and continuously mixed until material temperature reached 125°C, then the compound was further mixed in a two-

roller mill in 1.5 mm of roller gap for three times, finally pelletized into granule in the pelletizing machine (Model TKM-200-KE, Taiwan). The granule of mixed compound was prepared for torque rheometer analysis, or for preparation of high elasticity material by injecting and simultaneously cross-linking and blowing processes when mold temperature reached the required temperature (Table II). The formulations of blends were listed in Table I. All materials were in weight parts per hundred parts of the total content of EVA and EPDM. The material of Formula 1# was not a high elasticity material because its elasticity was not more than 45%. However, it was only used as a control experiment to compare.

Slab samples for mechanical property measurement were prepared by injecting, cross-linking, and blowing processes. These processes were carried out using an injection machine (Model KS-9000 made in Kingsteel, Taiwan) based on processing parameters in Table II.

Torque rheometer analysis

Torque rheometer was based on the fact that the cross-linking density was proportional to stiffness of polymers.¹¹ We assumed that the theoretical principle of blowing reaction was similar to cross-linking one. AC generated gases that dissolved in matrix polymer, and then gas cells were formed in matrix polymer. In the presence of DCP, the number of gas cells increased, but its size decreased. The cells were

TABLE II
Processing Parameters in Injecting, Cross-linking, and Blowing

Parameter	Value				
Extrusion pressure (MPa)	11.8	11.8	11.8	11.8	11.8
Extrusion temperature (°C)	80–95	80–95	80–95	80–95	80–95
Screw speed (rpm)	120	120	120	120	120
Hold time (s)	660	480	360	280	250
Mould temperature (K)	438	443	448	453	458
Hold pressure (MPa)	7.84	7.84	7.84	7.84	7.84
Thickness of mould (mm)	6.0	6.0	6.0	6.0	6.0

uniformly distributed in the matrix so that the dissolved gases were unable to escape from the mass. The average cell size and number of cells increased quickly at the blowing temperature. The gas cells gave the pressure to the die of rheometer.

Torque rheometer analysis was carried out using a type of torque rheometer (Model EKT-2000SP made in EKTRON, Taiwan) with a tightly closed nonrotor. Namely, there was an airtight component for the parallel plates and a pressure sensitive transducer on EKT-2000SP torque rheometer. The blowing reaction was monitored via this pressure sensitive transducer by determining gas pressure. On this rheometer, there was a concave die of 5 cm³, depth of 0.5–3.5 mm from the center to the edge, and the lower mold oscillated $\pm 1^\circ$ with 1.66 Hz of oscillating frequency to determine cross-linking torque. A sample in the die pressed with $4.90\text{--}5.39 \times 10^5$ Pa was heated by two precise heaters installed in the upper and lower molds and reached a required temperature in 20 s. Its precision of temperature was 0.1°C. At the required

cross-linking and blowing temperatures (T) of 438, 443, 448, 453, and 458 K, the cross-linking curve of torque-time and blowing curve of pressure-time were simultaneously analyzed, and then the cross-linking and blowing parameters could directly be obtained.

Mechanical property characterization

Mechanical properties of the injection molded slab sample at $(23 \pm 2)^\circ\text{C}$ were measured according to testing standard methods below. Tensile strength (T_S) and elongation at break (E_B) were measured according to ASTM standard 5035. Tear strength (T_R), tear parallel strength (T_P) and bonding to rubber (T_B) were measured according to DIN 53,329-A. T_S , E_B , T_R , T_P , and T_B were measured using Universal Testing machine (Model GT-7010-A2, made in Gotech, Taiwan) at a rate of 200 mm/min. Hardness (H), density (ρ), elasticity (E_L) and compression set ($C\text{-set}$) were measured according to ASTM standard D-2240, DIN 53,479, DIN 53,512, and ASTM standard

