

Phase morphology evolution and compatibility improvement of PP/EPDM by ultrasound irradiation

Yingzi Chen, Huilin Li*

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

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Abstract

The effects of ultrasonic irradiation on morphology and compatibility of polypropylene (PP)/ethylene–propylene–diene terpolymer (EPDM) blends were examined. Results show that ultrasound irradiation lead to stable morphology with reduced disperse phase size. Dynamic rheological analysis indicates the more homogeneous internal structure of PP/EPDM blend is obtained with ultrasonic irradiation. Increase the residence time of the blends in the ultrasound irradiating zone, the structure of the blends get even more homogeneous. The interfacial tension between PP and EPDM melts obtained from the Palierne emulsion model decreases with applying of ultrasound irradiation and increasing of residence time. The glass transition temperatures of PP and EPDM phase become closer to each other with ultrasonic irradiation. FTIR analysis indicates in situ copolymers formation between PP and EPDM happens with ultrasound irradiation and the copolymer consequently acts as compatibilizers for the blend.

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1. Introduction

Development of novel polymers by blending two or more polymers is a research field of considerable interest. The great majority of usable blends are thermodynamically incompatible. In these blends, mechanical properties depend greatly on the morphology, and are often very poor due to the lack of physical or chemical interactions between different phases and poor interfacial adhesion [1].

When two incompatible polymers are melting blended by extrusion or in a batch mixer, one component is mechanically dispersed inside the other. The size and shape of the dispersed phase depend on several processing parameters including viscosity ratio of the components, rheology, interfacial properties, and type of the flow field. It has been reported that, after the initial period, blend morphology does not change significantly over time in batch mixers [2–5], or over length in the twin-screw extruders [6]. This invariant morphology is due to a rapid

establishment of equilibrium between drop breakup and coalescence of the dispersed phase [7,8]. The ultimate morphology of the blend depends greatly on the design of the screw tip or the shaping head, and the operation [9,10].

In situ reaction to form copolymers in blending or adding premade diblock copolymers can suppress the dispersed phase coalescence effectively and result in smaller particle size and narrower particle size distribution [11]. That is the compatibility of the two phases in the blend is improved.

Ultrasound is a sort of elastic mechanic wave of frequency 10^4 – 10^8 Hz. It can influence a medium through which the waves propagate by sound streaming action, shatter, cavitations, etc. It has been shown that ultrasound-induced polymer breakage is a direct consequence of cavitation [12]. The breakage of the C–C bond by ultrasound usually leads to the formation of long-chain radicals in polymer solutions, which can cause the formation of copolymer by coupling of those long-chain radicals from different polymers [13,14].

Recently, high power ultrasound has been applied to the melt state polymer blends during processing. PP/PS [15] in batch mixing process and PP/rubber [16] in continuous extrusion process with ultrasound irradiation were reported, respectively. It was found that ultrasonic treatment during

* Corresponding author.

E-mail address: lihuilin5405136@sina.com (H. Li).

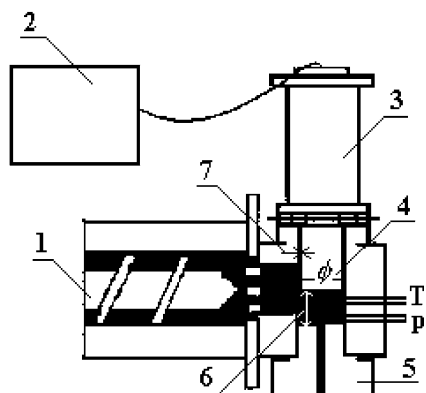


Fig. 1. Details of ultrasound-extrusion system. 1, Extruder; 2, ultrasonic generator; 3, piezoelectric transducer; 4, cylindrical horn with diameter $\phi = 10$ mm; 5, slit die; 6, gap between horn tip and entry to the slit die is 10 mm; 7, gap between the lateral surface of horn and the die wall is 1 mm; P, pressure transducer; T, thermocouple.

prolonged batch mixing (tens of minutes) or extrusion at a residence time of seconds can improve interfacial adhesion and compatibilization between different phases of immiscible polymer blends. PP/EPDM [17] in continuous extrusion process with ultrasound irradiation, which was reported by Wenlai Feng and Isayev, indicated the same effects as above. In this case, formation of copolymer in the ultrasound treated PP/EPDM sample was verified by IR spectra.

