Mixing Efficiency in Co-Rotating Batch Mixer for Preparation of NR/EPDM Blends

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ABSTRACT: An in-house developed co-rotating batch mixer was used to prepare the blends of natural rubber (NR) and ethylene-propylene-diene terpolymer (EPDM) in the present work. Phase morphology and magnitude of dispersive mixing efficiency offered by the in-house developed co-rotating batch mixer and a conventional counter-rotating batch mixer were compared. It has been found that the co-rotating batch mixer equipped with the MX2 rotor configuration could improve the dispersive mixing efficiency of NR/EPDM blends considerably. A poor state-of-mix in blends, particularly at high fill factor, could be overcome by the utilization of MX2 rotor configuration where the extensional flow is probably facilitated in the converging zones. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3688–3695, 2012

Key words: blends; mixing; rotor configuration; natural rubber; ethylene-propylene terpolymer

INTRODUCTION

One of the most important keys for achieving good state-of-mix in polymer blends in the polymer industry is a mixer which includes two-roll mills, non-intermeshing, and intermeshing internal mixers as well as single- and twin-screw extruders. There are generally a number of factors governing the mixing efficiency, namely, (i) mixer and rotor geometries, (ii) mixing conditions (i.e., temperature, time, speed, and fill factor), and (iii) material composition. Kim and White[1] investigated flow visualization of intermeshing and separated counter-rotating internal mixers. They found that the intermeshing rotors could homogenize pigmented rubber faster than the separated rotors. Maric and Macosko[2] compared dispersed-phase sizes of 80/20 polystyrene/polypropylene blends prepared from four different mixers, namely, cup and rotor mini-mixer, internal batch mixer, conical recirculation twin-screw extruder, and co-rotating twin-screw extruder. The smallest dispersed phase size was found in the specimens prepared from the co-rotating twin-screw extruder. Shon et al.[3] compared the development of phase morphology in polypropylene/polyamide-6 blend mixed by the uses of Buss Kneader, co-rotating twin-screw extruder, counter-rotating twin-screw extruder, and NEX-T Kobelco continuous mixer. They reported that the intermeshing counter-rotating twin-screw extruder produced the finest dispersed morphology.

Blends of elastomers have been widely prepared for manufacturing a variety of rubber products owing to their compromised properties.[4–6] For example, natural rubber (NR) has good tack, mechanical properties, and processability while ethylene-propylene-diene rubber (EPDM) possesses excellent heat and ozone resistances. Therefore, the blends of NR and EPDM would theoretically exhibit combined properties, i.e., good thermal–ozone resistance in conjunction with good tack, mechanical, and dynamic properties.[7] However, since the NR/EPDM blend is thermodynamically incompatible, the selection of a suitable vulcanizing system and the addition of a suitable homogenizing agent could significantly improve the homogeneity of the rubber blends, leading to the enhancement in properties of the blend vulcanizates.[6,8–11]

In this work, the in-house developed intermeshing co-rotating batch mixer and a tangential counter-rotating batch mixer were utilized to prepare 60/40 NR/EPDM blends. The phase morphology of NR/EPDM blends from both mixers was compared. The effects of mixing parameters, namely, fill factor and rotor configuration on phase morphology were also studied and discussed.

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TABLE I
Mixing Conditions Used for Preparing NR/EPDM Blends

Mixer	Co-rotating batch mixer, counter-rotating batch mixer
Material	NR/EPDM 60/40 by weight
Fill factor	0.6, 0.7, and 0.8
Rotor speed	40 RPM
Mixing temperature	100°C
Mixing time	6 min

EXPERIMENTAL

Materials

NR (STR 5L) was manufactured by Thai Hua Rubber Public Co., Ltd. (Bangkok, Thailand), and EPDM (Nordel IP 4725) with 4.9% ethylidene norbornene (ENB) content, 70% ethylene content, and 25 units of Mooney viscosity (ML (1+4) at 125°C) was purchased from Chemical Innovation Co., Ltd. (Bangkok, Thailand).

