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Study on the morphology, rheology and surface of dynamically vulcanized chlorinated butyl rubber/polyethylacrylate extrudates: effect of extrusion temperature and times

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Abstract A high-damping thermoplastic vulcanizate (TPV) composed of chlorinated butyl rubber (CIIR) and polyethylacrylate (PEA) was prepared by using a twin-screw extruder. The effect of extrusion temperature and times on the morphology, rheology and surface of the extrudates was examined and attempts were made to correlate the extrudate surface with the evolution of two-phase morphology and the rheological behavior. CIIR gel content of each extrudate was also analyzed. The result shows that CIIR gel content increases with increasing extrusion temperature or times; furthermore, extrusion at high temperature can produce numerous PEA and CIIR macromolecular radicals, thus chemical links take place between PEA and CIIR molecules. Morphological analysis indicates that phase inversion occurs at a gel content of around 68%, and with increasing extrusion times at high temperature the dispersed particles become larger and the particle edges become blurrier. All CIIR/PEA extrudates show pseudoplastic flow behavior. The extrusion temperature or extrusion times have a significant effect on melt viscosity of the extrudates. Surface analysis exhibits that co-continuous nature of the two-phase morphology results in melt fracture and periodic distortions on the extrudate surface, but with the increasing extrusion temperature or times the surfaces of the extrudates become gradually smooth.

Introduction

During the last few decades, thermoplastic elastomers (TPEs) have been of growing industrial importance, owing to the fact that TPEs possess the properties similar to conventional vulcanized rubbers while retaining the thermoplastic-like processability [1, 2]. Among various TPEs, thermoplastic vulcanizates (TPVs) with vulcanized rubber particles dispersed in thermoplastic resin possess higher tensile strength and elasticity, better thermal resistibility, improved media resistance and fatigue resistance, lower permanent compression deformation, greater stability of morphology and more consistent processability [2–4]. Dynamic vulcanization of TPVs can be conducted in devices of Brabender Plasticorder, Banbury mixer, Haake plasticorder or two-roll mill and so on. But in general the processing procedure in these internal or open mixers is discontinuous. In recent years, a continuous process of tailoring TPVs by using reactive extrusion has been widely reported. Cai and Isayev [5, 6] prepared a new TPV of copolyester/nitrile rubber alloys by using various dynamic vulcanization techniques, such as internal mixing, open mill mixing, and twin-screw extrusion, or their combinations. Furthermore, the effects of the various manufacturing techniques on rheological and mechanical properties of the TPV were compared, and their results of research indicated that the dynamic vulcanization method by a twin-screw extruder is most suitable for the manufacture of that TPV. Fritz [7, 8] also described preparing an innovative TPV composed of polypropylene and ethylene/octene copolymer by using a twin-screw extruder, and found that this TPV is easy to process into articles showing

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some attractive properties. Through optimizing the ingredient and technological conditions, Wu [9]prepared a low hardness TPV consisting of ethylene-propylene-diene monomer and polypropylene by employing a twin-screw extruder, and studied the effect of technological factors and accelerating agent content on the rheology, morphology and crosslinking density of the TPV. Pei and Basil [10] prepared a terephthalate/ethylene-ethyl acrylate-maleic anhydride terpolymer TPV by dynamical vulcanization in a one-step extrusion process and located the region of phase inversion. More recently, Agnes and coworkers [11] reported a new TPV of polypropylene/ethylene-vinyl acetate copolymer prepared by using a twin-screw extruder, and correlating the evolution of the two-phase blend morphology with respect to the extent of the crosslinking reaction on the elastomer phase. But for reactive extrusion, it is inevitable that when flowing through the die of an extruder, an extrudate can develop a surface with a more or less regular pattern of ridges resulting in an observable mattness, roughness or melt fracture due to melt flow instabilities. The phenomenon is often defined as the "sharkskin effect" and limit the development of polymer extrusion [12]. However none of the authors just mentioned above has given any detail concerning the extrudate surface. And correlation among the two-phase morphology, rheological behavior and the surface of TPV extrudate also remain undiscussed.