A previously reported study [18] of us has also revealed that applying of ultrasound vibration to PP/EPDM blend melt at the entrance of the shaping head (the die), morphology of smaller particle size and more homogenous dispersed EPDM phase, as well as good adhesion between EPDM and PP matrix were formed. In this paper, we try to illustrate how the ultrasound influences the morphology and compatibility of PP/EPDM blend during extrusion processing.

2. Experimental

2.1. Materials

The materials used in this study were commercial grades of PP (F401, Langang Chemical Co., Lanzhou, China) with MFR = 2.5 g/10 min as matrix polymer, and EPDM (NOR4725P, Dupont Dow Elastomers L.L.C., Wilmington, NC, USA) with MFR = 0.2 g/10 min. MFR were measured at 230 °C under load of 2.16 Kg with a American CS-127 MFR instrument.

2.2. Processing equipment

The ultrasound-extrusion experimental setup consists of a single-screw extruder with a variable cross-section capillary ($d = 3$ mm, $L/D = 8$) having high-temperature

pressure transducer and ultrasonic generator (Fig. 1). The ultrasonic frequency is 20 kHz and power ranges from 0 to 300 W. The direction of ultrasonic vibration coincides with that of the melt flow during extrusion.

2.3. Sample preparation

The virgin PP was physically mixed with EPDM at the ratios of PP/EPDM = 70/30 by weight, and extruded by single-screw extruder with screw rotation speed of 20 rpm, die temperature of 200 °C, then made pellets and extruded again with ultrasonic irradiation of various intensities. To increase the residence time of the blends in the ultrasound-irradiating zone, some of the blends prepared by preceding steps were extruded again with ultrasonic irradiation of various intensities.

The extrudates were then made pellets and compression molded into 1.5 and 4 mm plates. Compression molding was carried out using the following conditions: preheating at 190 °C for 10 min at low pressure, compression for 5 min at 10 MPa at the same temperature, and then cooling to ambient temperature with the cooling rate 30 °C/min in the mold at 10 MPa. Disk specimens with 25 mm in diameter for rheological experiments were cut from the 1.5 mm plates, and some SEM observed specimens were gotten from the 4 mm plates.

2.4. Morphological analysis

Japan JSM-5900LV scanning electron microscope (SEM) was used to observe blend morphology. The extrudates were cut at the exit of the die and immersed into liquid nitrogen immediately, then fractured longitudinally and transversely to get a longitudinal surface and a traversal surface. Fracture surfaces were etched by xylene to remove EPDM, and plated with gold before examination.

2.5. Rheological experiments

The frequencies sweep experiments of the melt samples were carried out on an Advanced Rheometrics Expansion System (ARES-9A, Rheometrics Co.) using the dynamic oscillatory mode with parallel plate fixture of 25 mm. The frequency ranged from 0.25 to 100 Hz. Sample response linearity with respect to temperature was verified and nitrogen gas was used to prevent thermal oxidation.

2.6. Thermal analysis

The thermal analysis of the materials was carried out in a NETZSCH DSC 204 (Germany) differential scanning calorimeter. To get the glass transition information of PP and EPDM phase of the blends, liquid nitrogen was used as refrigerating medium, the samples were heated from -80 to 20 °C at a rate of 10 °C/min.

