

Effect of additives on the morphology evolution of EPDM/PP TPVs during dynamic vulcanization in a twin-screw extruder

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Received: 9 April 2013 / Accepted: 4 September 2013 / Published online: 13 September 2013
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Abstract Ethylene-Propylene-Diene Monomer/Polypropylene thermoplastic vulcanizates (EPDM/PP TPVs) have been widely used as a kind of typical “green” elastomer because of their excellent mechanical properties and recyclability. The industrial TPVs always contain various types of additives, which influence the viscosity ratio of EPDM and PP and the morphology of TPVs. This work studied the morphology evolution of EPDM/PP TPVs with various amounts of curing agents, fillers, and plasticizer during dynamic vulcanization in a twin-screw extruder, which provides much more complicated dynamic vulcanization process than haaker rheometer. The results show that the increased curing agents content leads to the faster morphology evolution of TPV because it enhances the cross-linking speed and the viscosity of EPDM. The increased fillers content leads to the later breakup of EPDM and the bigger size of the rubber aggregation because it enhanced the modulus of EPDM and weakens the interfacial interaction between EPDM and PP. In addition, the increase in the plasticizer content leads to the earlier breakup of EPDM and the larger size of the rubber phase in TPV. Our work firstly demonstrates the morphology evolution of industrial EPDM/PP TPV, and thus can provide a guidance for the industrial production of high-performance EPDM/PP TPVs.

Keywords Thermoplastic vulcanizates · Dynamic vulcanization · Morphology evolution · Additives

Introduction

Thermoplastic vulcanizates (TPVs) based on polypropylene (PP) and ethylene-propylene-diene monomer (EPDM) have attracted much attention as a kind of typical “green” polymer material because they in use behave the same elasticity as the cured rubber and can be repeatedly processed as thermoplastic. Today, TPVs have been widely used in the fields such as automotive, building, and electronics, etc. The market for TPVs is increasing much faster than before due to more requirement for environmental protection and resource saving.

The properties of TPVs are influenced by many factors, such as the properties of rubber and plastic, the blend ratio, the compatibility between rubber and plastic, and the final morphology. Since the morphology of TPV plays a significant role in controlling the mechanical properties and the processability of TPVs, more researches have been focused on the TPVs’ morphology evolution in the earlier decades. Antunes and Goharpey proposed “fibrous model” and “four-stage model” to describe the morphology evolution of TPV composed of EPDM and PP during the dynamic vulcanization, respectively [1–3]. G. Martin studied the relationship between the phase inversion in TPV and the gel content of EPDM phase, and he found that the phase inversion in EPDM/PP TPV always took place when the gel content of EPDM was less than 60 % [4]. Antunes studied the viscosity ratio of EPDM and PP at phase inversion, and the results suggested that phase inversion driven by cross-linking of EPDM occurred at viscosity ratio lower than that estimated for the respective EPDM/PP blends at phase inversion [5]. Although there are some studies provided some new and clear insights for the relationship between TPVs’ composition and TPVs’

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morphology evolution, most of these studies were about the TPVs with simple composition processed in haake rheometer or internal mixer for easy controlling the process of dynamic vulcanization [2, 4–13]. It should be noted that in the industrial production, the TPV products always contain complicated composition, including various types of fillers and extending oil, which no doubt will influence the viscosity ratio of rubber phase and plastic phase, and further affect the morphology of TPV. In addition, for the high efficiency in large-scale, TPVs are preferably produced in twin-screw extruder, which allows continuous processing with high outputs and a large degree of process flexibility. Compared with the production in a haake rheometer or a internal mixer, it is harder to control the morphology formation caused by dynamic vulcanization in a twin-screw extruder, because the stay time of the blends in extruder is fairly short (generally less than 20 s), which always causes the insufficient cross-linking of rubber phase. What's more, under the extremely strong shear stress offered by the fast rotate rate of the screws, the cross-linking and the breakup of the rubber phase in TPVs both accelerate significantly. Unfortunately, the researches on dynamic vulcanization and morphology evolution of TPVs with complicated composition in twin-screw extruder were rarely reported [14–17].

In the present work, a group of dynamically cured EPDM/PP blends were prepared through a co-rotating twin-screw extruder, and the morphology evolution of EPDM/PP TPVs was studied by taking samples at different deliberately-set waypoints along the axis of the extruder during dynamic vulcanization. The effect of the amounts of curing agents, fillers, and plasticizer (paraffin oil) on the morphology evolution of TPVs during dynamic vulcanization was carefully studied in order to provide a guidance for the preparation of high-performance TPVs on large scale.