Sample preparation

Two types of mixers, the in-house developed co-rotating and commercial counter-rotating batch mixers, were utilized for preparing NR/EPDM blends at a given composition ratio of 60/40 giving the phase morphology with EPDM dispersed in NR matrix. The mixing conditions used are shown in Table I. Since the mechanical shear rate of mixers is required for an estimation of shear viscosities of NR and EPDM possessing pseudoplastic (shear-thinning) behavior during the blending process, the average of shear rate of mixer was calculated using eq. (1).[12] In addition, the maximum shear rate and the minimum shear rate taking place in the mixer was calculated using eqs. (2) and (3), respectively.[2,13] Such shear rates are known to affect the magnitude of dispersive mixing.

$$\gamma_{avg} = \frac{\pi \cdot D \cdot N}{H_{avg} \cdot 60} \quad (1)$$

$$\gamma_{max} = \frac{\pi \cdot D \cdot N}{H_{gap} \cdot 60} \quad (2)$$

$$\gamma_{min} = \frac{\pi \cdot D \cdot N}{H_{max} \cdot 60} \quad (3)$$

where: γ_{avg} = average of shear rate (s^{-1})
γ_{max} = maximum shear rate (s^{-1})
γ_{min} = minimum shear rate (s^{-1})
D = rotor outer diameter (mm)
N = rotor speed (rpm)
H_{avg} = average of channel depth of rotor (mm)
H_{gap} = clearance between rotor and chamber (mm)
H_{max} = maximum of channel depth of rotor (mm)

Co-rotating batch mixer

The intermeshing co-rotating batch mixer (MX) used in this research was in-house designed and developed as a model for mixing rubber. The mixing chamber bore diameter was 52.00 mm with the rotor diameter of 50.00 mm. The centerline distance between rotors was 41.00 mm. A pair of rotors was modular-type capable of providing the flexibility in configuration alteration. Temperature of a mixing chamber was set to 100°C, and the NR/EPDM blend composition ratio was kept constant at 60/40 by weight for all experiments. A fill factor used was varied from 0.6 to 0.8, and the mixing time was kept constant at 6 min. The rotors used in this work were a pair of MX1 and MX2 rotors (as illustrated in Fig. 1) with the arrangement of forward slotted screw parts, backward slotted screw parts, and kneading parts. The MX1 rotors represent a shear-flow configuration while the MX2 rotors represent a combination of shear-flow and extension-flow configuration. The rotor speed was set to 40 rpm with the speed ratio of 1 : 1 for both types of rotors. Additional data of mixing chamber and rotors are given in Table II. It must be noted that the clearance between rotor and chamber illustrated was obtained from a direct measurement. The average, maximum, and minimum shear rates were calculated using eqs. (1)–(3). The mixing capacity with the mounted specific rotors, the surface area of chamber, and the surface area of rotors were acquired from a commercial software (SolidWorks, Ver. 2008). A specific area

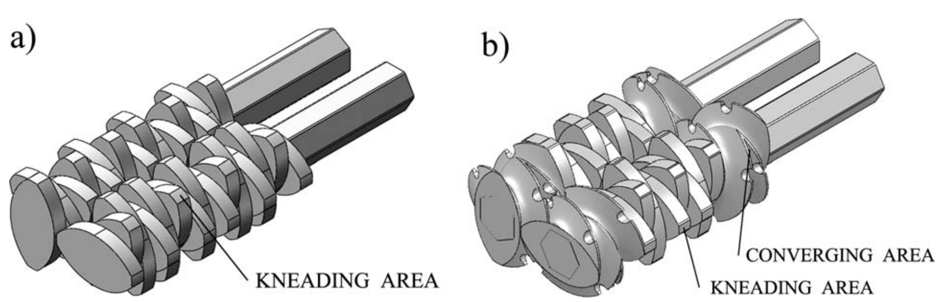

Figure 1 The intermeshing co-rotating batch mixer: (a) a pair of MX1 rotors; (b) a pair of MX2 rotors.