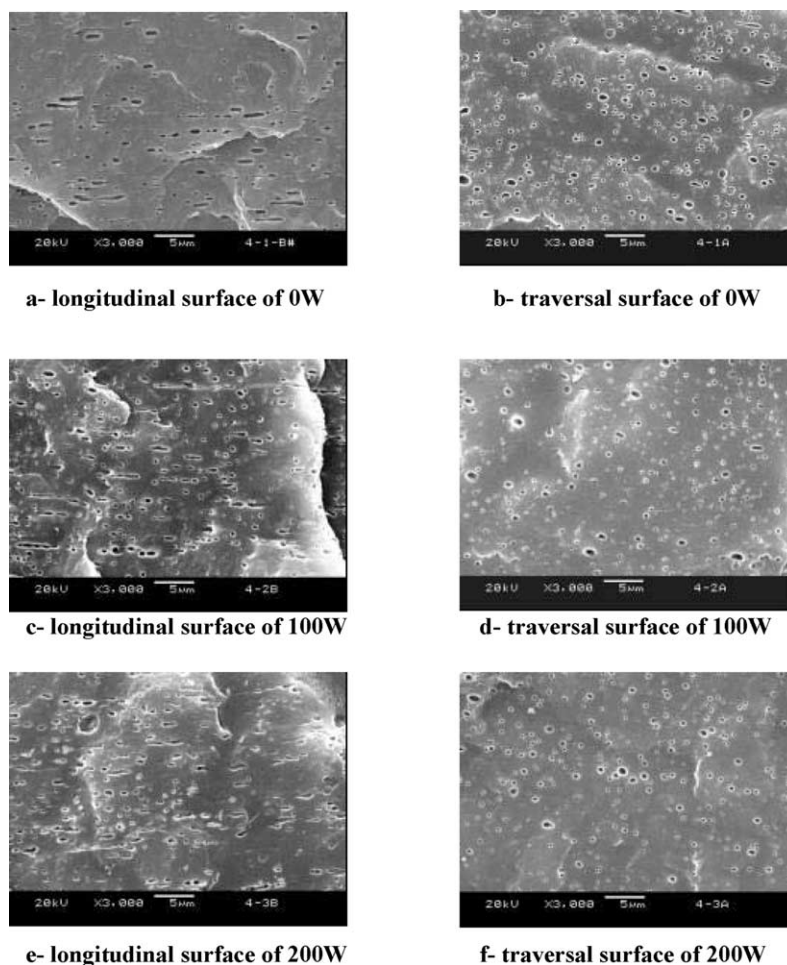


Fig. 2. SEM photos of brittle fractured surfaces of PP/EPDM extrudates.

2.7. Components separation experiment and FTIR analysis

To inspect the existence of PP-EPDM copolymer, the extrudates were put into a proper separation procedure, by which free EPDM was separated. After extruding, the samples were washed by extraction with cyclohexane for 72 h and dried in a vacuum oven at 100 °C for 12 h. The existence of EPDM units grafted to PP chains was investigated by FTIR (NICOLET-560).

3. Result and discussion

3.1. Fracture surface morphology observation

Fig. 2 shows the micrographs of brittle fractured surfaces of PP/EPDM blends extrudates. As it is shown in Fig. 2(a) and (b), elastic effect in the entry zone of the die and velocity gradient in the flow field made some of the EPDM drops deformed and oriented to the flow direction when the blends melt flow through the capillary die. The micrographs of the longitudinal surfaces are quite distinct from those of the traversal surfaces. When 100 W ultrasound is applied,

the direction of ultrasonic vibration coincides with that in which the melt flow through the die, and more EPDM drops were deformed and oriented by ultrasound vibration. The EPDM drops become into EPDM rods, expanding in length and contracting in diameter. The difference between the longitudinal surfaces and traversal surfaces is more notable, as seen in Fig. 2(c) and (d). With 200 W ultrasound intensity, the EPDM rods were stretched further, and broke at the weakness into smaller elliptical drops with the major axes orienting to the flow direction.

To quantify the phase morphology of a three-dimensional structure from micrographs showed in Fig. 2, the Chalkey method for estimation of the volume to surface ratio has been used [19,20]. Needles with a suitable length μ were dropped randomly on the SEM morphological structures and the amount of 'hits' and 'cuts' are counted. The total amount of the end of needles that lie in the interior of the feature of interest is called hits (N_h). The summation of the intersection points on the boundaries gives the number of cuts (N_c). Using formula (1), the volume (V) over surface (S) ratio (T^*) of the feature of interest, i.e. the EPDM phase for the PP/EPDM=70/30 blends can be calculated:

Table 1
Reciprocal Chalkey parameter as a function of the ultrasound intensity

Ultrasound intensity (W)	Reciprocal Chalkey parameter (cm^{-1}) $\times 10^{-6}$	
	Longitudinal surface	Traversal surface
0	37.71	76.21
100	45.33	169.78
200	53.54	312.00

$$(T^*) \equiv \left(\frac{V}{S} \right) = \frac{\mu N_h}{4vN_c} \quad (1)$$

where μ is the length of the needles, and v the total amount of the sampling points.

The reciprocal Chalkey parameter $(T^*)^{-1}$ is directly related to the relative surface fraction, because the volume fraction of EPDM phase in the PP/EPDM blends can be considered as constant on account of the incompatibility of the components. All SEM micrographs used to estimate the value of the Chalkey parameter have been taken in the middle of the fractured surfaces.