In our recent work, we have prepared a high-damping material composed of Chlorinated butyl rubber (CIIR) and Polyethylacrylate (PEA) [13], and if the blend ratio is 60/40 of CIIR/PEA, a high and broad damping peak around the room temperature can be achieved in the tanδ versus temperature curve. For the purpose of continuously producing the high-damping material, a twin-screw extruder is adopted in this article to prepare CIIR/PEA TPV extrudate with excellent surface quality, and a discussion is given to correlate the surfaces of these extrudates with the evolution of the two-phase morphology and the rheological behavior.

Experimental

Materials and preparation

CIIR (EXXON 1068) was supplied by Exxon Co. Phenolic resin 201 (PR 201) was commercially available from Chongqing Resin Plant. Other curing accelerating agent such as ZnO, MgO, stearic acid were offered by Kelong Chemical Industrial Plant. PEA initiated by $K_2S_2O_8$ and $FeSO_4$ was prepared by emulsion polymerization (the formulation is given in Table 1).

Melt-mixed CIIR/PEA blends with a ratio of 60/40 in weight were prepared on a two-roll mill at 160 °C. After cooling, PR201 and other accelerating agent were added to the resulting melt-mixed CIIR/PEA blends on the mill. The concentration of PR201, ZnO, SA, MgO are 5, 3, 1 and 0.25 wt%, respectively. The blends were then cut into particles for extrusion. Extrusion experiment was carried out with a co-rotating twin-screw extruder (TSSJ-25, made in Chengdu China). The screw L/D ratio is equal to 33/1 with D of 25 mm (L and D are, respectively, the length and the diameter of the screw). The barrel is divided into eight zones from the feeding hopper to the die. The screw speed was set at 160 rpm. The barrel temperature is set as shown in Table 2.

The CIIR/PEA TPV extrudates are denoted as $T1_1$, $T2_1$, $T3_1$, $T4_1$, $T2_1T4_1$, $T2_1T4_2$, $T2_1T4_3$, and $T2_1T4_4$ respectively, where T and the Arabic numerals are indications of the extrusion temperatures and the subscripts are corresponding to the extrusion times, for example, $T1_1$ is extruded at temperature T1 for one time, and $T2_1T4_4$ is first extruded at temperature T2 for one time and then extruded at temperature at T4 for four times.

Rheological measurement

The rheological measurement of the extrudates was carried out in a RHEOGRAPH 2002 High Pressure Rheometer at a temperature of 160 °C. Before measurement, 0.5 wt% of diphenyl carbamidine was added to in each extrudate to retard or prevent the CIIR phase from further crosslinking in the rheometer.

Morphology analysis

A scanning electron microscopy (SEM, Hitachi X-650, made in Japan) was used to study the morphology of extrudates. To prepare samples for SEM analysis, the

Table 1 The formulation of emulsion polymerization

Composition	Content/g
EA	100
$K_2S_2O_8$	0.05
$FeSO_4$	0.1
EDTA	0.025
$NaHSO_2CH_2O$	0.1
Na_2HPO_5	0.2
$C_{18}H_{29}NaO_3S$	4
H_2O	150

Table 2 The barrel temperature

Temperature	Zone I (°C)	Zone II (°C)	Zone III and IV (°C)	Zone V and VI (°C)	Zone VII (°C)	Die (°C)
T1	90	100	100	110	110	100
T2	100	110	110	130	130	120
T3	120	130	130	150	150	140
T4	140	150	150	170	170	160

extrudates were quenched in liquid nitrogen and cryogenically fractured. The fractured samples were eroded with acetone for 30 min and the PEA was extracted preferentially. Before testing, these samples were sputter coated with Au.

Determination of CIIR gel content

The extrudates were cut into small particles. About 1 g particles of each extrudate were accurately weighted and extracted first with acetone for 72 h, and then with cyclohexane for the same time. The samples was completely dried after extraction and weighted. Then the CIIR gel content can be calculated from W_r/W_c, where W_r is the weight of residual CIIR and PR201 and W_c is the original weight of CIIR and PR201 contained in the sample.

Fourier transform infrared spectroscopy (FTIR) analysis

A Nicolet Magna 360 FTIR spectrometer was used to analysis the gel after extraction.