Experimental

Materials

Table 1 lists the properties of an injection-grade PP and an oil-extended EPDM used in this study, which were bought from Basell Co., Ltd. (Bangkok, Thailand) and ExxonMobil Co., Ltd. (USA), respectively. The curing agents composed of resol and SnCl₂ were supplied by XinJiang Karamay Oilfield. Paraffin oil used as the plasticizer, was supplied by Shanxi provincial research institute of chemical industry. Pottery clay and the anti-oxdyant were commercially available.

Samples preparation

In this study, TPVs were prepared in a intermeshing co-rotating twin-screw extruder with L/D of 52 and a throughput

Table 1 Characteristics of the used materials

	MFI ^a (g/10 min)	Crystallinity (%)	T _m (°C)	Mooney viscosity [ML(1+4) 125 °C/ Pa·s]	PP content (%)
PP	0.35	42	168	–	–
EPDM	–	–	–	25	36

MFI Melt flow index; T_m Melting point

^a At 230 °C and 2.16 kg

of 100 kg/h, a screw speed of 600 rpm and a barrel set of 200 °C.

In order to study the morphology evolution of TPVs during the process of dynamic vulcanization, the EPDM/PP blends were firstly prepared in the laboratory-sized two-roll mill according to the quality ratio of 70/30 at 180 °C, meanwhile the anti-oxidant was added to prevent the aging of PP. After that the blends were transferred to another two-roll mill at ambient temperature and cooled down. The different amounts of curing agents, fillers, and plasticizer were added into the blends in order to guarantee these additives being dispersed into EPDM rather than PP. The composition of the achieved premixes prepared for dynamic vulcanization are shown in Table 2.

Then the premixes were dynamically vulcanized in a specific twin-screw extruder with five sampling exits along the screw axis at the rotate speed of 600 rpm, and the temperature in extruder was set as 200 °C. The samples were taken out at the different curing times during dynamic vulcanization (Fig. 1), and they were cooled down immediately in liquid nitrogen to stop the cross-linking of EPDM phase and avoid further morphological changing.

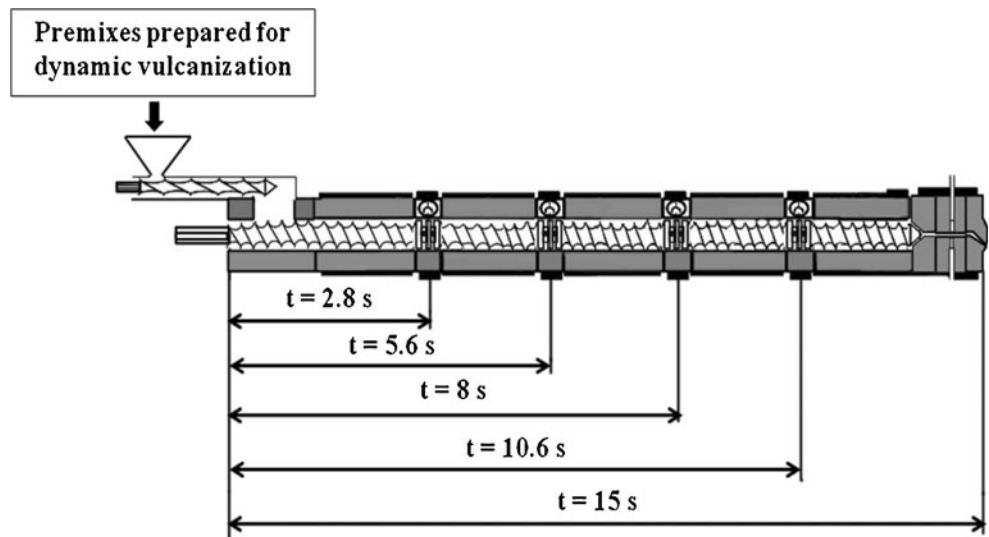
Morphological studies

To study the effect of TPVs' composition on TPVs' morphology evolution, H-800-I-type transmission electron microscopy

Table 2 The composition of premixes prepared for dynamic vulcanization

Coding	EPDM (g)	PP (g)	Resol (g)	SnCl ₂ (g)	Pottery clay (g)	Paraffin oil (g)
C1	50	22	0.1	0.025	10	20
C2	50	22	0.4	0.1	10	20
C3	50	22	0.7	0.175	10	20
F1	50	22	0.4	0.1	0	20
F2	50	22	0.4	0.1	10	20
F3	50	22	0.4	0.1	20	20
P1	50	22	0.4	0.1	10	0
P2	50	22	0.4	0.1	10	20
P3	50	22	0.4	0.1	10	40

Fig. 1 Twin-screw extruder layout with five sampling exits at different curing times (*t*)



(TEM), which was supplied by Japan’s Hitachi company, was performed. Before observation, the samples were cryomicrotomed into 100-nm-thick sections at $-130\text{ }^{\circ}\text{C}$ and then vapor stained with ruthenium tetroxide for 25 min.