The estimated surface to volume ratio of EPDM phase in the PP/EPDM blends is listed in Table 1 as a function of ultrasound intensity. As can be seen, the reciprocal Chalkey parameters, obtained both from the longitudinal surfaces and from the traversal surfaces, increase with ultrasound intensity. That means the size of EPDM particles are much smaller and the dispersions of EPDM phase in PP matrix are more homogenous with ultrasound irradiation than that without ultrasound.

In practical blend processing, it is very hard to obtain good dispersion if viscosity of the disperse phase is much higher than that of the matrix. In this case the stress required to break the disperse phase cannot be satisfied, although there are some other reasons, such as the viscoelasticity and complexity of the flow field. When ultrasound is applied, its powerful vibration and jet current help to deform and shear cut EPDM in PP matrix. When the blend melt goes into the ultrasound effect zone (i.e. entrance of the die), ultrasonic

vibration leads to disentanglement of molecular chains and interpenetration of the two phases by dynamics controlling process. Once the melt flows out of the zone, thermodynamics process become dominant, and the chains get entangled again. This gives the chance to PP and EPDM molecules near the interface to entangle with each other. Therefore, interfacial thickness of PP/EPDM blend is improved by applying of ultrasonic vibration, that means compatibility of EPDM and PP matrix is improved. The elastic recoil of the entangled molecules at the interface helps to separate the EPDM drops during the initial collision step. And the increased interfacial effect helps to suppress coalescence of EPDM phase.

Fig. 3 shows the phase morphology of PP/EPDM blends reprocessed by compression molding. As it is shown that the elongated EPDM particles in the extrudates were contracted to be spherical, and coalescence of EPDM drops happened in a certain extent. But it still can be seen that the EPDM particles are much smaller in PP/EPDM blend with ultrasonic irradiation [Fig. 3(B) and (C)] than in that without ultrasonic irradiation [Fig. 3(A)]. This means strong interactions between PP and EPDM phases and preferable interfacial adhesion are achieved by ultrasound irradiation, which helps in the stability of the morphology.

3.2. Dynamic rheological analysis

The frequency dependence storage modulus G' and loss modulus G'' of PP/EPDM blends were measured at various temperatures ranged from 175 to 220 °C. These temperature curves can be superposed onto master curves by a horizontal shift along the frequency axis. That is, time–temperature superposition principle can be applied. Fig. 4 shows the master curves of G' and G'' of PP/EPDM blends with different ultrasound intensities at reference temperature 190 °C. For the master curves of the blend without ultrasound irradiation (Fig. 4, 0 W), the superposition of different curves are not so well, especially in high frequency region. But for the blend with 150 W ultrasonic irradiation, the master curves obtained from time–temperature

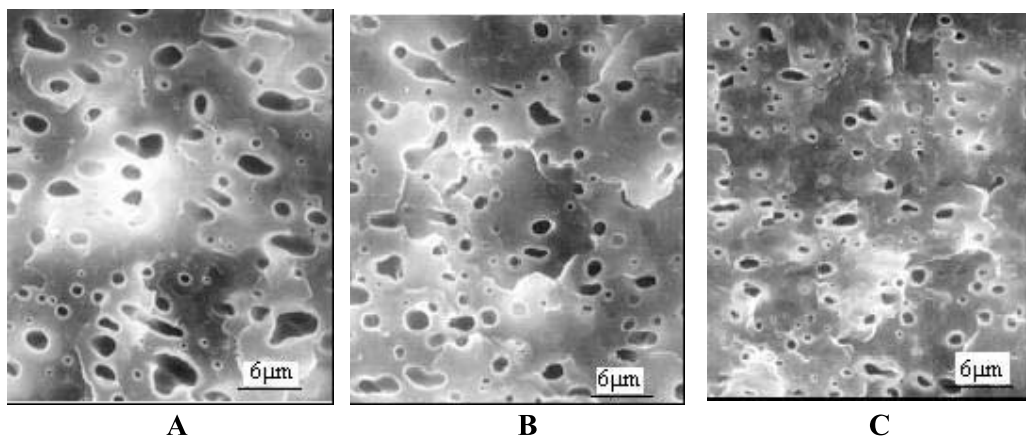


Fig. 3. SEM of brittle fractured surfaces of PP/EPDM (70/30) blends (A) 0 W, (B) 100 W, (C) 200 W.