Determination of extrudate swell

The extrudates were carefully collected as they emerged out from the die of the extruder, taking care to avoid any deformation. The diameters of the extrudates were measured after cooling. The die swell value is calculated from d_e/d_d, where d_e and d_d are the diameter of the extrudate and the diameter of the die, respectively.

Results and discussion

Analysis of CIIR gel content

The influence of extrusion temperature and times on the CIIR gel content is shown in Table 3. For T1$_1$, extrusion at the temperature of T1 for once time is just like a further blending process, and the CIIR gel content is little, but for other samples, the CIIR gel content increases with increasing temperature or times of extrusion. However, it is still unexpected to note that CIIR gel content exceeds 100% for T2$_1$T4$_3$ and T2$_1$T4$_4$. The cause may lies in the fact that numerous macromolecular radicals from PEA and CIIR are formed due to the long-time strong sheer stress and high temperature in the extruder. As a result, chemical links take place between CIIR and PEA molecules and some amounts of copolymer are produced. In other words, the gel of T2$_1$T4$_4$ and T2$_1$T4$_3$, or even T2$_1$T4$_2$, T2$_1$T4$_1$ contains not only CIIR molecules but also part of PEA molecules. To testify this speculation, FTIR was used to analysis the pure CIIR and the gel of T4$_1$ and T2$_1$T4$_1$, the result is shown in Fig. 1. Compared with pure CIIR, the gel of T4$_1$ shows three weak vibrational band at 1,731, 1,650 and 1,600 cm^{-1}, which are attributed to the C = O vibration and the C = C vibration of crosslinking agent of phenolic resin. However, we can observe a relative strong band at 1,708 cm^{-1} in the gel of T2$_1$T4$_1$, which is the superimposed band of the C = O vibration of PEA and phenolic resin. Furthermore, in the IR spectrum of the gel of T2$_1$T4$_1$, we can still notice two characteristic bands of C–O–C vibration of PEA at 1,260 and 1,098 cm^{-1}, suggesting that some PEA molecules are grafted on to CIIR molecules and a quantity of copolymer is formed. Because strong shear stress and high temperature are exerted on the CIIR/PEA blend in the extruder, the processes of mechanochemical and thermal degradation happen simultaneously. As a result, there may be three ways to form macromolecular radicals of CIIR and PEA. First, chlorine atoms in CIIR or α-Hydrogen atoms in PEA are easy to break off due to high temperature, which gives rise to macromolecular radicals. Second, compared with end groups and side groups, chemical bonds at the middle of main chains of both PEA and CIIR bear stronger shear stress, thus they

Table 3 The CIIR gel content of the phase of different extrudates

Sample	Gel content (%)
T1$_1$	6.9
T2$_1$	68.8
T3$_1$	75.8
T4$_1$	78.9
T2$_1$T4$_1$	81.2
T2$_1$T4$_2$	93.7
T2$_1$T4$_3$	106.2
T2$_1$T4$_4$	117.3

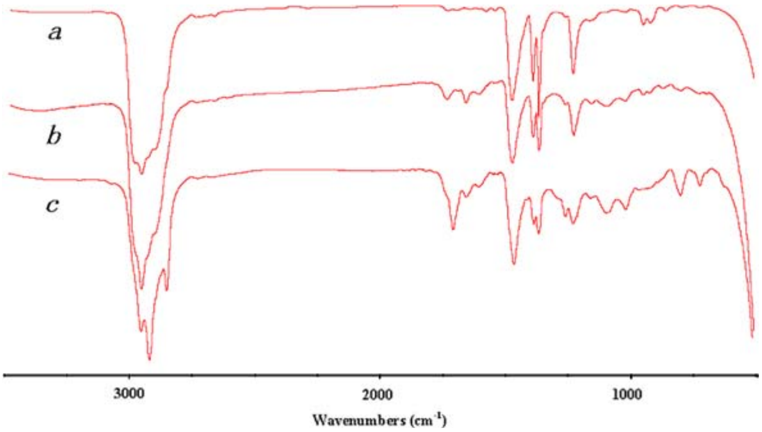

Fig. 1 IR spectra of **a** (pure CIIR), **b** (gel of T4$_1$) and **c** (gel of T2$_1$T4$_1$)

tends to rupture and yield macromolecular radicals. Third, the network of crosslinked CIIR can easily fracture under strong shear stress, and produce macromolecular radicals of CIIR. Some macromolecular radicals of CIIR can attack the α-Hydrogen of PEA, so graft polymer is produced. On the other hand, some macromolecular radicals of PEA can react with phenolic resin or attack Cl–C bond of CIIR, consequently, direct or indirect chemical links are formed between CIIR and PEA.

