Macromol. Symp. 2012, 321-322, 225–230 DOI: 10.1002/masy.201251141

Droplet Breakup Theory as a Method to Predict the Processing Conditions of Polymer Blends

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Sumary: The droplet breakup theory has been investigated in predicting processing conditions of polymer blends. A ternary blend of polystyrene/styrene-butadiene rubber/natural rubber (PS/SBR/NR) was used with a constant content of every component [PS/SBR/NR 80/(30/70) wt.%] while changing mixing temperature, time and rotor speed. The experimental design was applied to optimize mixing conditions where izod impact and tensile strength were the targets. The mixing conditions from theory calculation: 190 °C, 56.5 rpm, 3.47 ÷ 5.47 min. Suitable blending conditions resulting in the experiments were: 190 °C, 60 rpm, 5.44 min.

Keywords: blends; mixing; particle size distribution

Introduction

Polymer blending is a way of improving deficient properties of some traditional polymers. Development of a blend is more economical than that of a new polymeric resin.[1] The blends properties, to great extent, are controlled by morphology, which depends on the thermodynamic and the rheology.[2] The development of morphology in two-phase liquid/liquid systems, and blends has been studied and experimented for over 100 years. The droplet breakup theory has been used to predict the development of morphology.[3–7] On the other hand, the final morphology also can be predicted by interfacial tension theory.[8–12] The morphology of blends must consider not only component polymers and their blend ratios but also processing conditions (time of mixing, screw rotation speed, temperature…).

L. A. Utracki al et[13] said that "Currently, selection of screw configurations as well as the operating conditions for compounding polymer blends with desired morphology in a co-rotating twinscrew extruder is an art based on experience". During the last few years, there is a need to examine the processing conditions by experiments, Sabu Thomas and Susan Joseph[14] used classical experiment design to seek processing conditions for (PS/PB) blends.

In this study, we used NR to improve impact strength for PS and SBR as a compatibilizer. Droplet breakup theory was used to predict mixing conditions for PS/SBR/NR blend, later these mixing conditions were verified again by the experiment design.

Theoretical Background

When droplets are suspended in another liquid and a shear stress is applied, they deform and then breakup into smaller droplets. Taylor calculated the velocity and pressure fields inside and outside the droplet and noted that: at low flow rates the deformation degree can be expressed by two dimensionless microrheological parameters: the viscosity ratio:

$$\lambda = \frac{\eta_d}{\eta_m}, \tag{1}$$

and the capillarity (or Taylor) number:

$$\kappa = \frac{\eta_m \dot{\gamma} d_n}{2\gamma_{dm}}, \tag{2}$$

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where, η_d and η_m are the dispersed and matrix phase viscosity, respectively, $\dot{\gamma}$ is the shear rate, d is the droplet diameter, γ_{dm} is the interfacial tension coefficient. λ is optimum at 1.[14,15] The mixing temperature can be controlled via viscosity ratio and equation:

$$\log\left(\frac{\eta}{\eta_T}\right) = \frac{-C_1' C_2' (T - T_T)}{\left[C_2' + (T - T_g)\right]\left[C_2' + (T_T - T_g\right]'} \tag{3}$$

where, C_1' and C_2', are constants that depend on kind of polymer, η and η_T are the viscosity at the temperature which unknown viscosity and known viscosity, respectively.

The equation (2) indicates that the smaller shear stress ($= \eta_m \dot{\gamma}$) or the smaller the droplet dimension, the more difficult the dispersed phase deform. On the other hand, the higher the interfacial tension, the more difficult the deformation of dispersed phase.

It is convenient to introduce the capillarity number in its reduced form:

$$\kappa^* = \kappa / \kappa_{cr}, \tag{4}$$

where, κ_{cr} is defined as the minimum capillarity number sufficient to cause breakup of the deformed drop droplets, can further deform and break-up. The critical capillarity number for droplet breakup tends to show a minimum at a viscosity ratio around 1. However, that a minimum in the critical capillarity number is not directly related to the smallest obtainable droplet diameter in the case of a varying matrix viscosity, it depends on minor phase composition. Taylor derived a function for the value of κ_{cr} in the case of Newtonian systems under simple shear flow:[15]

$$\kappa_{cr} = \frac{1}{2}\,\frac{16\lambda + 16}{19\lambda + 16}, \tag{5}$$

For blend systems with a high viscosity ratio ($\lambda \geq 2$), the prediction of Taylor clearly underestimates κ_{cr} value.[15] Critical capillarity number was also given by de Bruijin:[16]

$$\log(\kappa_{cr}) = -0.506 - 0.0994\log(\lambda) + 0.124\log^2(\lambda) - \frac{0.115}{\log(\lambda) - \log(4.08)}, \tag{6}$$

When: $0.1 > \kappa^*$ droplets do not deform,

$0.1 < \kappa^* < 1$ droplets deform but they do not break.

$1 < \kappa^* < 2$ droplets deform then split into two primary droplets, an equilibrium drop shape will no longer exist and the droplet splits into two primary droplets by a necking mechanism if the time of the deformation process is long enough.