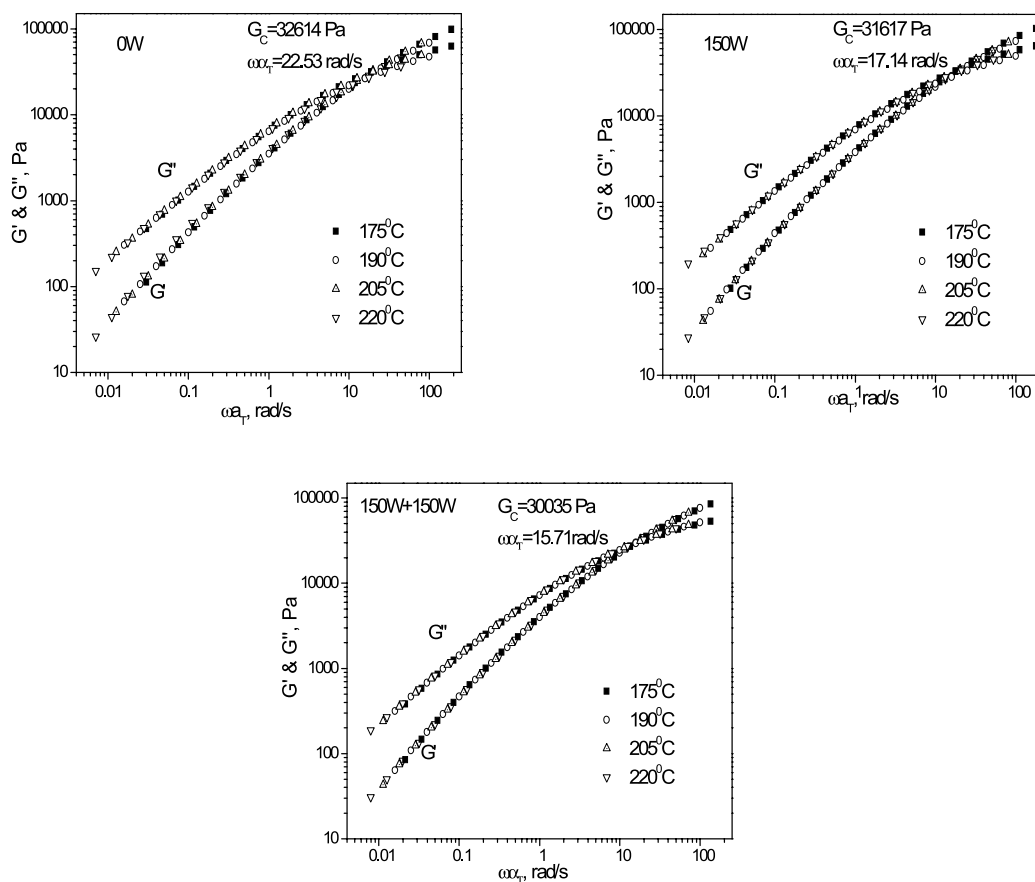


Fig. 4. Master curves of G' and G'' of PP/EPDM blends with different ultrasound intensities at reference temperature 190 °C.

superposition is better than that of the blend without ultrasound irradiation. In the case of blend with twice 150 W ultrasonic irradiation, the master curve is quite smooth all over the frequency region concerned. That means with ultrasound irradiation, the structure of PP/EPDM blend become more homogeneous. With twice ultrasonic irradiation, which means with increased residence time of the blends in the ultrasound irradiating zone, the structures of the blends get even better.

The crossing of G' and G'' curves was defined as dynamic intersection M_C indicating the separation of viscosity and elasticity [21]. At this point

$$G_C(\omega_C) \equiv G'(\omega_C) = G''(\omega_C) \quad (2)$$

G_C was called dynamic intersection modulus and its value depends on the disparity of the system. Bigger the value of G_C , broader the disparity of the system, which means the structure of the system less homogeneous.

As indicated in the Fig. 4, with applying of ultrasound irradiation (150 W) and increasing of the residence time (150 W + 150 W), the dynamic intersection modulus G_C is getting smaller and smaller than that of the blend without ultrasound irradiation (0 W). That confirms the structure of the blends become more homogeneous with ultrasound irradiation.