TABLE II
Parameters of Mixers and Rotors

	MX1	MX2	CM
Rotor rotation	Co-rotation	Co-rotation	Counter-rotation
Clearance between rotor and chamber (mm)	1.0	1.0	1.5
Minimum shear rate (s^{-1})	9.3	9.3	7.2
Maximum shear rate (s^{-1})	105	105	94
Average shear rate (s^{-1})	13	13	12
Mixing capacity (cm^3)	212.4	212.4	388.3
Surface area of chamber (cm^2)	389.5	389.5	334.9
Surface area of rotors (cm^2)	478.3	519.3	298.4
Specific area of mixer without rotors (cm^{-1})	1.8	1.8	0.9
Specific area of mixer with rotors (cm^{-1})	4.1	4.3	1.6

of mixer was defined as a ratio of surface area to mixing capacity.

Counter-rotating batch mixer

The counter-rotating batch mixer equipped with a cam rotor configuration (CM) was a commercial plasti-corder lab-station with a W350E (three zones) mixer head manufactured by Brabender OHG (Duisburg, Germany). The rotors were a pair of cam type with the rotating speed of 40 rpm with the speed ratio of 2 : 3. The CM rotors represent a shear-flow configuration. Further details regarding the mixing chamber and rotors are illustrated in Table II. The mixing chamber temperature was set to 100°C while the material fill factor was varied from 0.6 to 0.8. The mixing time is kept constant at 6 min similar to the case of co-rotating batch mixer.

Rheological investigation

Rheological behavior of raw rubbers was investigated by the Rubber Process Analyzer (RPA) model RPA2000 as manufactured by Alpha Technologies (USA) and a rate-controlled capillary rheometer (Göttfert model Rheo-Tester 2000, Germany). The former and latter were used to determine rheological properties of rubbers under low-to-moderate and moderate-to-high shear rate ranges, respectively.

With the use of RPA2000, three test modes were performed, namely, time-sweep, strain-sweep, and frequency-sweep tests. The time-sweep test performed under the test frequency of 40 rad/s at 130°C for 15 min was used for determining the thermal stability of raw rubbers. The strain-sweep test was carried out at test temperature and angular frequency of 100°C and 5 rad/s, respectively. The frequency-sweep test was performed at 100°C under the deformation strain within the linear viscoelastic (LVE) region in order to monitor the flow behavior as a function of shear rate. The capillary test was conducted using three dies with different L/D ratios of 10/2, 20/2, and 30/2 at the test temperature of 100°C.

Mixing pressure investigation

It is known that extensional flow could enhance the degree of phase dispersion in polymer blending.[14–17] However, it is not easy to measure the degree of extensional flow, especially in the system with the combination of shear and extensional flows. One practical way to compare the existence of extensional flow affected by rotor configurations is the measurement of pressure entry at the investigated zones of rotors with a given shear rate.[18–20] Therefore, in the present work, the mixing pressure generated by kneading elements and converging elements was measured during the mixing process and compared at similar shear rate. Typically, at any given shear rate, the elements generating higher pressure should offer greater magnitude of extensional flow. Figure 2 shows the location of pressure transducers installed at the apex of the intermeshing zone. A commercial CT-Pressure monitoring software with a fast acquisition-time data logger (Chareon Tut Co., Ltd., Thailand) was used to monitor and record the pressure continuously at 24 readings/s. The blending of 60/40 NR/EPDM at rotor speed, fill factor, and chamber temperature of 40 rpm, 0.7, and 100°C, respectively, was performed for measuring the pressure development in the intermeshing areas of co-rotating batch mixer. The pressure was recorded after the mixing time of 6 min, which is analogous to the mixing conditions as illustrated in Table I.

Morphological observation

Phase morphology of NR/EPDM blends was observed using a scanning electron microscope (JEOL Model JSM 6301F, Japan) at an acceleration voltage of 15 kV. Samples were cryogenically fractured and stained with osmium tetroxide prior to

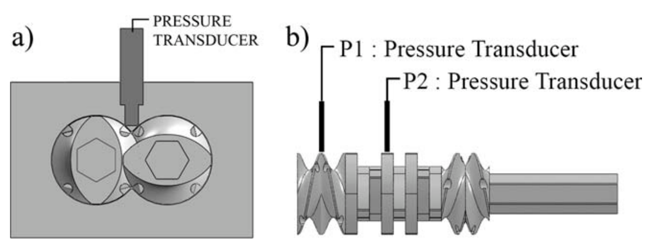

Figure 2 The location of pressure transducers installed at the apex of intermeshing zone: (a) front view; (b) side view.