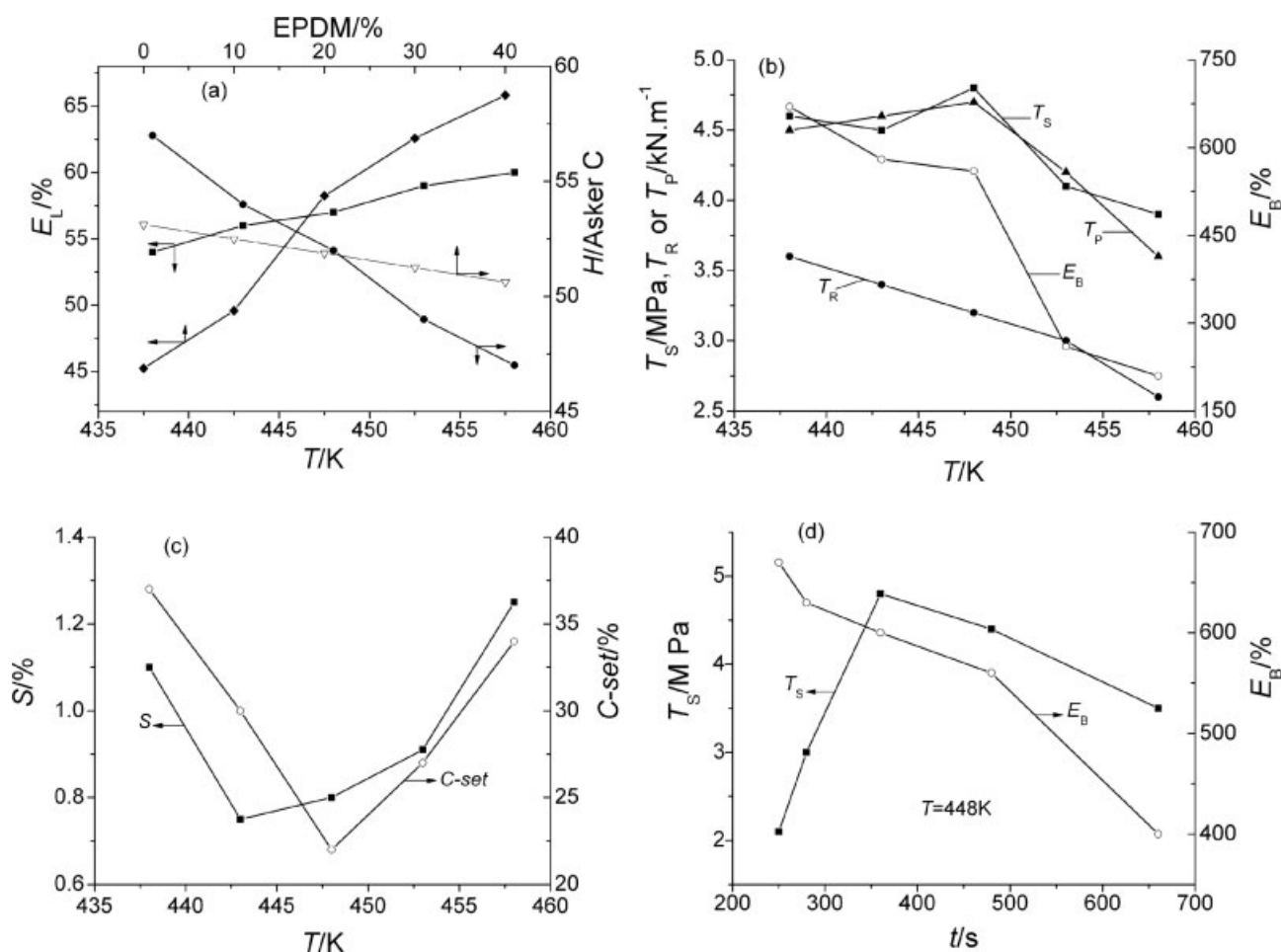


Figure 1 Mechanical property as a function of T , t , and formula: (a) E_L and H versus T and EPDM content; (b) T_S , T_R , T_P , and E_B versus T ; (c) S and $C\text{-set}$ versus T ; (d) T_S and E_B versus t ; (e) E_L and $C\text{-set}$ versus t ; (f) T_S , T_R , T_P , and E_B versus DCP content; (g) E_L and H versus DCP and AC content; (h) T_S , T_R , T_P , and E_B versus AC content.

D 395-B, respectively. E_L was measured using Frank Elasticity Tester (Model GT-7042-SF, Gotech).

The shrinkage (S) of the sample was measured according to the following standard operation procedure. A test plate sample of 150 mm (l) \times 50 mm (w) \times 10 mm (h) was stored at 50°C in an air circulating oven for 24 h, the loss of dimension in percent for length shrinkage (L_S) and for width shrinkage (W_S) were obtained, then S was the average of L_S and W_S .

Scanning electron microscopy characterization

SEM examination of the gas cell of a cross section of the high elasticity material sample was carried out using a scanning electron microscope (Model XL30 ESEM TESTER) made in PHILIP. All samples were examined at 20.0 kV after they were coated with gold to avoid electrostatic charging and poor image resolution.

RESULTS AND DISCUSSION

Mechanical property

This high elasticity material had over 60% of elasticity and a low density of 0.22–0.25 g/cm³. The T_B of

Formula 3#, 4#, and 5# was in the range of 3.4–3.8 kNm⁻¹, whereas that of Formula 6# was in the range of 3.0–3.2 kNm⁻¹, suggesting that CPE increased T_B by 10–25%.

Mechanical properties were shown in Figure 1. If T was lower than 438 K, it took longer than 660 s to cross-link and blow the blend, resulted from low cross-linking and blowing reaction rates. However, it was difficult to control the cross-linking and blowing reactions at higher temperature. For example, the cross-linking and blowing reaction rates were fast if temperature was over 453 K. From Figure 1(b,c), as T was in the range of 440–450 K, T_S and T_P were higher, S and C -set were lower, and T_S and T_P also reached maximum at 448 K. From Figure 1(d,e), as T was 448 K and the cross-linking and blowing time (t) was 360 s, T_S reached maximum, while C -set reached minimum. Therefore, a good temperature range was 440–450 K, the optimum temperature and time were 448 K and 360 s, respectively.

E_L increased with increase of EPDM [Fig. 1(a)]. With increase of DCP and AC content [Fig. 1(g)] E_L increased first and then declined after it reached maximum at 0.80% of DCP and 2.50% of AC. However, at DCP content of 1.20% [Fig. 1(f)], T_S , E_B , T_R ,