According to linear viscoelasticity theory [22], at the terminal region ($\omega \rightarrow 0$), storage modulus G' and loss modulus G'' of homogeneous polymers have the relation as following:

$$\log G' \propto 2 \log G'' \quad (3)$$

That means for monodisperse system the $\log G' \sim \log G''$ plot is linear with the slope of 2. For polydisperse system, the terminal region of $\log G' \sim \log G''$ approximates to be linear but the slope is smaller than 2, and drops with the increases in polydispersity [23]. Here the slopes of the terminal region of $\log G' \sim \log G''$ plots are used to obtain some information about the internal structure of PP/EPDM blends. Fig. 5 is the logarithmic plots of $G' \sim G''$ of PP/EPDM blends with different ultrasound intensities at reference temperature 190 °C. The slopes are indicated in the figures. As can be seen, for the blend with ultrasonic irradiation (150 W, 150 W + 150 W) the slope of the terminal region is larger and closer to 2 than that of the blend without ultrasonic irradiation (0 W). This also gives the information that the internal structure of PP/EPDM blend is more homogeneous than that of the blend without ultrasonic irradiation.

The rheological model presented by Palierne [24,25] was developed for incompressible viscoelastic disperse phase

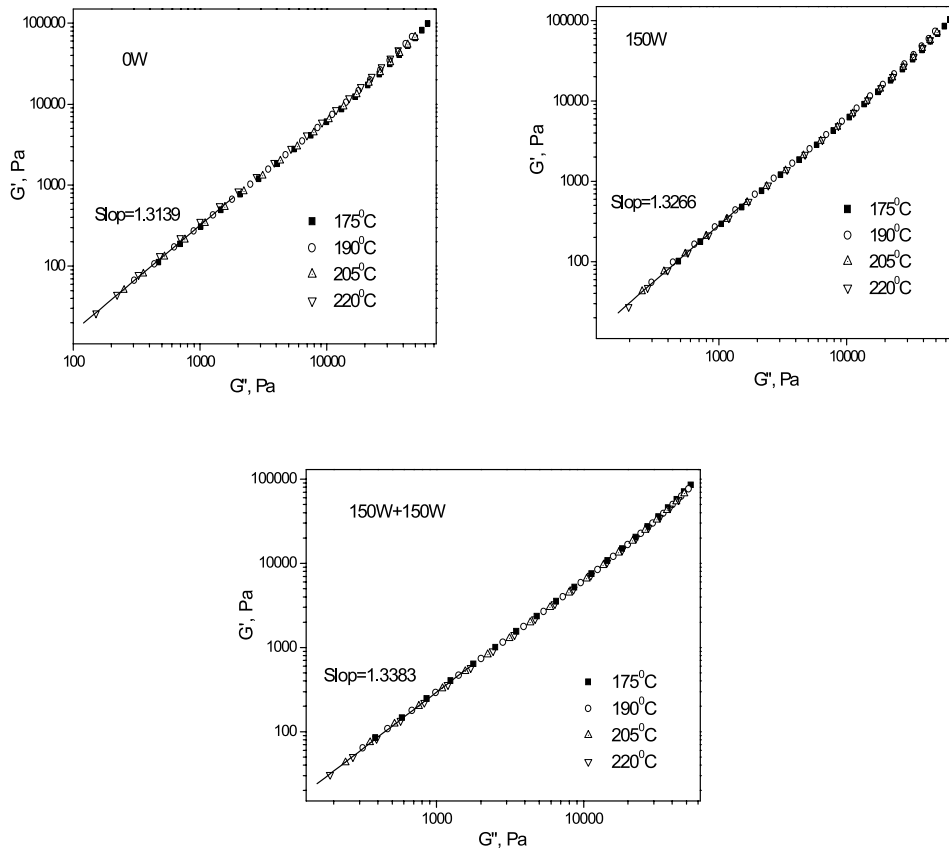


Fig. 5. Logarithmic plots of $G' \sim G''$ of PP/EPDM with different ultrasound intensities at reference temperature 190 °C.

that is spherical at equilibrium in an incompressible matrix. For the emulsion model, the complex shear modulus G^* of the blend at a given temperature is expressed as a function of the interfacial tension Γ , the complex shear moduli of matrix G_M^* , and the complex shear moduli of the disperse phase G_I^* at the same temperature.

$$G^* = G_M^* \frac{1 + 3\phi H}{1 - 2\phi H} \quad (4)$$

$$H = \frac{(4\Gamma/\bar{R}_V)(2G_M^* + 5G_I^*) + (G_I^* - G_M^*)(16G_M^* + 19G_I^*)}{(40\Gamma/\bar{R}_V)(G_M^* + G_I^*) + (2G_I^* + 3G_M^*)(16G_M^* + 19G_I^*)} \quad (5)$$

Table 2

Glass transition temperature of PP and EPDM Phase in PP/EPDM=70/30 blend

Sample code	T_g of PP (°C)	T_g of EPDM (°C)	ΔT_g (°C)
Virgin PP	-12.37		
Virgin EPDM		-44.26	31.89
0 W	-13.49	-42.94	29.45
150 W	-15.92	-41.46	25.54
150 W + 0 W	-15.04	-42.27	27.23
150 W + 100 W	-16.79	-40.17	23.38

with ϕ the volume fraction of the disperse phase, \bar{R}_V the average radius of the disperse phase.