Analysis of the extrudate morphology

In order to trace the evolution of the two-phase morphology with variation of crosslinking density of CIIR phase during extrusion undergoing different temperature or different times, the morphologies of extrudates are characterized by SEM.

Figure 2 shows the effect of extrusion temperature on the extrudate morphology. For T1$_1$, two distinct phases can be observed. At this extrusion condition, the major phase of uncured CIIR forms a continuous phase in which PEA spherical particles are dispersed. While for T2$_1$, its gel content has reached 68.8%, under this case, PEA domains are not spherical any more, but look as if they interpenetrate with CIIR domains, thus, a co-continuous structure is generated, indicating the beginning of phase inversion. This phenomenon demonstrates that CIIR domains have begun to breakup and PEA particles have been coalesced under high shear stress. It can be interpreted by the fact that the crosslinking network of CIIR phase behaves like a viscoelastic solid, which is fragile under high shear stress; furthermore, the crosslinking of the CIIR phase under shearing breaks the coalescence/breakup equilibrium process of PEA particles. For T3$_1$, with a gel content up to 75.8%, the CIIR network looks like a structure of more or less broken domains. However, it's still co-continuous. For T4$_1$, when the CIIR gel content reaches 78.9%, the CIIR network has broken up completely into particles dispersed in the continuous PEA matrix. The morphology in this stage is opposite to T1$_1$, indicating that the phases have been inversed. This phenomenon is consistent with the result of Danesi and Porter [14], who point out that: when the two components have different melt viscosities, the morphology of the binary blend depends on whether the minor one has lower or higher melt viscosity than that of the major one; in general, the less viscous component tends to form the continuous phase while the more viscous one tends to be dispersed phase, irrespective of composition. Obviously, in the CIIR/PEA blend, the viscosity of the major phase of cured CIIR network is much higher than that of uncured PEA phase.

Figure 3 exhibits the effect of extrusion times on the TPV extrudate morphology. For the four samples, extruded at the temperature of T2 and T4 for more than one time, all exhibit morphologies of CIIR particles dispersed in the continuous PEA matrix. But it is worth to note that with increasing extrusion times the domains of the dispersed phase become larger, instead of the general tendency of becoming smaller, and also the particle edges become blurrier. With the increasing of extrusion times, more and more PEA molecules are linked and attached to the dispersed CIIR particles, and these PEA molecules can't be etched out. So the reason why dispersed particles seem to become larger is not that coalescence takes place in CIIR phase but that PEA molecules are chemically linked and attached to CIIR particles. Finally, it is clear in the SEM photograph of T2$_1$T4$_4$, which are magnified to 1000 times, that the PEA phase is difficult to be etched out.

Analysis of the viscosities of the extrudates

As can be seen in Fig. 4, the viscosities of the four extrudates, extruded at different temperatures,