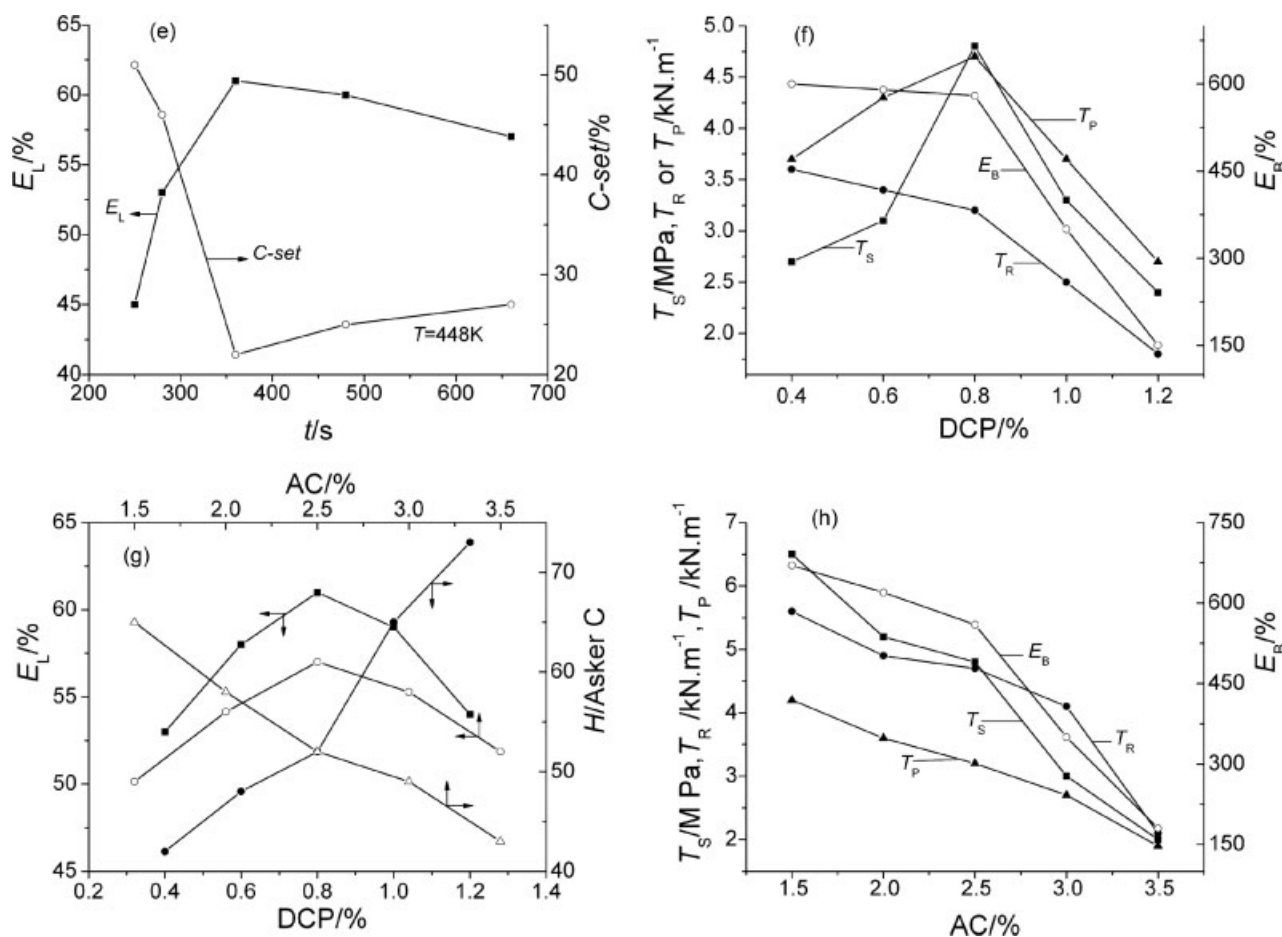


Figure 1 (Continued)

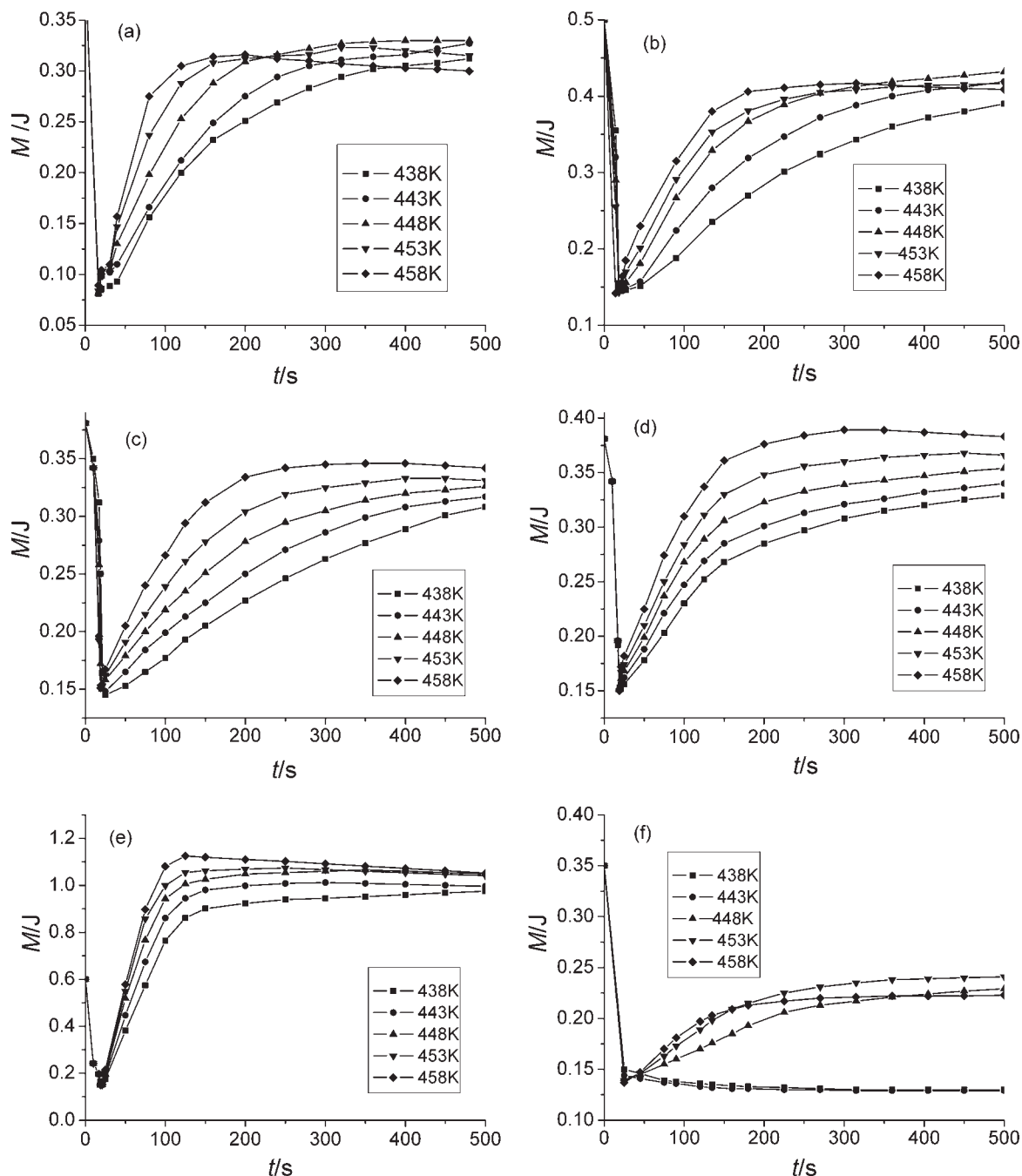


Figure 2 Crosslinking curves of M versus t of different formula: (a) 3#, (b) 4#, (c) 10#, (d) 11#, (e) 13#, (f) 7#.

and T_P decreased to 2.4 MPa, 150%, 2.7 kNm⁻¹, 1.8 kNm⁻¹, respectively, because there was over cross-linking. In Figure 1(g), it was observed that H increased rapidly with DCP, suggesting that the blowing reaction could not normally take place because of strong cross-linking. Mechanical properties were decreased with increase of AC content [Fig. 1(h)], on the other hand, if AC content was smaller than 2.0%, the blowing reaction was insufficient [Fig. 1(g)] and H was bigger. Mechanical properties were a function of T , t , and formula.

Kinetics of cross-linking reaction

The torque rheometer analysis was based on the fact that the cross-linking density was proportional to the stiffness of the polymers.¹¹ The curing reaction of hard rubber followed a kinetic equation^{11,12}

$$M = M_H[1 - e^{-k(t-t_0)}] \quad (1)$$

where M was the torque at time t , M_H was the maximum torque, k was the cross-linking reaction rate constant, t_0 was the induction time.