RPA analysis

The changes in the storage modulus of samples with strain were analyzed by Rubber Process Analyzer (RPA 2000). The temperature was controlled at $190\text{ }^{\circ}\text{C}$, and the frequency was controlled at 0.2 Hz. Before the determination the samples were preheated for 5 min.

Volume swelling ratio measurement

The volume swelling ratio (*Q*) of the blends was measured as a measure of the cross-linking degree of EPDM phase by

extraction in cyclohexane at room temperature. For swellings, rectangular test pieces with dimension of $10 \times 10 \times 2\text{ mm}^3$ were immersed for 48 h under gentle stirring; the solvent was refreshed after 24 h to remove extracted components. The swelling mass (*m_s*) and the residual mass (*m_d*) of the samples were determined before and after drying the swelling sample in vacuum oven at $80\text{ }^{\circ}\text{C}$ for 12 h, respectively. The volume swelling ratios (*Q*) of the blends were calculated by using the Eqs. (1)–(2) [18]:

$$\varphi_P = \frac{V_P}{V_S} = \frac{1}{1 + \frac{m_S - m_d}{m_d} \times \frac{\rho_P}{\rho_S}} \tag{1}$$

$$Q = \frac{V_S}{V_P} \tag{2}$$

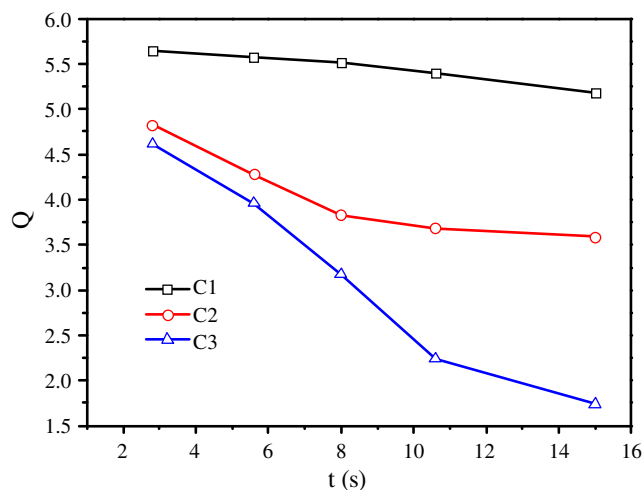


Fig. 2 Volume swelling ratios of the samples at different curing times for C1 (squares), C2 (circles), and C3 (triangles) systems

where φ_p is the volume fraction of polymer in the whole sample after swelling; V_p and V_s are the volume of sample before and after swelling, respectively; ρ_p and ρ_s are the density of the sample and the solvent (cyclohexane) respectively. With the values of m_s , m_d , ρ_p , and ρ_s , the values of *Q* can be obtained. For example, ρ_s is commercially provided, which is 0.78 g/cm^3 . The density of the dynamically vulcanized blend (ρ_p) with least curing agents contents (C1) was measured to be 0.96 g/cm^3 . After extracted in cyclohexane for 48 h, the masses of the C1 sample before and after drying (*m_s* and *m_d*) were 229 g and 52 g respectively. With the Eqs. (1)–(2), the *Q* of C1 can be calculated to be 5.2.

When the *Q* of the blends with different fillers contents (F1, F2, and F3) were compared, the ratios of the volume swelling ratio and the EPDM volume fraction–relative volume swelling ratios–of the TPVs were measured and compared in order to avoid the influence of fillers added.

Results and discussion

Effect of curing agents

The morphology and the properties of TPVs were proved to be strongly influenced by the amount of curing agents [9–11, 19]. It is well-known that the morphology evolution of TPV during dynamic vulcanization is determined mainly by the blend ratio and the viscosity ratio of EPDM and PP

[3, 13]. Reasonably, the increasing amounts of curing agents increases the cross-linking degree of EPDM, accompanying with the viscosity ratio of EPDM and PP. So the curing agents content is the key factor for the morphology formation of TPVs.