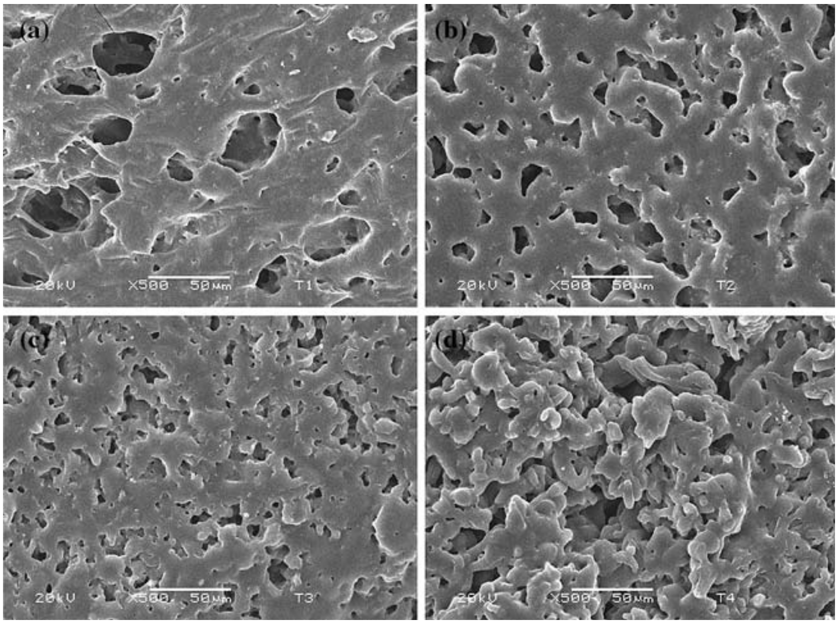

Fig. 2 Effect of extrusion temperature on the extrudate morphology: (**a**) $T1_1$, (**b**) $T2_1$, (**c**) $T3_1$, (**d**) $T4_1$

decrease with increasing shear rate, suggesting a feature of pseudoplastic flow. For $T1_1$ $T2_1$, $T3_1$ and $T4_1$, as the extrusion temperature decreases, the extrudate viscosity increases at the same shear rate. However, the rheological behavior of $T1_1$ is more complex. At low shear rates, it is lower than that of $T2_1$, $T3_1$, $T4_1$, and goes down more slowly; while at high shear rates, the viscosity of $T1_1$ goes higher than that of $T2_1$, $T3_1$, $T4_1$ and finally parallel with $T2_1$. These behaviors can be explained in terms of phase morphology of these TPV extrudates. In polymer blends, the viscosity depends on interfacial thickness, interface adhesion and morphology in addition to the characteristics of the component polymers. When a shear stress is exerted on a polymer blend, it undergoes an elongational flow. If the interface between the components is not strong, there will be interlayer slip along with orientation and disentanglement on the application of shear stress. As a result, the viscosity is lower than the log-additive value of the components. But if the interface is strong enough, the deformation of the dispersed phase will make it be effectively transferred to a continuous phase. As a result, a co-continuous morphology is formed, which can prevent the interlayer slip effectively and make

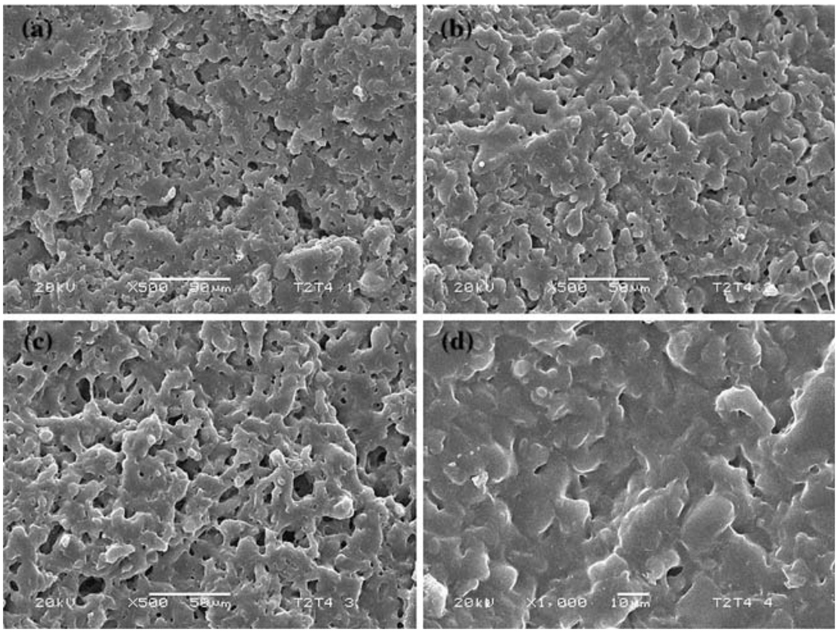

Fig. 3 Effect of extrusion times on the extrudate morphology: (**a**) $T2_1T4_1$, (**b**) $T2_1T4_2$, (**c**) $T2_1T4_3$, (**d**) $T2_1T4_4$