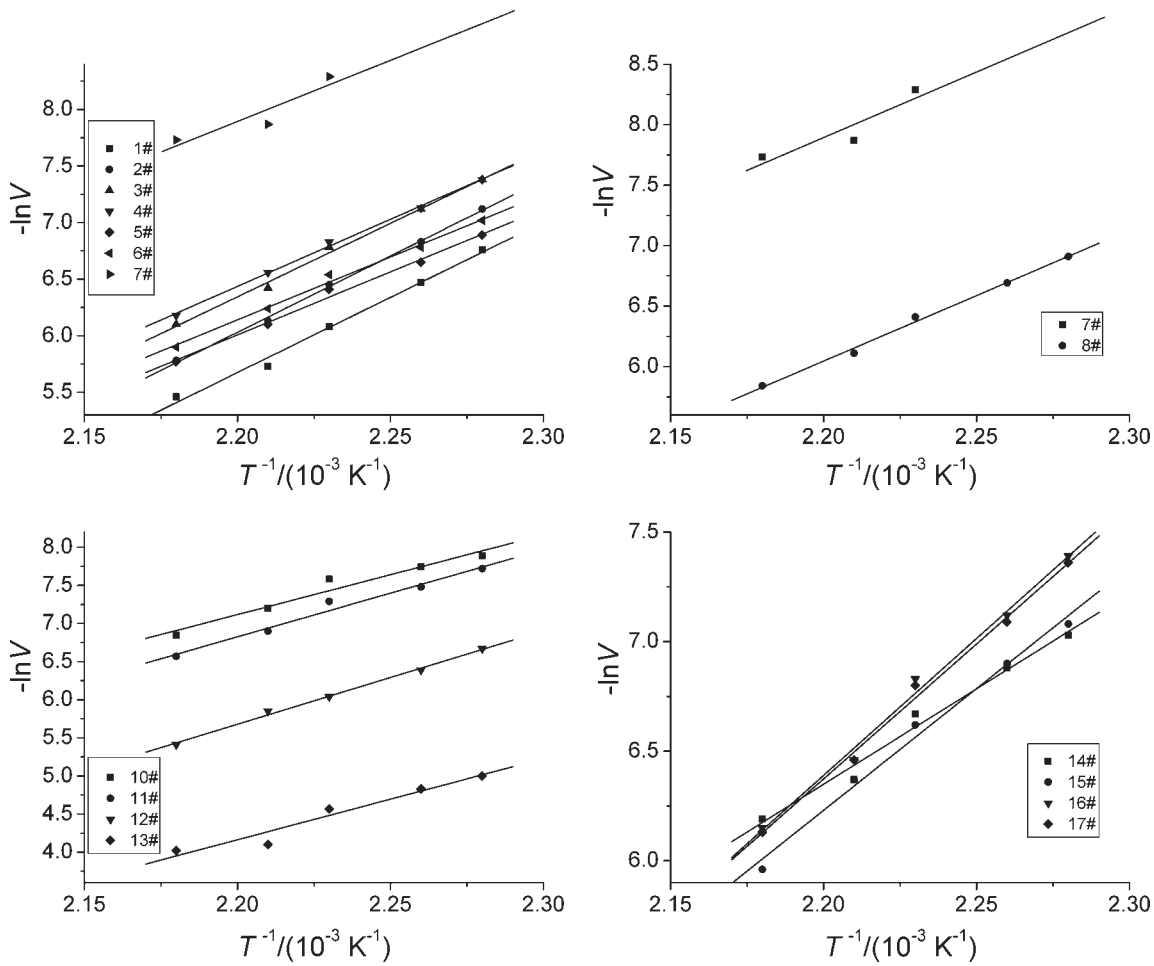


Figure 3 Plots of $-\ln V$ versus T^{-1} of different formula.

We assumed the cross-linking reaction was first order reaction in its torque rising stage. For this high elasticity material, typical cross-linking curves of M versus t were shown in Figure 2. It was observed that the cross-linking curve was linear as M was in the torque rising stage, where, the differential coefficient of M over t was given by

$$\frac{dM}{dt} = k. \tag{2}$$

$$M_{90} = (M_H - M_L) \times 90\% + M_L \tag{3}$$

where M_{90} was the torque at the cross-linking stage corresponding to 90% crosslinking, M_L was the lowest torque. It was observed that there were different slopes of cross-linking curves in their torque rising stage at different T (Fig. 2). This revealed that k changed with T . According to Arrhenius relation

$$k = Ae^{-E/RT} \tag{4}$$

where E was activation energy, A was frequency factor, R was gas constant, 8.314 J/(molK), respectively.

Within the ranges of $[M_L, M_{90}]$ and $[t_0, t_{90}]$, there was $M = M_{90}$ as $t = t_{90}$, integral of eq. (2) gave

$$\ln \frac{M_{90} - M_L}{t_{90} - t_0} = \ln A - \frac{E}{RT}, \tag{5}$$

in which t_{90} was the technology normal crosslink time.

The cross-linking reaction rate was defined as

$$V = \frac{M_{90} - M_L}{t_{90} - t_0}. \tag{6}$$

Thus,

$$-\ln V = -\ln A_V + \frac{E_V}{RT}, \tag{7}$$

in which E_V was the activation energy, A_V was the frequency factor. Equation (6) can be used to decide whether the cross-linking reaction rate was appropriate or not as fast as possible.