$\kappa^* > 2$ droplets deform into stable filaments, the droplet will deform into a fibril and disintegrates into several small droplets at long times leading to very fine dispersions.

So that, $\kappa^* = 2$ is the ultimate value to obtain the droplets deform, break up and stability. With this ultimate value and κ_{cr} which was calculated from Eq. (6), κ can be calculated by Eq. (4). Final, shear rate (or mixing speed) can be recorded by Eq. (2).

But droplets breakup occurs when the time required to reach this stage can be expressed as a dimensionless time:

$$t^* = \frac{t\dot{\gamma}}{\kappa} = 84\lambda^{0.345}\left(\frac{\kappa}{\kappa_{cr}}\right)^{-0.559}, \tag{7}$$

So, the time at least is to deform and break up droplets from the original d_1 diameter to the final d_2 diameter can be introduced:

$$t = \int_{d_1}^{d_2} t(d)dd = 84\lambda^{0.345}\left(\frac{\kappa}{\kappa_{cr}}\right)^{-0.559} \frac{\eta_m}{2\gamma_{dm}} \frac{\left(d_1^2 - d_2^2\right)}{2}, \tag{8}$$

Experimental Part

Materials

PS (PG-80 from CHI MEI), SBR (Europrene 1502 from POLIMERI EUROPA)

Table 1.
Characteristics of the materials.

Polymer	10^{-3} M_w, (g/mol)	M_w/M_n	Density, (g/cm^3), 20 °C
PS	362	2.77	1.05
SBR	617	3.86	0.91
NR	1486	3.36	0.92

random copolymer contained 23.5 wt.% bound styrene and NR (3L from Dong Nai Rubber). Characteristics of material used are given in (Table 1). All the blends were investigated in this study had composition ratio of PS/SBR/NR 80/(30/70) wt.%.

Blend Preparation

Blends were performed in a Haake Polydriver R600. First, PS was melted for 2 min to turn it into a melt and then both rubbers were introduced. The mixing time was recorded from the moment that SBR and NR were introduced.

Mechanical Properties

After mixing, the molten materials were sheeted out through a lab mill (NeoPlast) at nip setting of 4.5 mm, later it is pressed in a mold at 20 MPa for 2 min. Tensile and Notched Izod Impact strength test specimens were punched out from sheets of 120 × 115 × 3.5 mm. Blends for mechanical testing were prepared at each point of experimental matrix.

Tensile testing of the samples was performed at room temperature according to ASTM D638 (Type IV) test method with SHIMADZU testing machine at a tensile speed of 5 mm/min. Izod impact was determined as ASTM D256, also measured at room temperature with DTS-AST testing machine. Each value is the average of six to ten independent measurements after analyzing the number by Student distribution means.

Results and Discussion

Mixing Conditions from Theory

Mixing temperature

Table 2.
The characteristic of materials.

	T_T (°C)	η_o ($T = T_T$) (Pa.s)	C_1' a)	C_2' a)	T_g (°C)
PS	190	5.22 10^4	14.50	50.40	100 a)
SBR	200	2.64 10^4	17.44	51.60	−52 b)
NR	25	1.25 10^8	16.70	53.60	−73 a)

a) Ref. [17] p533.
b) Ref. [18] p985.

Table 3.
λ at the different temperatures.

Temperature, °C	λ_1, (SBR/PS)	λ_2, (NR/PS)	$D = \sqrt{\lambda_1 \lambda_2}$
150	0.02	0.04	0.03
160	0.05	0.15	0.09
170	0.15	0.42	0.25
180	0.33	0.99	0.57
190	0.64	2.00	1.13
200	1.12	3.64	2.02
210	1.81	6.06	3.31
220	2.74	9.40	5.08

From η_0 (viscosity at zero shear rate) of PS; SBR and NR depends on temperature (Table 2), λ at the different temperatures were calculated by Eq. (3) (Table 3). In a ternary blend system, SBR/PS and NR/PS are two viscosity ratio noted, so the system viscosity ratio reaches to 1 when general response ($D = \left[\prod_{i=1}^{n} \lambda_i\right]^{1/n}$) reaches to 1. In (Table 3) D = 1.13 at 190 °C is the closest to 1, so the most adaption mixing temperature is 190 °C.

Mixing speed

The droplets only break up and are stable when $\kappa^* \geq 2$ or κ at least equals double κ_{cr}. Replacing λ (190 °C) into Eq. (6) κ_{cr} is obtained. κ was calculated from Eq. (4) with $\kappa^* = 2$. The final, shear rate was recorded from Eq. (2) (Table 4). The mixing speed could get approximately with shear rate if mixing zone is small like internal mixer machine of Lab. According to Table 4, the NR droplets will be broke gradually from the original diameter 0.8 cm to the final diameter 3.5 μm when the shear rate is 56.5 s^{-1}.