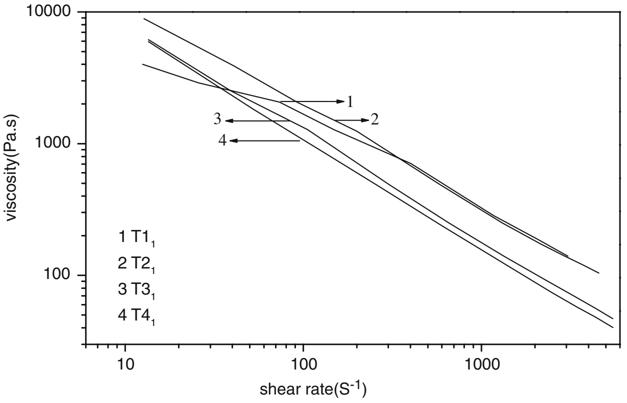

Fig. 4 Effect of extrusion temperature on the viscosities of $T1_1$, $T2_1$, $T3_1$ and $T4_1$

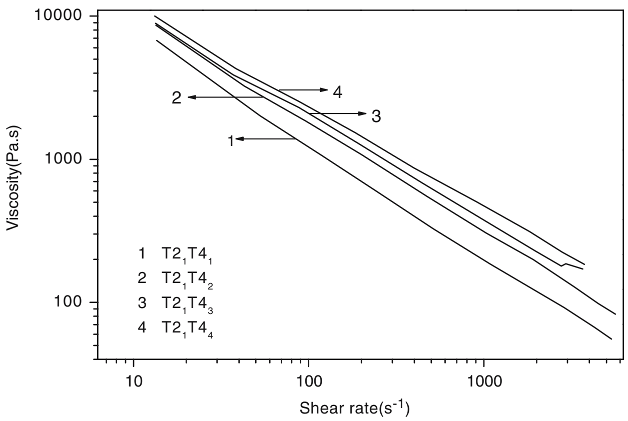

Fig. 6 Effect of extrusion times on the viscosities of $T2_1T4_1$, $T2_1T4_2$, $T2_1T4_3$ and $T2_1T4_4$

disentanglement more difficult. So the co-continuous morphology is responsible for higher viscosity.

As to $T2_1$ and $T3_1$, the co-continuous nature of CIIR and PEA is the reason why their viscosities are higher than that $T4_1$. But the continuous CIIR phase of $T3_1$ is more or less broken, so its viscosity is lower than that of $T2_1$. As to $T1_1$, there probably are two causes to explain its unusual rheological behavior: (1) the interface adhesion is strong between CIIR and PEA, because CIIR is not vulcanized. With the growth of shear rate, the PEA phase becomes continuous gradually and finally a co-continuous phase is formed (as shown schematically in Fig. 5), consequently, with increasing shear rate, the viscosity of T1 decrease more slowly than that of other samples and finally goes higher than that of other extrudates. (2) The addition of diphenyl carbamidine cannot completely prevent the CIIR phase from further crosslinking, so the odd rheological behavior of T1 can be attributed to the fact that crosslinking density of the almost unvulcanized T1 rises with increasing test time.

The effect of extrusion times on the viscosity of the extrudate is shown in Fig. 6. As can be seen, $T2_1T4_1$, $T2_1T4_2$, $T2_1T4_3$ and $T211_1T4_4$ also show pseudoplastic flow behavior. As the extrusion times increases, the extrudate viscosity increases, which is probably resulted from two aspects: (1) With increasing crosslinking density of CIIR phase, it is more difficult for the extrudates to flow. (2) As mentioned previously, chemical links takes place between CIIR and PEA molecules due to strong shear stress, and the PEA molecules chemically linked and attached to CIIR particles may behave as a compatilizer, which lead to a reduction in interfacial tension, an improvement in interfacial adhesion and an increase in interfacial thickness. As a result, stress transfer between the dispersed phase and continuous phase is greatly improved. This contributes to the reduction in interlayer slip and therefore gives rise to an increase in viscosity. The more times the CIIR/PEA TPV is extruded, the more macromolecular radicals are produced and the more PEA molecules are chemically linked and attached to CIIR particles. Consequently, with increasing of extrusion times, the viscosity of the TPV goes up.