Figure 2 shows the development of volume swelling ratios of the blends with different curing agents contents (C1, C2, C3). The premixes of C1, C2 and C3 disintegrated in cyclohexane because unvulcanized EPDM phase is the matrix, so

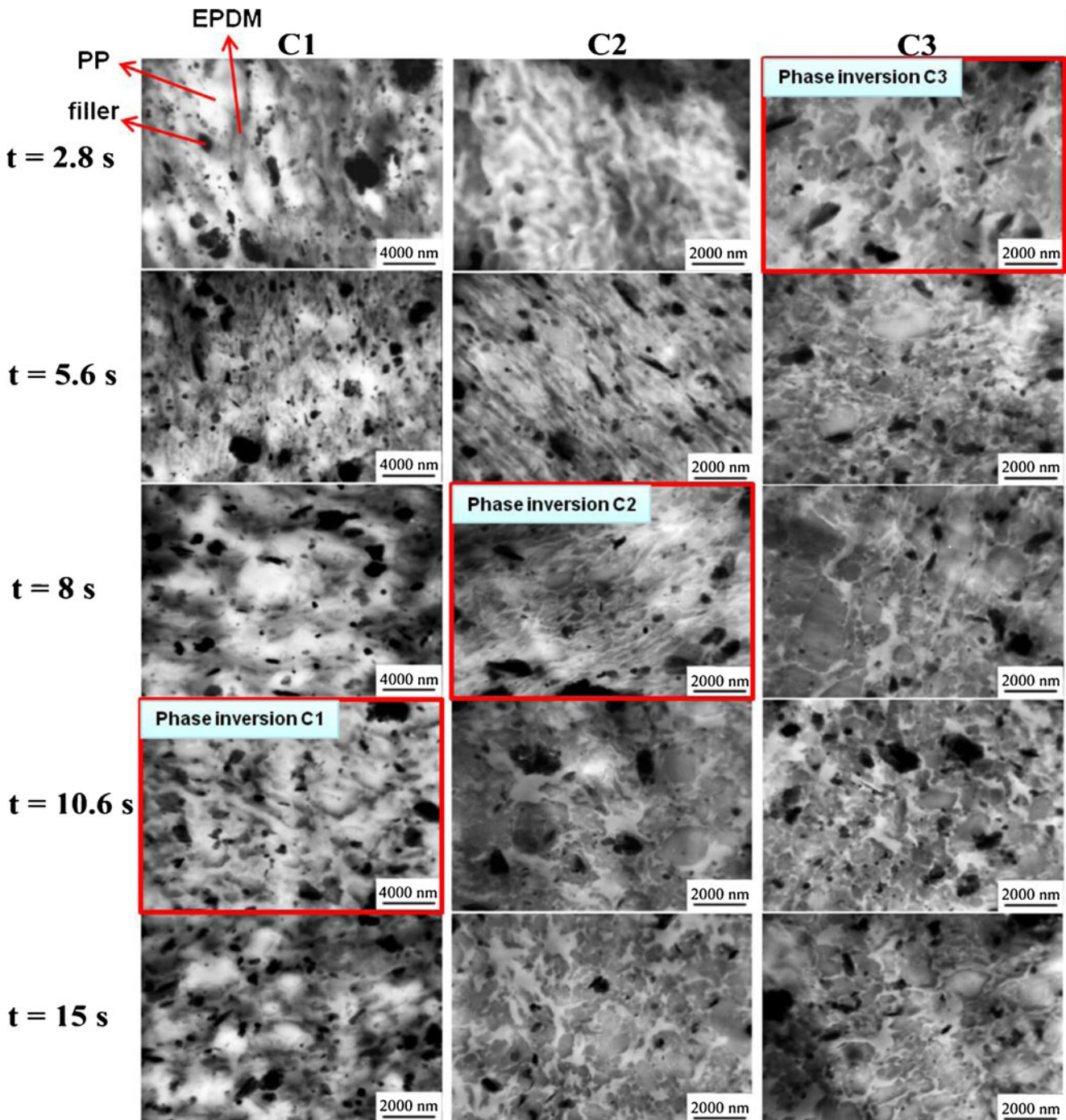


Fig. 3 TEM micrographs of samples with different curing agents contents taken at different curing times (t)

the volume swelling ratios of the premixes cannot be measured. It is well known that the higher volume swelling ratio represents the lower cross-linking degree of the rubber phase. Figure 2 shows that during dynamic vulcanization, the volume swelling ratios of the blends reduce obviously, which demonstrates the increase of the cross-linking degree of EPDM phase in C1, C2, and C3. It also can be seen from Fig. 2 that at the same curing time, the volume swelling ratio of the blend with high curing agents content is higher than those of the blends with low curing agents content, which demonstrates that the cross-linking degree of EPDM phase increases with the increase of the curing agents content at the same curing time. In addition, Fig. 2 shows that with the development of dynamic vulcanization, the volume swelling ratio of C3 declines faster than those of C2 and C1, which indicates that the curing speed of EPDM phase in blends raises with the increase of curing agents content.