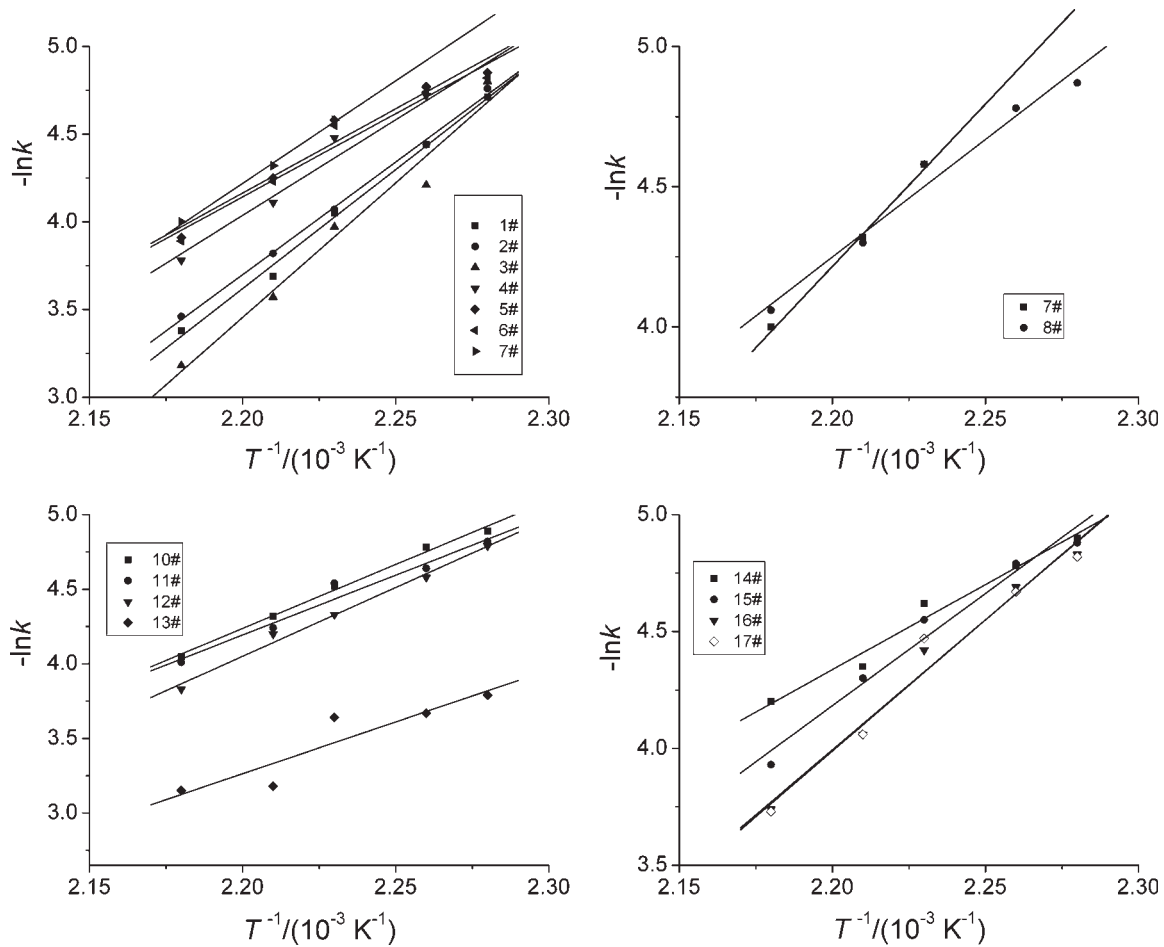


Figure 4 Plots of $-\ln k$ versus T^{-1} of different formula.

From eq. (1), k could be calculated as

$$k = \frac{\ln \frac{M_H - M_{90}}{M_H}}{t_0 - t_{90}} \tag{8}$$

$$-\ln k = -\ln A_k + \frac{E_k}{RT} \tag{9}$$

in which E_k was the activation energy, A_k was the frequency factor.

From Figure 2, the crosslinking torque (e.g., M_H) increased with increasing of EPDM and DCP content. On the other hand, with addition of AC content the cross-linking torque decreased. It was observed that the cross-linking reaction did not take place if there was no DCP in the blend system, as in the case of Formula 9#, the cross-linking curves were horizontal lines ($M = 0.123\text{--}0.145$ J, respectively). Moreover, in the case of Formula 18#, its cross-linking curves were also some horizontal lines ($M = 0.113\text{--}0.131$ J, respectively). Here they were not shown out. Thus, it was considered that TA could slightly affect M (e.g., M_L) and the effect of TA was

counteracted in $M_H - M_L$ or $M_{90} - M_L$, namely, the cross-linking reaction initiated by TA or additives such as ZnO, ZnST, and ST might not be considered. However, the cross-linking reaction took place [Fig. 2(f)] by incorporating 5 wt % of CPE when the cross-linking temperature was 448–458 K. It might be that CPE eliminated HCl to generate molecular radical and then to initiate cross-linking or maybe there were some ionic bonds to generate when temperature was 448–458 K. But the cross-linking torque increase cross-linked by CPE was smaller [Fig. 2(f)].

From cross-linking curves, M_H , M_L , t_{90} , and t_0 were directly obtained. The torque range of [M_L , M_{90}] and the time range of [t_0 , t_{90}] were used to calculate V , $-\ln V$, k , and $-\ln k$ based on eqs. (3)–(9). Plots of $-\ln V$ versus $1/T$ and $-\ln k$ versus $1/T$ were shown in Figures 3 and 4, respectively. These plots were straight lines and consistent with Arrhenius relation. $-\ln V$ versus $1/T$ was also consistent with $-\ln k$ versus $1/T$. These results demonstrated that the cross-linking reaction was first order reaction during the torque rising stage. Thus, the apparent activation energy, E_V and E_k , and frequency factor, A_V and A_k , were calculated (Table III).

TABLE III
Apparent Activation Energy and Frequency Factor

Formula	E_V (kJ mol ⁻¹)	A_V	E_k (kJ mol ⁻¹)	A_k	E_b (kJ mol ⁻¹)	A_b
1#	107	5.60×10^{10}	108	6.81×10^{10}	58.2	8.10×10^7
2#	112	1.84×10^{10}	107	4.69×10^{10}	71.7	2.95×10^7
3#	112	1.32×10^{10}	103	2.17×10^{10}	69.4	1.65×10^6
4#	99.0	3.84×10^8	101	7.68×10^9	71.5	2.94×10^6
5#	93.0	1.20×10^8	98.1	2.99×10^9	73.7	5.49×10^6
6#	92.6	9.60×10^7	96.8	1.82×10^7	68.3	1.22×10^6
7#	95.8	3.85×10^7	99.0	3.52×10^9	121	9.28×10^{12}
8#	91.0	6.92×10^6	88.8	2.33×10^8	0	0
9#	0	0	0	0	104	9.50×10^{10}
10#	87.0	7.97×10^6	71.3	2.28×10^6	69.9	1.84×10^6
11#	95.3	9.70×10^7	66.7	7.03×10^5	67.5	9.90×10^5
12#	102	1.76×10^9	76.7	1.14×10^7	55.7	3.69×10^4
13#	88.5	2.31×10^8	57.8	1.67×10^5	81.5	4.43×10^7
14#	72.4	3.70×10^5	60.5	1.17×10^5	59.6	1.07×10^5
15#	92.3	8.02×10^7	79.8	2.28×10^7	64.2	3.92×10^5
16#	104	1.47×10^9	93.4	9.93×10^9	69.3	1.70×10^6
17#	102	9.89×10^9	69.8	1.67×10^6	73.0	4.84×10^6
18#	0	0	0	0	0	0

It should be noted that the apparent activation energy and frequency factor were the total apparent activation energy and frequency factor including

those of the cross-linking reaction initiated by CPE even though the cross-linking caused by CPE was smaller.