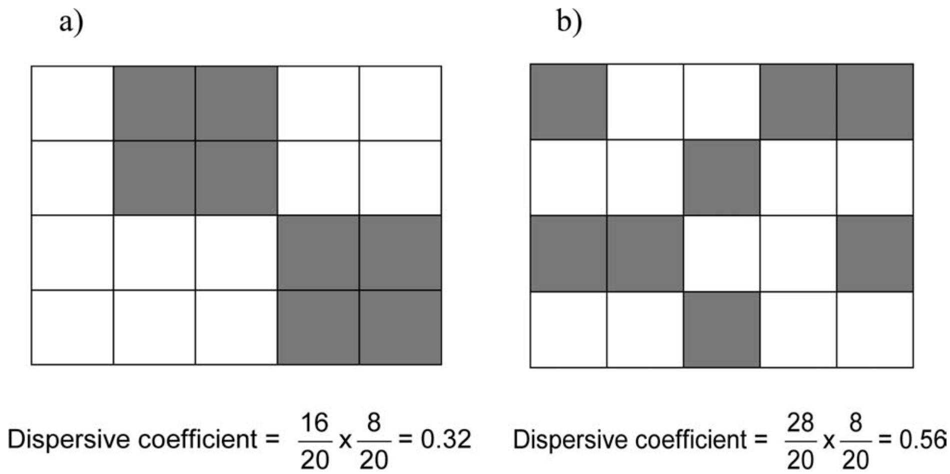

Figure 3 Schematic representation of dispersive mixing determination in specimen with different state-of-mix: (a) low state-of-mix; (b) high state-of-mix.

the morphological observation in order to enhance phase contrast.

Determination of dispersive mixing quality

In general, the improvement in mixing efficiency in incompatible polymer blends with two-phase morphology would lead to a decrease in size of the dispersed phase. In the present work, the quality of mixing is determined both qualitatively and quantitatively. The qualitative examination was carried out by the direct observation of SEM images, i.e. the appearance of EPDM phase size in NR matrix. The 2-dimentional SEM images can be converted to quantitative values by collecting the inter-phase distance via an image analysis program. In practical, quantitative examination was performed by calculating the sum of dispersed particle perimeter per image area in SEM images as represented by eq. (4) where ϕ_d represents a volume fraction of dispersed phase. By this means, a coefficient of dispersive mixing (CDM) was resulted. According to a schematic representation of phase size and CDM correlation as illustrated in Figure 3, the blend with relatively large phase size would give a relatively small sum of dispersed particle perimeter and thus a small value of CDM [see Fig. 3(a)]. With increasing degree of dispersion, the droplet break-up process gives a decrease in phase size, and thus a rise in CDM value, as represented in Figure 3(b).

$$\text{Coeff. of dispersive mixing} = \frac{\sum(\text{Dispersed particle perimeter})}{\text{Image observed area}} \times \phi_d \quad (4)$$

RESULTS AND DISCUSSION

In order to study the phase morphology of blends, there are a number of controlling factors, including bulk viscosity, mixing temperature, flow pattern, mixing force, and strain rate.[2,14,21–26] Referred to previous work,[12] both types of mixers provide a broad range of shear rates depending on the position in the mixers, i.e., low shear rate at rotor root and maximum shear rate at rotor tip. As evidenced in Table II, among the three rotor configurations, the minimum shear rate at rotor root and the maximum shear rate at rotor tips are 7.20 s^{-1} and 105 s^{-1}, respectively. Therefore, the rheological behavior under a broad shear rate range in the present work was measured with the utilization of both RPA2000 and capillary rheometer. The interconnection of oscillatory and steady shear results was carried out with the application of Cox-Merz rule to the apparent data, as exhibited in Figure 4.[27] Evidently, NR demonstrates the greater magnitude of pseudoplasticity than EPDM which is caused probably by the broader molecular weight distribution of NR. Because the phase morphology of 60/40 NR/EPDM blend systems studied is in a way that the EPDM phase is dispersed in NR matrix (see Figs. 6–8), the viscosity ratio of the blends is defined as the ratio of