The TEM micrographs of the samples with different curing agents contents taken at different curing times are shown in Fig. 3, which indicates the effect of different curing speeds of rubber phase on the morphology evolution of TPV during dynamic vulcanization. In the TEM micrographs, the darker phase is EPDM phase, the light phase is PP phase, and the totally opaque black particles are the fillers added into TPV (marked in Fig. 3). In order to make it easy to recognize the change of blends' morphology, the TEM micrographs of the samples taken at the stages when the phase inversion firstly observed during dynamic vulcanization are marked with red boxes. C1 is the blend with least amounts of resol and SnCl₂. The TEM micrograph of the sample of C1 collected at 2.8 s shows the PP phase as the dispersed phase, and at 8 s the sample becomes to be a co-continuous structure. The phase inversion of C1 does not take place until 10.6 s, and the EPDM phase still looks as irregular bulks with large size at

the end of dynamic vulcanization. Because of the higher curing agents content, the speed of the morphology evolution of C2 is faster than that of C1, obviously. The samples of C2 collected at 2.8 s and 5 s are observed as a co-continuous structure, and EPDM and PP are both stretched, resulting in elongated structures. The phase inversion of C2 takes place before 8 s, where EPDM has already dispersed in PP, the matrix. The sequential increase of curing agents added further accelerates the morphology evolution of the blends. The phase inversion of C3 takes place much earlier than that of C2, and it's obvious that at 2.8 s EPDM phase has already broken up as rubber particles dispersed in PP phase.

The differences between these morphology evolution processes of three blends are attributed to the different curing speeds of EPDM, which is observed in Fig. 2. The phase inversion takes place when the viscosity ratio of EPDM and PP is as high as a critical value. In the curing process with the same temperature and shear rate, the higher amount of curing agents leads to the faster cross-linking of EPDM phase in TPV, thus the viscosity ratio in TPV with high curing agents content (C3) reaches this critical value earlier than that in TPVs with low curing agents content (C2, C1), thus the phase inversion of TPV with higher curing agents content also takes place earlier. In addition, because EPDM phase is under the shear stress which is in proportion to its viscosity, the high curing agents content promotes the breakup of EPDM. As a result, the morphology evolution speed of C3 is higher than those of C2 and C1.

From Fig. 3 it also can be seen that the diameter of EPDM particles in C1 obtained at the end of extruder is larger than that of the EPDM particles in C2 and C3 finally obtained. This is because the cross-linking degree of EPDM in C1 is low, and the collided rubber particles coalesce again and become a whole rubber particle with large size. While it can be observed from Fig. 3 that because of the high viscosity and high

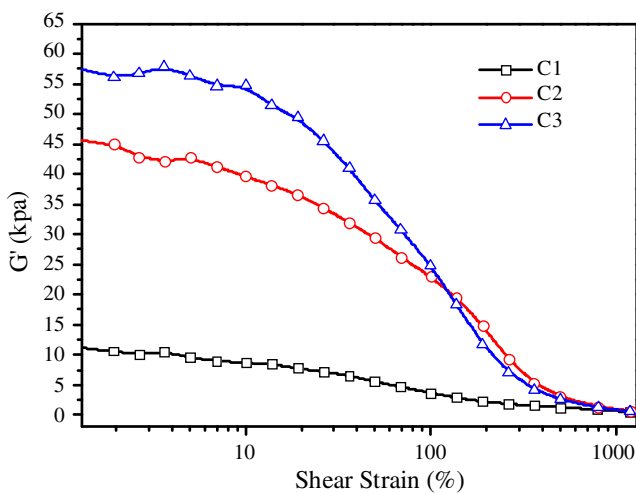


Fig. 4 Storage modulus as a function of strain for TPV with 0.1 g resol and 0.025 g SnCl₂ (squares), TPV with 0.4 g resol and 0.1 g SnCl₂ (circles), and TPV with 0.7 g resol and 0.175 g SnCl₂ (triangles)

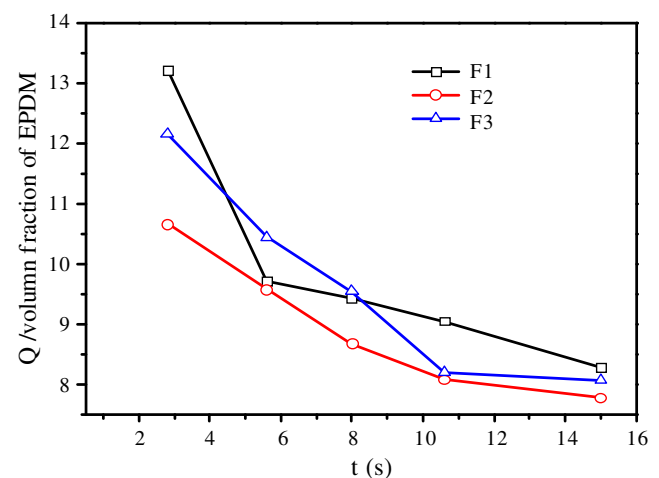


Fig. 5 Relative volume swelling ratio of samples taken from extruder at different curing times of F1, F2, and F3

modulus of the rubber particles in C2 and C3, they tend to aggregate rather than coalesce after collision.