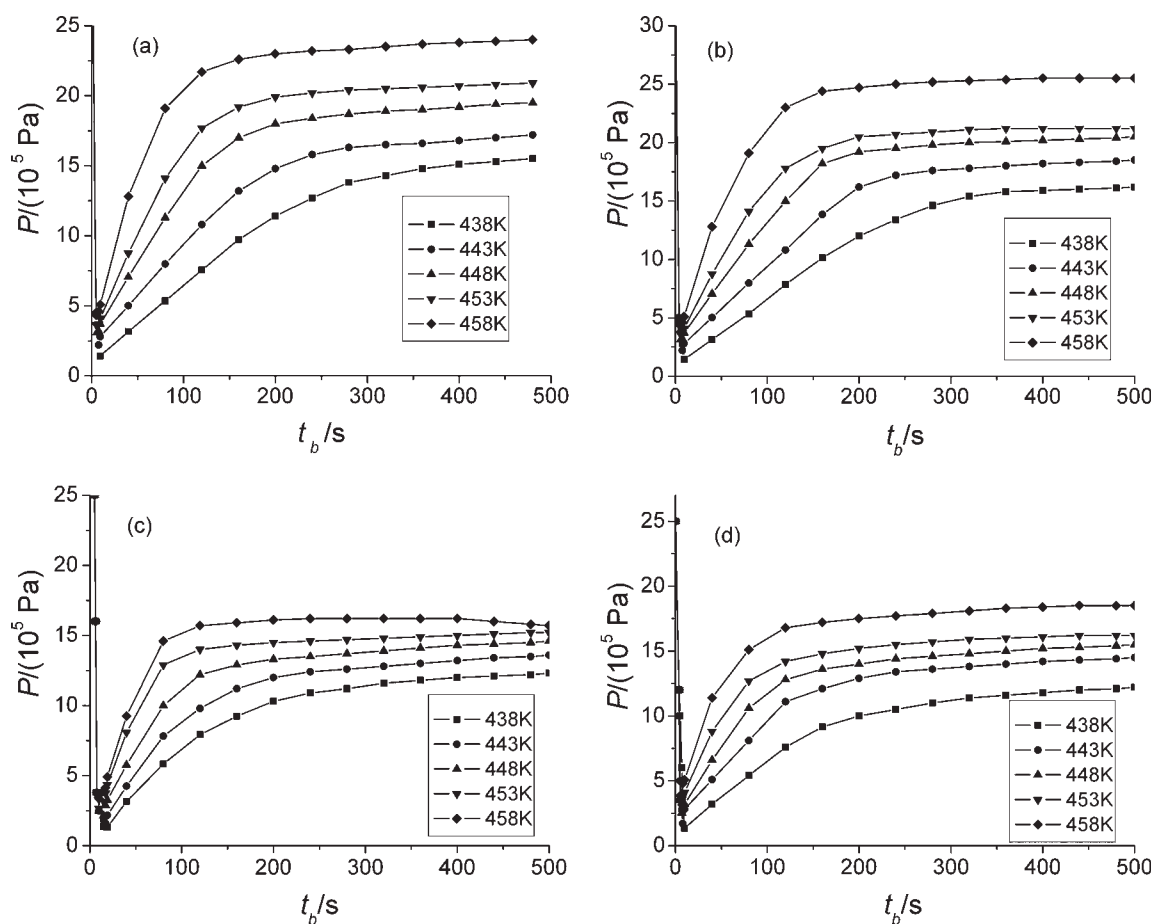


Figure 5 Blowing curves of P versus t_b of different formula: (a) 3#, (b) 4#, (c) 13#, (d) 14#, (e) 15#, (f) 16#, (g) 17#, (h) 7#.

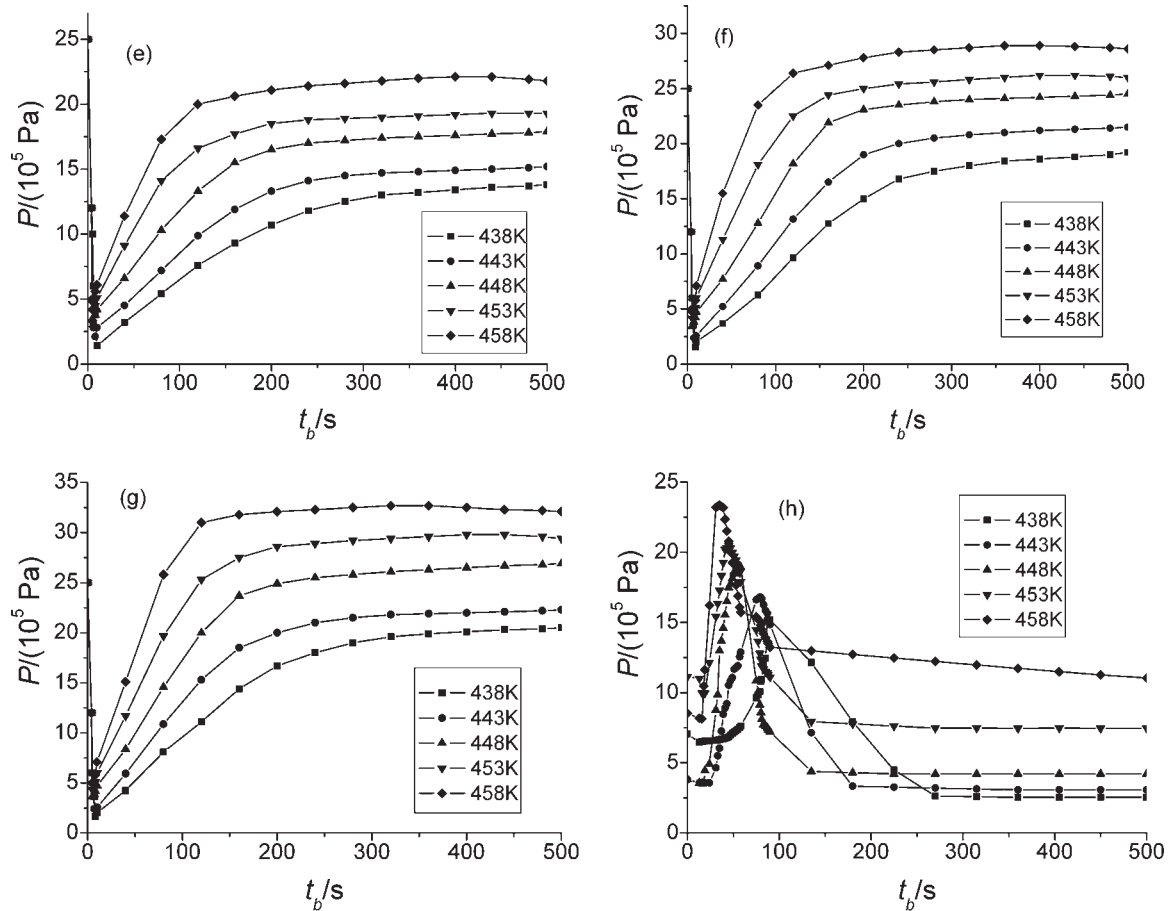


Figure 5 (Continued)