The surfaces of the extrudates

In the barrel and die of the extruder the polymer molecules undergo orientation under the action of shear stress, when emerging from the die, the oriented molecules have a tendency to recoil, because of the melt elasticity of polymers, especially rubbers. As a result, phenomena like extrudate swell, melt fracture, shark skin, etc. take place. The surfaces of the extrudates are shown in Fig. 7, from which it can be seen

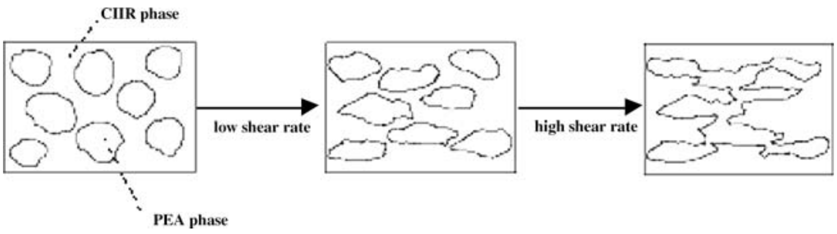

Fig. 5 Schematic representation of morphology development of T1 under shearing

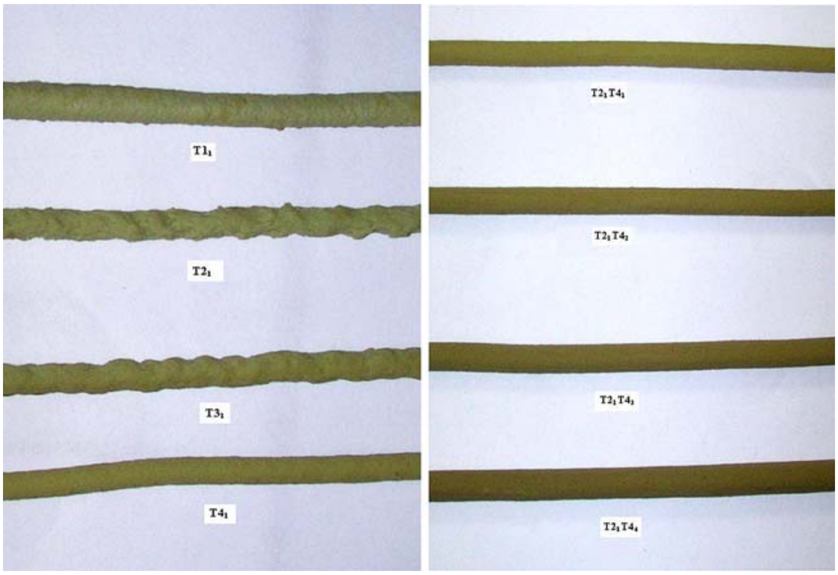

Fig. 7 The surfaces of the extrudates

that with the increasing extrusion temperature or times, the surfaces of the extrudates become gradually smooth. It is suggested from the Fig. 7 that higher extrusion temperature or more extrusion times are favorable for smoothing the extrudate surface and reducing the extrudate deformation. A rough surface can be observed from T1$_1$. With spherical PEA particles dispersed in the continuous CIIR phase, CIIR plays a dominant role in the flow behavior, however, the high melt elasticity of CIIR is disadvantageous to extrusion. For T2$_1$ and T3$_1$, it is unexpected that the formation of a co-continuous phase is unfavorable to form a smooth extrudate surface, as can be seen that periodic distortions appear on their surfaces, implying that melt fracture takes place. For the rest of the samples, the extrudate surface becomes gradually smooth and glossy with increasing temperature or extrusion times, which can be interpreted by the change of the morphology. As mentioned above, for these samples, CIIR particles are dispersed in the continuous PEA matrix, therefore less elastic PEA phase play a predominant role in the flow behavior. Furthermore, with the increase of extrusion temperature or times, the CIIR particles become smaller and smaller. For T4$_1$, because the CIIR particles are larger, they are easily to undergo a larger extent of deformation and orientation, and after emerging from the die the recoil of these particles result in a rough surface (as shown schematically in Fig. 8a). On the contrary, for T2$_1$T4$_1$, T2$_1$T4$_2$ T2$_1$T4$_3$ and T2$_1$T4$_4$, the CIIR particles are smaller and suffer less deformation and orientation during extrusion through the die, and the recoil extent of the particles is smaller, therefore their surfaces are relatively glossy and smooth (as illustrated schematically in Fig. 8b). Among all of these extrudates, the surfaces of T2$_1$T4$_3$ and T2$_1$T4$_4$ are the best. It can be explained by the fact that the numerous PEA molecules chemically linked and attached to CIIR particles act as a function of compatilizer, which can improve the extrudate surface and reduce the extrudate deformation, as suggested by George [15].