To verify these conjecture, RPA was performed on the dynamically crosslinked samples—C1, C2, and C3, as illustrated in Fig. 4, which indicates the interaction of the high cross-linked rubber particles and the strength of the rubber networks (the Payne effect) in C1, C2, and C3 [20]. Due to the densely dispersion of the rubber particles with high modulus in PP phase, the initial storage modulus (G') of C1, C2, and C3 are high. With the increase of the strain, the rubber networks are destroyed, and the storage modulus of the blends decline

rapidly. The more significant decrease in the storage modulus with the increase of the strain, the stronger rubber network in TPV and the stronger Payne effect. It is evident from this figure that the storage modulus of TPV increases obviously with the increase of the curing agents content. This is explained to be attributed to the higher modulus of EPDM phase in TPV with higher curing agents content. What's more, the storage modulus platform of TPV shortens with the increase of the curing agents content, which indicates that the rubber network in TPV with high curing agents content is stronger than that in TPV with low curing agents content. This

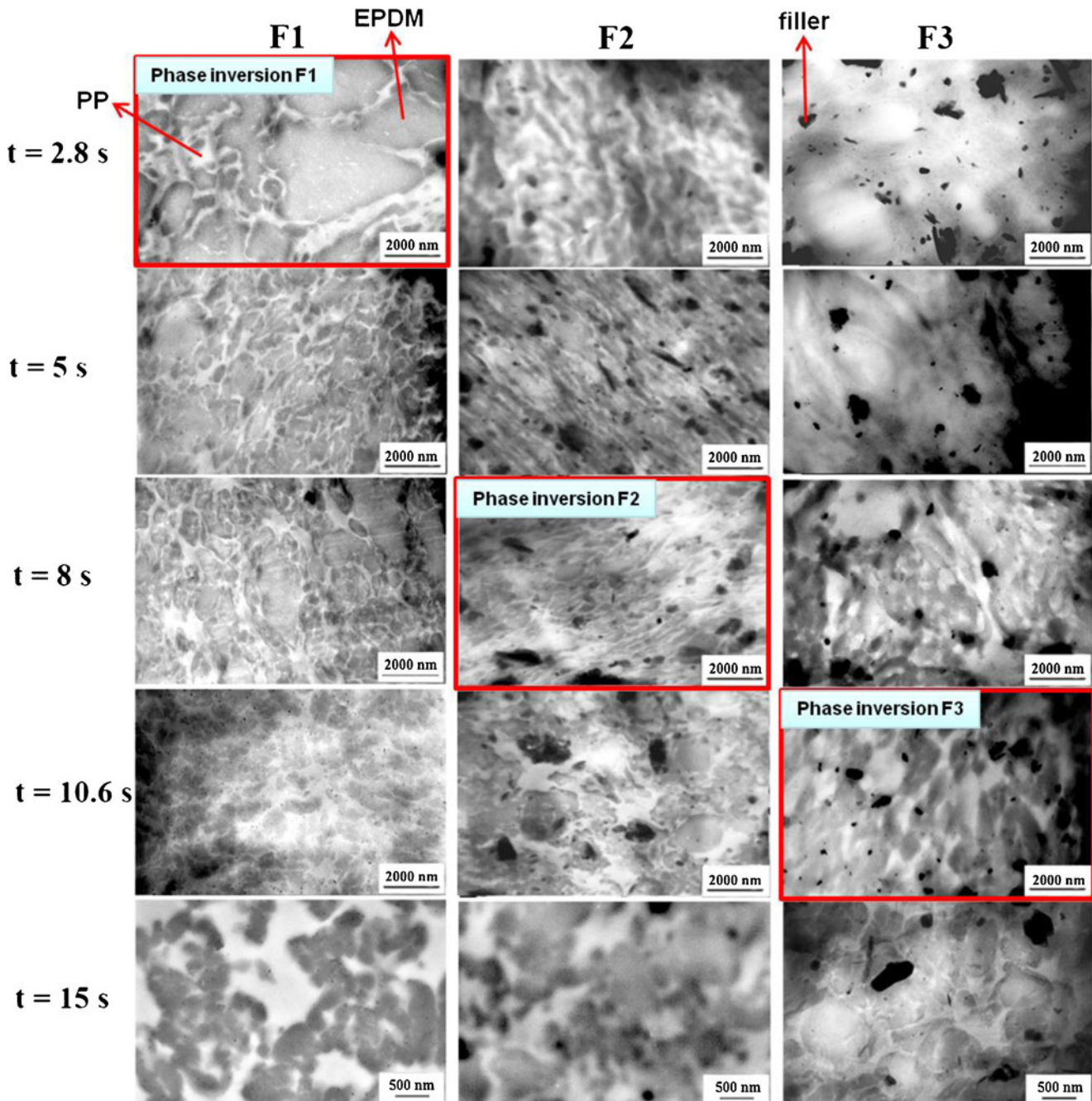


Fig. 6 TEM micrographs of samples with different fillers contents taken at different curing times (t)

is due to the more complete breakup of EPDM phase and the more uniform distribution of EPDM particles in TPV with higher curing agents content.

Effect of fillers

There were a large amount of studies proved that the amounts of fillers added strongly affected the mechanical properties and crystallization behavior of EPDM/PP blends without and with curing agents [7, 8, 21, 22]. From Fig. 5

it is obvious that the amount of fillers added almost has no effect on the volume swelling ratio of TPVs, which proves that the fillers content has no effect on the curing speed of the rubber phase in TPV.

Figure 6 indicates the TEM photomicrographs of the blends with different fillers contents taken from the twin-screw extruder at different curing times during dynamic vulcanization. The TEM micrographs of the blends at phase inversion are also marked by using red boxes, as shown in Fig. 6. It can be observed in this figure that the breaking speed