Kinetics of blowing reaction

The cross-linking and blowing reactions took place simultaneously in this blend system. Typical blowing curves of the blowing pressure (P) versus time (t_b) were shown in Figure 5. From Figure 5, the blowing pressures (e.g., P_H and P_L) increased with increasing of EPDM and AC content because EPDM had higher elasticity than EVA and P was proportional to AC content. If there was DCP in the blend, the number of gas cells in the blowing material increased and the cell size decreased and the cells were uniformly distributed in the matrix. With addition of DCP the torque of the compounds increased, and thus the dissolved gases were unable to escape from the mass.¹³ Consequently, it was observed that the blowing pressures increased with increase of DCP content (Formula 10# to 12#). It was also observed that P_H was lower if there was no DCP in the blend compound [Fig. 5(h)] and that the blowing pressure reduced rapidly after it reached P_H . The blowing curves of Formula 9# were similar to Figure 5(h). It revealed that the blowing material would break up if there was no DCP in the blend compound. So did the experimental truth of Formula 7# and 9#. This

might be that the number of gas cells increased and the average cell size expanded quickly at blowing temperature of 438–458 K so that the dissolved gases were able to escape from the mass, finally the blowing material broke up.

The blowing curves of Formula 8# and 18# were those horizontal lines at the pressure of $1.45\text{--}2.07 \times 10^5 \text{ Pa}$. Here, those blowing curves of Formula 8#, 9#, and 18# were not shown out. Similarly to that of cross-linking reaction, it was considered that TA could slightly affect P (e.g., P_L) and the effect of TA was counteracted in $P_H\text{--}P_L$.

Decomposition reaction of AC depended on temperature. If temperature was higher, the starting point of the blowing reaction would be very much earlier, resulting in that the gases decomposed from AC dissolved on the surface of material. As a consequence, there were many bigger pores on the surface of the material and the gas cell size inside material was not uniform. On the other hand, if temperature was lower or not propitious to decomposition of AC and blowing reaction, it certainly caused blowing reaction to take place behind cross-linking. Third, if the cross-linking torque was much higher than that

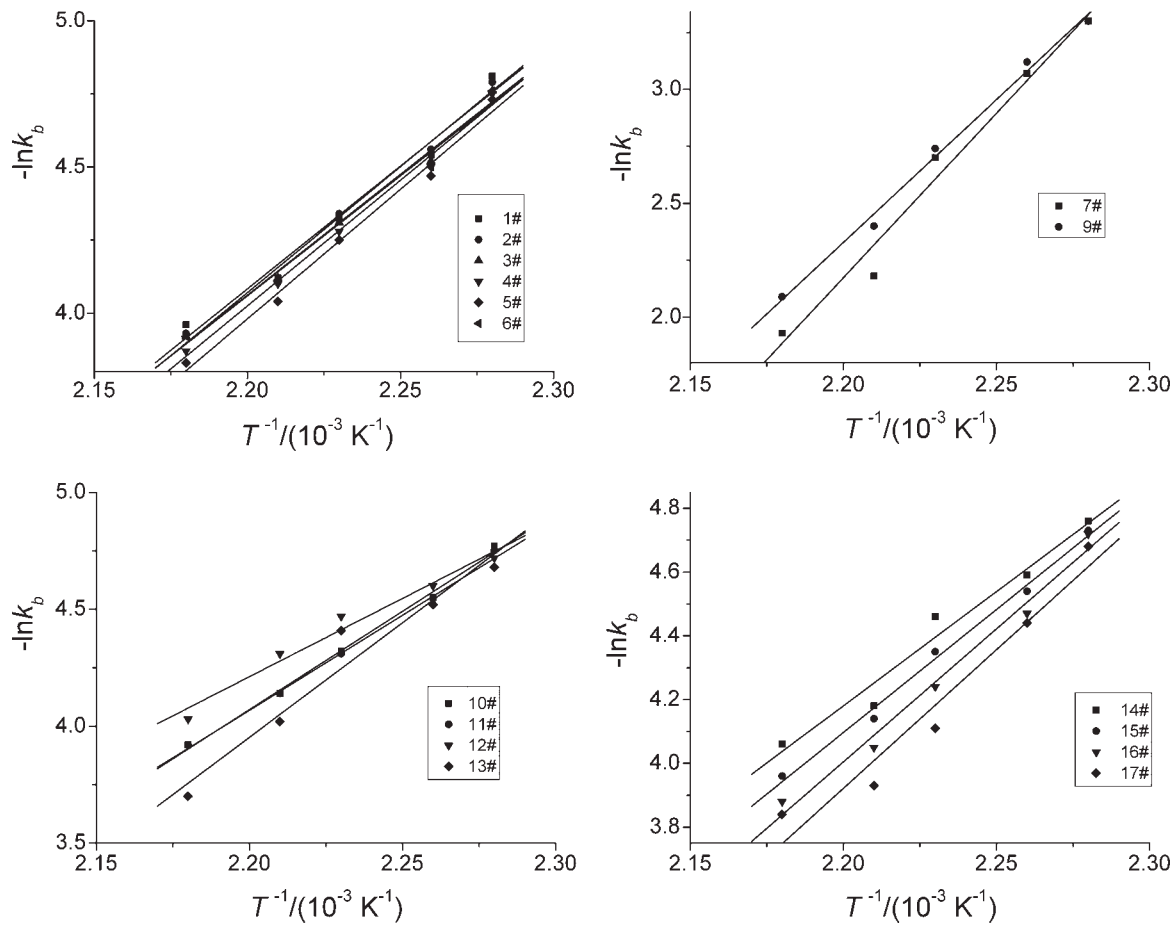


Figure 6 Plots of $-\ln k_b$ versus T^{-1} of different formula.

required [Fig. 2(e)], it would not bring about an effective blowing reaction [Fig. 5(c), the blowing pressures were lower] and produced a relative hard blowing material. It was very important to find an optimum temperature for both cross-linking and blowing reactions and make the two reactions take place simultaneously. It was preferred that the blowing reaction took place a bit earlier than the cross-linking reaction (t_{b0} was smaller than t_0).

We supposed there was a relation

$$P = P_H [1 - e^{-k_b(t_b - t_{b0})}] \quad (10)$$

where P_H and P were the maximum pressure and the pressure at time t_b , respectively, k_b was the blowing reaction rate constant, t_{b0} was the time corresponding to the lowest pressure.

$$P_{90} = (P_H - P_L) \times 90\% + P_L \quad (11)$$

where P_{90} was the pressure corresponding to 90% blowing reaction, P_L was the lowest pressure. Thus,

$$k_b = \frac{\ln \frac{P_H - P_{90}}{P_H}}{t_{b0} - t_{b90}} \quad (12)$$

where t_{b90} was the time corresponding to 90% blowing reaction. According to Arrhenius relation,

$$-\ln k_b = -\ln A_b + \frac{E_b}{RT} \quad (13)$$

where E_b was the blowing reaction activation energy, A_b was the blowing reaction frequency factor.