It is shown that dynamic shear measurements can be used as an original method for determining the interfacial tension between two polymers melts.

Fig. 6 shows the way in which the interfacial tension between PP and EPDM melts affected by ultrasound irradiation. The interfacial tension between PP and EPDM melts reduce markedly with 150 W ultrasound irradiation, and reduce even more with twice 150 W ultrasound irradiation. Ultrasound vibration acts on the blends melt; change the viscoelasticity of the components to a less non-Newtonian way. The viscosity ratio between the two phases reduces and so does the interfacial tension.

3.3. Glass transition temperature

The glass transition temperatures of PP and EPDM phase in the blends from differential scanning calorimetry analysis are listed in Table 2. As can be seen, with ultrasonic irradiation, the glass transition temperature of PP and EPDM phase all change and get closer to each other. The longer the residence time, the more the glass transition temperature of PP and EPDM phase move to each other. That means compatibility of EPDM and PP matrix is improved.

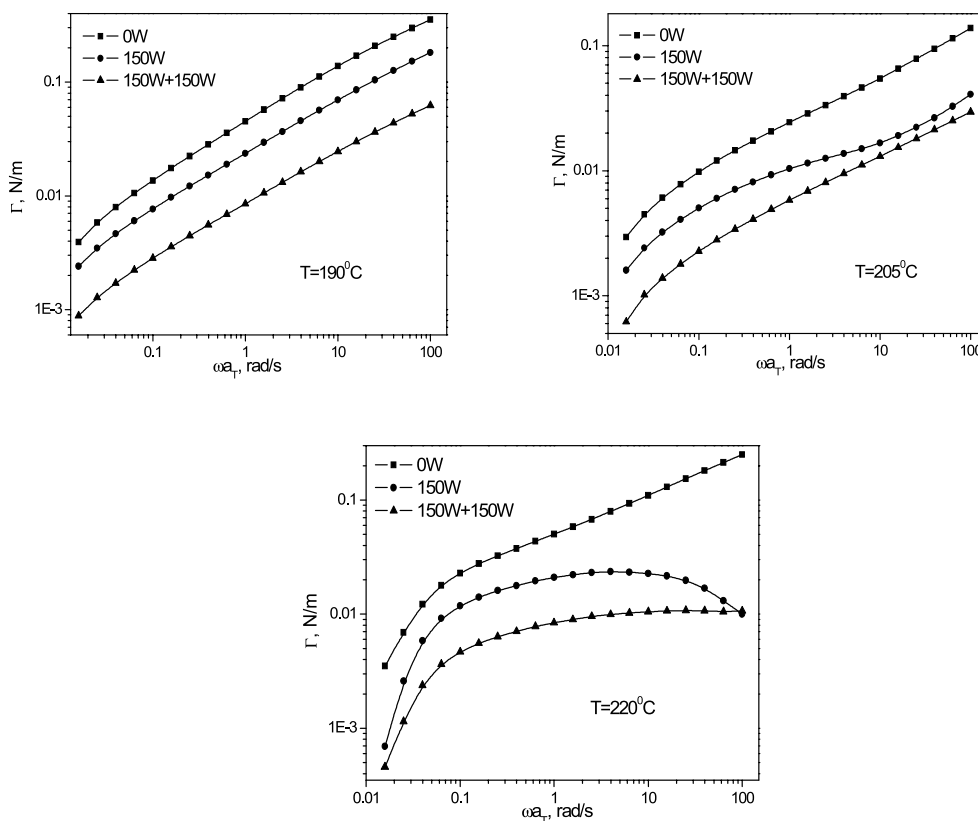


Fig. 6. Log–log plots of Γ vs. $\omega\alpha_T$ of PP/EPDM blends with different ultrasound intensity at various temperatures.

Upon irradiation of ultrasound, molecules are exposed to alternate compression and expansion modes, by which bubbles are formed and eventually collapsed. On the molecular level, this implies a rapid strike to the molecules impeded by surrounding molecules cannot adjust. Thus, friction is generated which causes strain and eventually bond rupture in the macromolecules. Therefore, it is supposed that in situ copolymers are formed by PP and

EPDM macroradicals that occur with ultrasonic irradiation in this study. The copolymers acts as a compatibilizer to PP/EPDM blend to improve and stabilize the morphological structure.