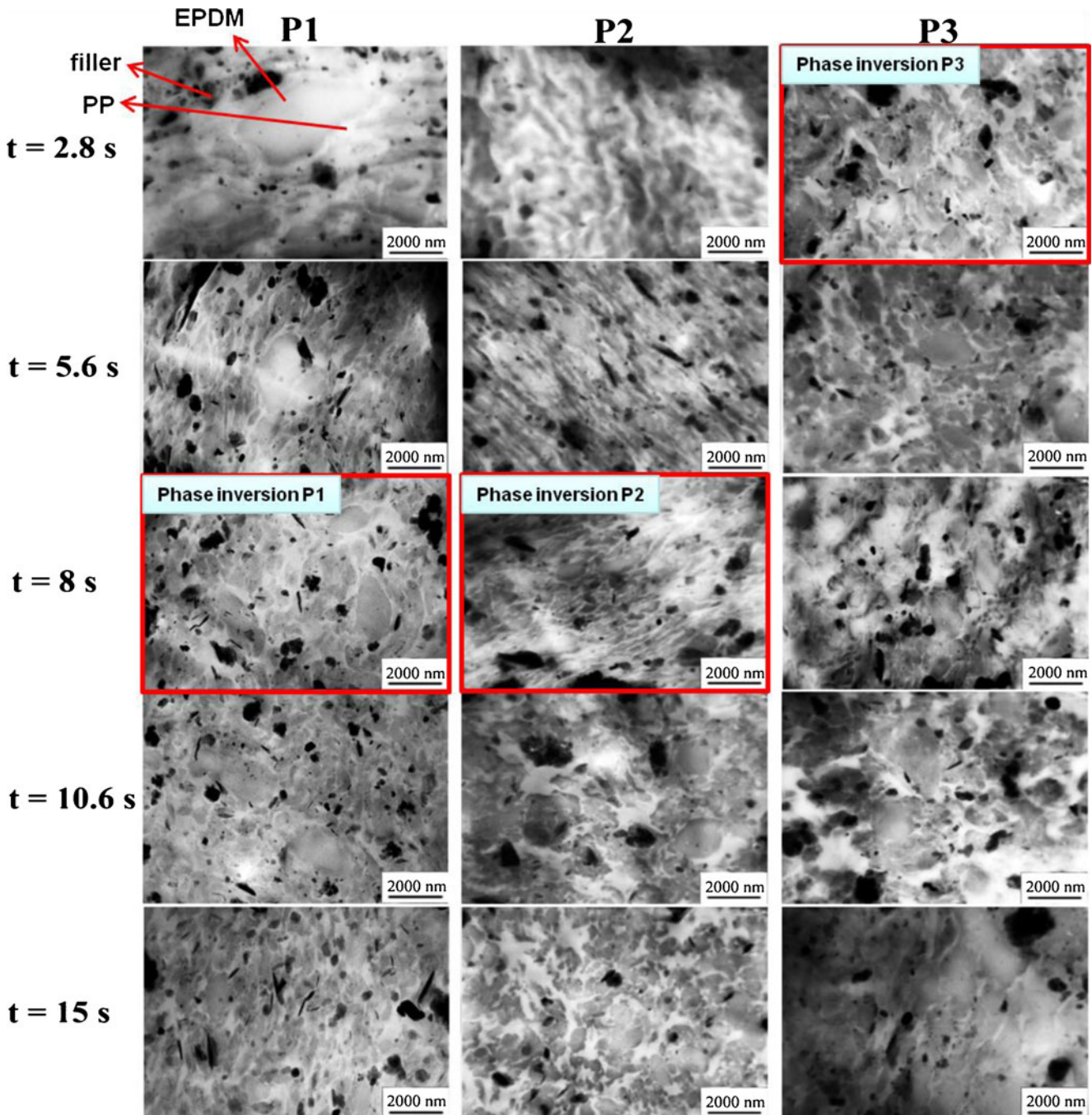


Fig. 7 TEM micrographs of samples with different plasticizer contents taken at different curing times (*t*)

of EPDM phase in blends gets later with the increase of fillers content. The TEM micrograph of the sample of F1 collected at 2.8 s shows that the rubber phase in the blend has broken and dispersed in PP, which indicates that the phase inversion of F1 happens before 2.8 s. At 5 s EPDM has broken into particles with the diameter of 0.5 μm –2.0 μm . The phase inversion of F2 happens between 5 s and 8 s, which is later than that of F1. When the fillers content increases to 40 g/50 g EPDM in F3, the morphology evolution speed of the blend reduces significantly. At 2.8 s the EPDM (the dark phase) is still observed as matrix, and the sample of F3 taken at $t=8$ s is observed as a co-continuous structure. The EPDM does not break into dispersed particles until $t=10.6$ s, where the phase inversion is observed. Because it is evident from Fig. 4 that the increase of fillers content does not affect the curing speed of EPDM in blends, the results observed in Fig. 5 are attributed to the fact that the increase of fillers content enhances the modulus of EPDM, and then makes the breakup of EPDM more difficult.

What's more, the size of the dispersed rubber particles in the samples taken at $t=15$ s increases with the increase of the fillers content. This is because the increase of fillers content weakens the interfacial interaction between the PP and EPDM phase, which results in the formation of the larger-size rubber droplets [23].

Effect of plasticizer

The rheological properties and the mechanical properties of EPDM/PP TPV will be affected by the amount of oil and its distribution between EPDM and PP [6]. In Fig. 7 the TEM micrographs of samples with different plasticizer content which were taken at different curing times were presented and compared. It is clearly observed that in the blend with high plasticizer content the breakup of EPDM phase happens at the earlier stage during dynamic vulcanization than in the blend with low plasticizer content or with no plasticizer. The phase inversions of P1 and P2 take place between 5 s and 8 s, while the phase inversion of P3 takes place at 