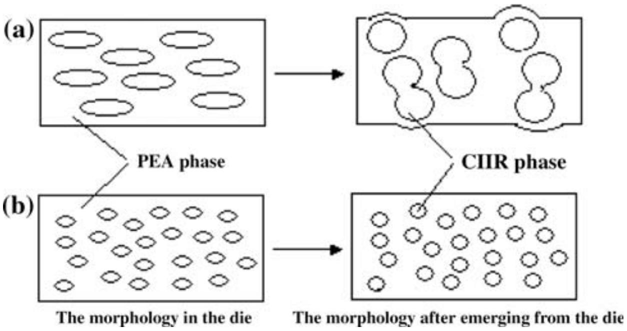

Fig. 8 Schematic representation of development of morphology of the extrudates: (**a**) extruded for once time, (**b**) extruded for three times

The extrudate swells are shown in Table 4, the dynamic vulcanization has a significant effect on the extrudate swell values. As the gel content increases, the extrudate swell values decrease firstly and then increase. Since CIIR is continuous in T1$_1$ and T2$_1$, it high melt elasticity dominates the recovery process of molecular orientation after extrusion and finally results in the high extrudate swell. The swell values of T3$_1$, T4$_1$, T2$_1$T4$_1$, T2$_1$T4$_2$ and T2$_1$T4$_3$ are relatively low. This result is in accord with the research of Coran et al. [16], who reported that in the case of dynamically vulcanized thermoplastic elastomers, the die swell

Table 4 The extrudate swell values

Sample	Extrudate swell values
$T1_1$	1.33
$T2_1$	1.26
$T3_1$	1.16
$T4_1$	1.14
$T2_1T4_1$	1.13
$T2_1T4_2$	1.16
$T2_1T4_3$	1.17
$T2_1T4_4$	1.33

values are very low or can't be detected. But for $T2_1T4_4$, its swell ratio is relatively high, such a phenomenon can be deduced by that with a gel content of 117.3%, the extrudate as a whole may form a network, which possesses fairly high elasticity and thus has a tendency to recover from orientation.

Conclusion

It can be summarized from the experimental results that:

(1) The CIIR gel content increases with increasing extrusion temperature or times; extrusion at high temperature produces numerous PEA and CIIR macromolecular radicals, thus chemical links take place between PEA and CIIR molecules;

(2) the phase inversion takes place at a gel content of around 68%, where a co-continuous morphology is formed; when the CIIR gel content reaches around 79%, the CIIR network is completely broke into particles dispersed in the continuous PEA matrix; with the increasing extrusion times at high temperature the dispersed domains become larger and the particle edges become blurrier;

(3) CIIR/PEA TPVs show a feature of pseudoplastic fluid; with the decrease of extrusion temperature or increase of extrusion times, the melt viscosity of these TPVs increases; but the rheology behavior of the extrudate prepared at the lowest temperature is somewhat complex.

(4) a morphology of PEA particles dispersed in the continuous CIIR phase is unfavorable for smoothing the extrudate surface; and the co-continuous nature of the morphology also results in melt fracture and periodic distortions on the extrudate surface; on the other hand, with the increasing extrusion temperature or times, the surfaces of the extrudates become gradually smooth; and as the gel content increases, the extrudate swell values decrease firstly and then increase.

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