3.4. FTIR analysis

An evidence for the copolymer formation was found by

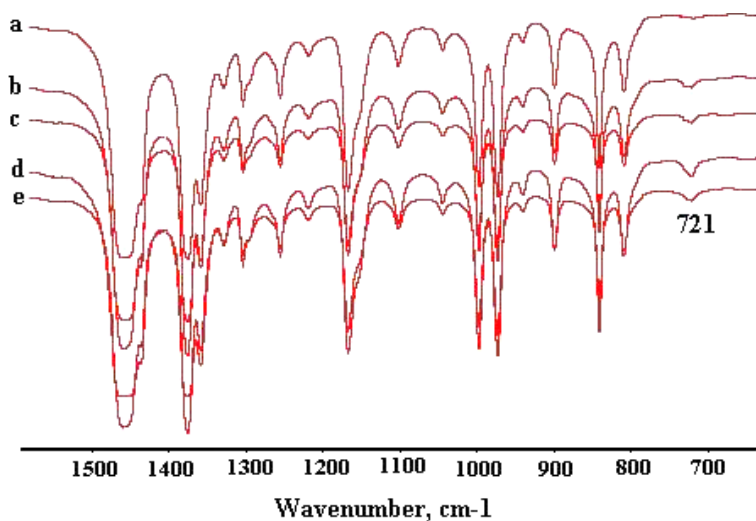


Fig. 7. FTIR spectra of PP in PP/EPDM blends extruded with different ultrasound intensity (a) 0 W; (b) 100 W; (c) 200 W; (d) 150 W + 100 W; (e) 150 W + 200 W.

Table 3
Relative absorbance intensity of EPDM and PP in the extracted samples with various ultrasound irradiation

	0 W	100 W	200 W	150 W + 100 W	150 W + 200 W
A_{973}	592.865	592.632	429.224	636.222	458.218
A_{721}	–	53.240	54.590	119.680	91.384
A_{721}/A_{973}	–	0.090	0.127	0.188	0.199

FTIR analysis of PP/EPDM blends, in which free EPDM had been removed. As shown in Fig. 7, the characteristic absorption band of $[\text{CH}_2]_n$ ($n \geq 4$) appeared at 721 cm^{-1} in the spectra of the samples with ultrasound irradiation, which confirms the existence of EPDM component grafted to the PP chains.

Since, the absorption bands at 973 cm^{-1} are associated with $[\text{CH}_2\text{CH}(\text{CH}_3)]_n$, the ratios of 721 cm^{-1} absorbance bands area to that of 973 cm^{-1} are employed to denote the relative content of EPDM that reacted with PP, as shown in Table 3. The ratio rises up with the increase of ultrasound intensity and residence time, which indicates that amount of EPDM reacted with PP increases as ultrasound intensity and residence time increasing.

Copolymers formed at the interface would stabilize the interface by enhancing the entanglement between the disperse phase and the matrix, and coalescence of the dispersed phase can be suppressed effectively during the mixing or reprocessing.

4. Conclusion

In the extrusion of PP/EPDM blend, ultrasound irradiation led to stable morphology with reduced disperse phase size. Dynamic rheological analysis indicates time–temperature superposition principle was applied to the PP/EPDM blend and smoother master curves were obtained for the blend with ultrasonic irradiation. The slopes of the terminal region of $\log G' \sim \log G''$ plots were used and obtained the information that more homogeneous internal structure of PP/EPDM blend is obtained with ultrasonic irradiation. The interfacial tension between PP and EPDM melts obtained from the Palierne emulsion model decreases with ultrasound irradiation. The glass transition temperatures of PP and EPDM phase become closer to each other with ultrasonic irradiation. FTIR analysis indicated that copolymers of PP and EPDM were formed by combination of the corresponding macroradicals. Elongated residence time of the blends in the ultrasound irradiating zone makes all the effects mentioned above even better. The copolymers consequently act as compatibilizers for the blend. The powerful vibration and jet current of ultrasound help to deform and shear cut EPDM in PP matrix. It also changes

the viscoelasticity of the components and result in the decreasing of interfacial tension between PP and EPDM melts and increasing of the compatibility of the two components.

Acknowledgements

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