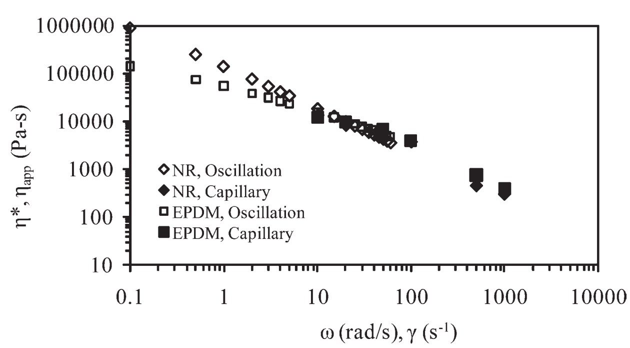

Figure 4 Complex and steady shear viscosities of NR and EPDM at 100°C.

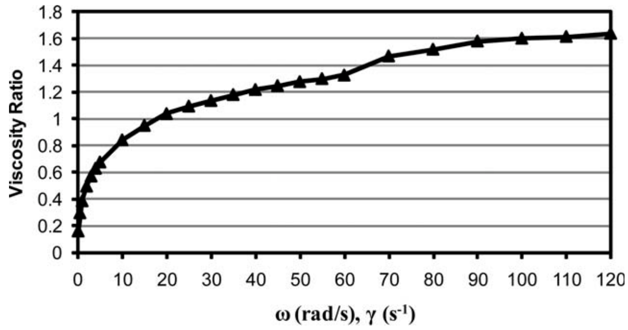

Figure 5 Shear viscosity ratio of NR/EPDM as measured at test temperature of 100°C.

EPDM to NR viscosities, which appears to increase with increasing shear rate, as shown in Figure 5.

Phase morphology and dispersive mixing quality

Figures 6–8 illustrate the SEM images of the blends prepared from the mixers equipped with MX1, MX2, and CM rotor configurations, respectively, at various fill factors. The dark and bright phases represent EPDM and NR components, respectively. As mentioned previously, the direct observation of SEM images is taken as the qualitative examination of dispersive mixing quality in this work. At a given rotor configuration, phase size of EPDM dispersed in NR matrix appears to increase with increasing fill factor which is probably due to the increased potential of the droplet coalescence process promoted by the decreased bulk viscosity via the generated shear heating. The fill factor of 0.6 appears to give the finest phase morphology. It is worth noting that a high value of the fill factor of batch mixers, i.e. 0.75–0.80, is normally used to prepare polymer blends. However, the better mixing efficiency can be obtained by lowering the value of fill factor, especially when blending a highly incompatible mixture. Also, at any given fill factor, the MX2 rotor configuration provides the finest phase morphology whereas the MX1 and CM configurations give similar phase morphology with large phase size.

As a quantitative examination of magnitude in dispersive mixing efficiency, the CDM values in the blends prepared from different rotor configurations are represented in Figure 9. Apparently, the MX2 rotors provide the highest CDM value whereas the CDM values of MX1 and CM rotors are comparable. In other words, the mixing efficiency for dispersing the EPDM phase is highest with the utilization of co-rotating mixer equipped with the MX2 rotor configuration followed by both MX1 and CM configurations. It is evident that the CDM results as a quantitative examination and SEM images as a qualitative examination of dispersive mixing efficiency are in good agreement.