From blowing curves, blowing parameters of P_H , P_L , t_{b90} , and t_{b0} were directly obtained. P_{90} , k_b , and $-\ln k_b$ were calculated based on eqs. (11) and (12). Plots of $-\ln k_b$ versus $1/T$ were shown in Figure 6. These results demonstrated that eq. (10) was consistent with Arrhenius relation and the blowing reaction was first order reaction during the pressure rising stage. Thus, the results of E_b and A_b of the blowing reaction were calculated (Table III).

With the increase in EPDM content, E_V and E_k declined while E_b increased, suggesting that the blend with higher EPDM content needed much more energy to blow it and might result in a coarser gas pore of blowing material. E_V and E_k were higher than E_b except for Formula 7#. It was found that the activation energy of the cross-linking reaction was higher than that of the blowing reaction. It indicated that we

should pay more attention to the cross-linking reaction and should choose a blowing agent that its decomposition temperature suited for the technology processes. By comparing the E_v , E_{kr} and E_b of Formula 4# with those of Formula 6#, it was found roughly that the cross-linking initiated by CPE contributed 6.4, 4.2, and 3.2 kJ/mol to E_v , E_{kr} and E_{br} , respectively. But, it

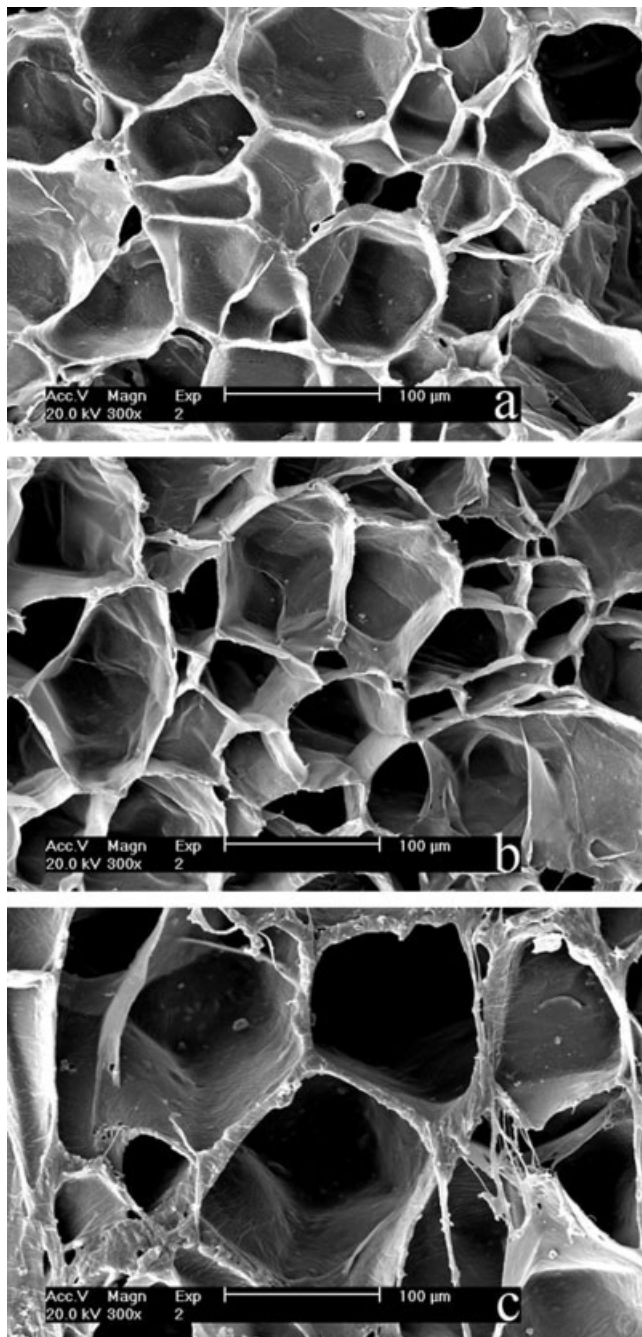


Figure 7 SEM images of the cross section of blowing material sample of different formula: (a) 70% EVA + 30% EPDM of 6#, (b) 70% EVA + 30% EPDM + 5% CPE of 4#, (c) 60% EVA + 40% EPDM of 5#.

needed more additional study to distinguish perfectly the cross-linking and blowing reactions.

SEM analysis

SEM images of the gas cell morphology of a cross section of the high elasticity material sample were shown in Figure 7. Figure 7(b), the diameter of gas cell size was 20–60 μm , the wall thickness of the gas cell was 2–3 μm when 5 wt % of CPE was added. The gas cells were uniform and finer. As EPDM content was no more than 30 wt %, the diameter of gas cell size was 20–90 μm , the wall thickness of the gas cell was 3–6 μm [Fig. 7(a)]. As EPDM content, however, reached 40 wt %, the diameter of gas cell size was 80–130 μm , the wall thickness of the gas cell was 5–10 μm [Fig. 7(c)] and the gas cells were bigger and a bit coarse. After CPE was incorporated, the polarity of the blend was increased and AC was dispersed thoroughly.⁷ It gave the finer and homogeneous gas cell morphology, as a consequence, mechanical properties were improved by incorporating 5 wt % of CPE.

CONCLUSIONS

A cross-linking and blowing high elasticity material of EVA/EPDM/CPE had been developed and its elasticity was over 60%. Its mechanical properties were greatly improved in the presence of CPE, which served as a compatibilizer and improved the polarity of EVA/EPDM so that AC was dispersed perfectly in EVA/EPDM/CPE. Formulation and cross-linking and blowing temperature and time affected mechanical properties.

It was possible to find a way in controlling AC content by determining the blowing pressure with a torque rheometer because the blowing pressure was proportional to AC content. So, mechanical properties were improved.

Kinetics of both cross-linking and blowing reactions were investigated. Both cross-linking and blowing reactions were first order. The activation energy of the cross-linking reaction was higher than that of the blowing reaction. We should pay more attention to the cross-linking reaction and should choose a blowing agent that its decomposition temperature suited for the technology processes. But it needed more additional study to distinguish perfectly the cross-linking and blowing reactions.

SEM analysis revealed that finer and homogeneous gas cell morphology and excellent mechanical property could be obtained by incorporating CPE.

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