2.8 s, where the rubber phase has completely broken. This difference between the blends with different plasticizer content is due to the increase in the plasticizer content, which reduces the viscosity and the modulus of the rubber phase in the blends, and then makes the breakup of EPDM phase easier. What's more, the EPDM aggregation in the samples obtained at the end of extruder were also observed and compared, and it is obvious that the EPDM particles dispersed in TPV with higher plasticizer content are larger than those dispersed in TPV with low plasticizer content. This is suggested to be attributed to the softening effect of plasticizer on the rubber phase in the samples, which promotes the flowability of EPDM phase and the aggregation of EPDM particles.

Conclusion

Clearly, the use of a series of sampling devices along the extruder axis allowed a detailed investigation of the morphology evolution of EPDM/PP blends during dynamic vulcanization. Our investigation shows that the morphology evolution of the blends was strongly influenced by the different amounts of ingredients, including curing agents, fillers, and plasticizer. Increased curing agents content enhances the cross-linking speed and the viscosity ratio of EPDM and PP, thus it leads to the earlier breakup of EPDM phase and the faster morphology evolution of TPVs. The increase in the fillers content leads to the later breakup of EPDM and the bigger size of rubber aggregates, the reason is that the increased fillers content enhances the modulus of the rubber phase and weakens the interfacial interaction between EPDM and PP. In addition, the plasticizer content affects the viscosity and the flowability of EPDM phase, thus affects the breakup of EPDM and the distribution of rubber particles in TPV. It is evidenced that the increase in the plasticizer content leads to the earlier breakup of EPDM and the larger size of EPDM phase in TPV.

Acknowledgments We would like to acknowledge the National Basic Research Program of China (Grant No. 2011CB606003) for financial support, and the financial supports of the National Natural Science Foundation of China under Grant No. 51221002 are also gratefully acknowledged.

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