Factors probably affecting the results include: (i) specific area of mixer with rotors (as shown in Table II), (ii) flow pattern in the mixing chamber, (iii) rotation pattern of rotors, and (iv) generated temperature via the viscous dissipation taking place during the mixing process. As for the effect of specific area of mixer with rotors on mixing efficiency, Ratnagiri et al.[13] investigated the mixing efficiency in PS/PE blends by varying the specific area of mixer via the alteration of chamber and rotor dimensions at constant mixer and rotor geometries. They found that the mixing efficiency increases with increasing specific area of mixer with rotors. However, in this work, the specific areas of mixers with rotors of MX1, MX2, and CM rotor configurations are of 4.1, 4.3, and 1.6 cm^{-1}, respectively, which are not in accordance with the CDM results, as shown previously in Figure 9 (i.e., CDM of MX2 >> MX1 ~ CM configurations). This implies that the dispersive mixing efficiency in this work is not dominated by the mixer specific areas.

Regarding the flow pattern effect, Figure 10 demonstrates the pressure profiles generated by the

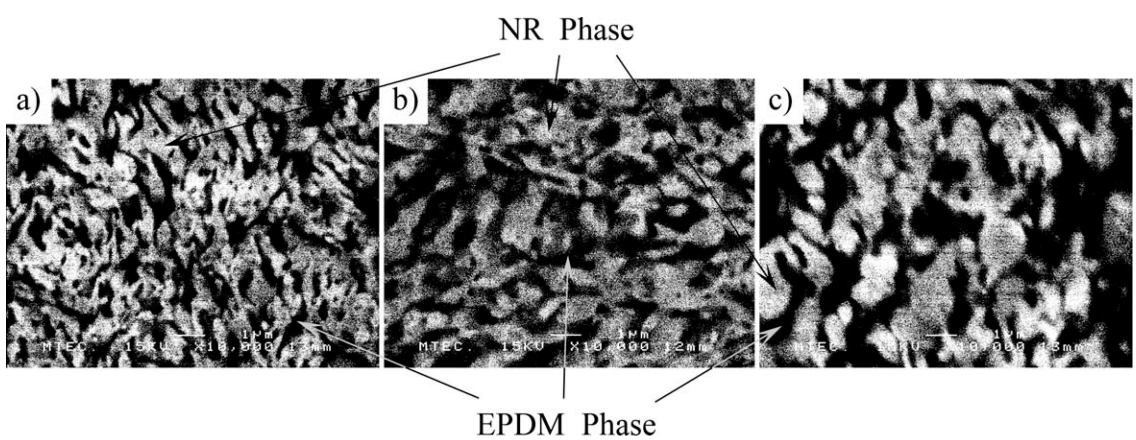

Figure 6 SEM images of NR/EPDM blends prepared from the co-rotating mixer equipped with the MX1 rotor configuration at various fill factors: (a) 0.6; (b) 0.7; (c) 0.8.

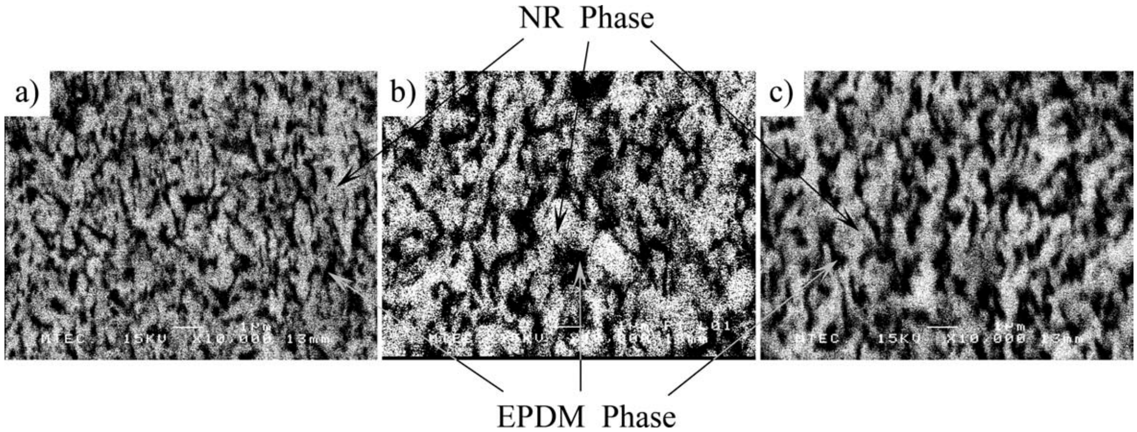

Figure 7 SEM images of NR/EPDM blends prepared from the co-rotating mixer equipped with the MX2 rotor configuration at various fill factors: (a) 0.6; (b) 0.7; (c) 0.8.

kneading and converging elements. It is evident that the converging elements are capable of generating the pressure much higher than the kneading elements. This suggests that the converging elements might generate the higher magnitude of extension rate. The flow patterns offered by MX1 and CM rotors are believed to be controlled mainly by shear rather than extensional flows via the kneading action occurring on the kneading elements. By contrast, the MX2 rotors with the combination of kneading zones and converging zones probably provide the additional magnitude of extensional flow, especially in the converging area.[18–20,28] Therefore, the existence of converging zones is evidently the main factor for the dispersive mixing efficiency. The explanation proposed is in good agreement with previous work reporting the improvement in state-of-mix via extensional flow.[14–17]

Mixing efficiency offered by two different rotation patterns of mixers, the co-rotation and counter-rotation, was also compared in this work. The MX1 and MX2 rotors were mounted in the co-rotating mixer while the CM was mounted in the counter-rotating mixer. From the results, the CDM value of MX2 configuration is the highest while those of MX1 and CM configurations are comparable. The results imply that the rotation pattern of mixer is not the main factor for the dispersive mixing efficiency, especially at low rotor speed.

Lastly, the increase in temperature during the mixing process caused by viscous dissipation (or the so-called shear heating) is thought to influence mixing efficiency through the alteration in viscosity ratio. Figure 11 illustrates the dump temperatures of the blends after mixing for 6 min, as prepared under the different fill factors. Apparently, at any given fill factor, the dump temperature is highest in the blends prepared from the CM followed by MX2 and MX1 rotor configurations, respectively. Also, with increasing fill factor, the dump temperature appears to increase via the viscous dissipation during blending. This is probably because of the increased

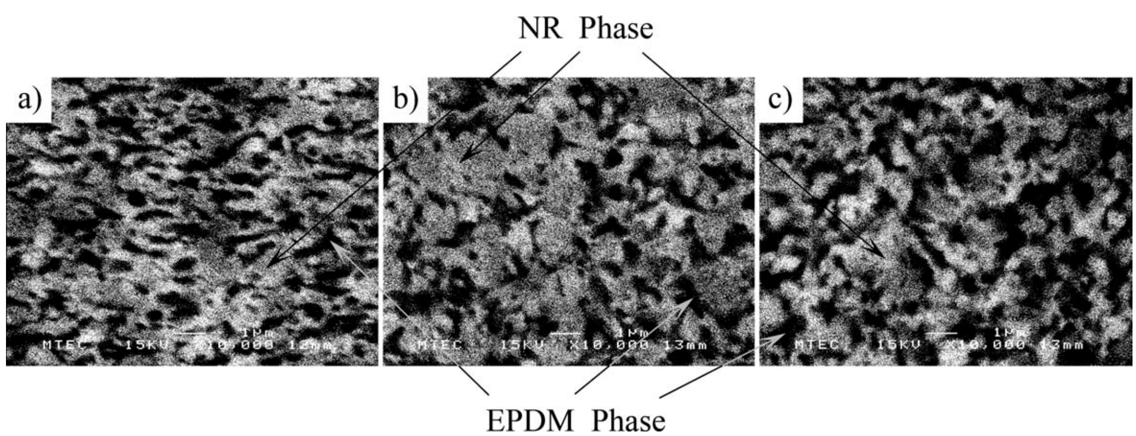

Figure 8 SEM images of NR/EPDM blends prepared from the counter-rotating mixer equipped with the CM rotor configuration at various fill factors: (a) 0.6; (b) 0.7; (c) 0.8.

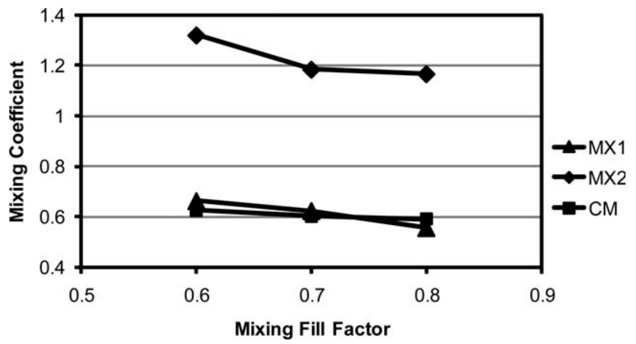

Figure 9 Dispersive mixing quality of NR/EPDM blends prepared from the co- and counter-rotating mixers at various fill factors.

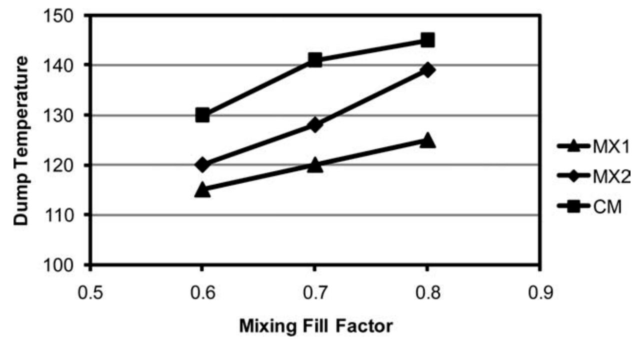

Figure 11 Dump temperatures of the blends at mixing time of 6 min prepared from different rotor configurations and fill factors.

compaction of polymer bulk. Such high batch temperature would yield a reduction in bulk viscosity and so the domination of phase coalescence over the droplet break-up process. The proposed explanation is also supported by the SEM images and CDM results, as discussed previously. In the comparison of MX1 and MX2 rotor configurations, although the former gives the lower dump temperature, the latter provides superior mixing performance as evidenced by the CDM results (see Fig. 9). This implies the domination of rotor configuration over the viscous dissipation effects.

CONCLUSION

The 60/40 NR/EPDM blends were prepared from different mixers, namely, the in-house developed co-rotating batch mixer equipped with MX1 and MX2 rotor configurations and a conventional counter-rotating batch mixer equipped with cam rotor configuration (CM). Also, fill factor was varied from 0.6 to 0.8. SEM images were investigated as a qualitative examination of dispersive mixing efficiency. The CDM was proposed as a quantitative examination of dispersive mixing efficiency. Results obtained reveal that the dispersive mixing efficiency in terms of phase morphology and CDM values of NR/EPDM blends is dominated mainly by rotor configuration. The finest dispersed-phase size is observed in the blends prepared from the co-rotating batch mixer equipped with MX2 rotors where the extensional flow may be facilitated in the converging zones. By contrast, the conventional counter-rotating batch mixer equipped with CM rotor configuration appears to give the coarsest phase morphology. At a given rotor configuration, the increase in fill factor leads to the decrease in state-of-mix. Additionally, a remarkable increase in batch temperature observed in CM rotor configuration tends to coarsen the phase morphology.

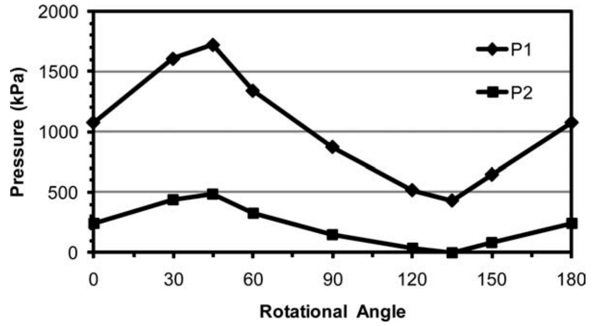

Figure 10 Pressure generated by the converging elements (P1) and the kneading elements (P2) at different rotational angles

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