Mixing time

In the (Table 4), the droplets could deform and break up from 0.8 cm to 3.5 μm diameter when the minimum time is 1.47 min. It is also satisfied with the

Table 4.
Shear rate and droplet breakup time at 190 °C.

Couple polymers	κ_{cr}	κ	γ_{dm} a), (mN/m)	$\dot{\gamma}$, (s^{-1})	t b), (min)
NR/SBR	2.98	5.96	0.51	52.1	1.47
SBR/PS	0.46	0.92	2.52	25.4	0.27
NR/PS	0.70	1.40	3.69	56.5	0.27

a) Ref. [19].
b) They have been calculated from Eq. (8).

experiments of Sabu Thomas et al.[14] PS/PB blends, the droplets breakup occur within the first 1–2 min of mixing time and they need 2–4 min to be homogeneous and stable. So that, in this blend system, the mixing time needs within 3.47–5.47 min.

Mixing conditions from experiment

The experimental design considered in this research was three-factor design (temperature, time and rotor speed), where each factor is set at two different level. Blend temperature is in [180;200] °C, time is in [6;10] min, rotor speed is in [40;80] rpm, this operation conditions was referred from research of Sabu Thomas et al.[14] for PS/PB blends. The design matrix is in (Table 5). We obtained the first degree of response surface from above experimental matrix with authenticity 95%:$\hat{y}_I = 78.17 - 7.12x_1 - 7.37x_1x_2$, (9) and $\hat{y}_T = 18.4$, (10) where, $\widehat{y}_I$ and $\widehat{y}_T$ are izod impact and tensile strength, x_i ($-1 \leq x_i \leq 1$) are the coded variables, the subscripts i = 1; 2; 3 represent the temperature, time and rotor speed, respectively.

After estimating regression function by Fisher model, the first degree model is suitable, however $F_0 = 101.39$ (is the test statistic for the hypothesis of no differences in treatment mean) is relatively high compared with $F_{0.05}^{4,1} = 224.6$. So that, we continued to plan the Box-Wilson second degree response surface in this region without finding out optimal area. The Box-Wilson experimental matrix is in (Table 6).

The second degree of response surface from Box-Wilson experimental matrix with authenticity 95%:$\hat{y}_I = 96.17 - 9.42x_1 - 7.37x_1x_2 - 12.61x_3^2$, (11) and $\hat{y}_T = 18.24$, (12)

Tensile strength does not almost depend on mixing conditions so that we only optimize mixing conditions from izod impact strength. On the other hand, Eq. (11) is maximum as $x_3 = 0$ correspond with 60 rpm and $\hat{y}_{Ia} = 96.17 - 9.42x_1 - 7.37x_1x_2$ is maximum. $\hat{y}_{Ia}$ is a saddle function, having two doubt point. One is the saddle point (0, −1.278) correspond with (190 °C; 5.44 min) and another is the conditional maximum point (−1,1) correspond with (180 °C;

Table 5.
The design matrix of mixing conditions.

Run	Experimental matrix			Mechanical strength	
	Temperature, (°C) Z_1	Time, (min) Z_2	Speed, (rpm) Z_3	Izod impact, (J/m)	Tensile (MPa)
1	180	6	40	74.55	18.32
2	200	6	40	91.10	15.47
3	180	10	40	101.29	17.86
4	200	10	40	53.38	18.93
5	180	6	80	85.92	18.56
6	200	6	80	70.37	16.82
7	180	10	80	79.39	21.64
8	200	10	80	69.38	19.62
9	190	8	60	80.04	19.52
10	190	8	60	78.39	18.62

Table 6.
The Box-Wilson design matrix of mixing conditions.

Run	Experimental matrix			Mechanical strength	
	Temperature, (°C) Z_1	Time, (min) Z_2	Speed, (rpm) Z_3	Izod impact (J/m)	Tensile (MPa)
1	180	6	40	74.55	18.32
2	200	6	40	91.10	15.47
3	180	10	40	101.29	17.86
4	200	10	40	53.38	18.93
5	180	6	80	85.92	18.56
6	200	6	80	70.37	16.82
7	180	10	80	79.39	21.64
8	200	10	80	69.38	19.62
9	190	8	60	80.04	19.52
10	190	8	60	78.39	18.62
11	203	8	60	93.14	15.42
12	177	8	60	131.71	18.76
13	190	10.6	60	100.18	18.02
14	190	5.5	60	108.61	16.85
15	190	8	86	90.75	18.33
16	190	8	34	87.79	19.04

Table 7.
Izod impact and tensile strength at the saddle and the conditional maximum point.

	Saddle point 190 °C, 5.44 min, 60 rpm		Conditional maximum point 180 °C, 10 min, 60 rpm	
	Value	Standard deviation	Value	Standard deviation
Izod impact strength, (J/m)	137.27	7.64	83.95	2.00
Tensile strength, (MPa)	19.09	0.84	19.28	0.76

10 min). Izod impact and tensile strength of these points are in (Table 7). From (Table 7), the optimum mixing conditions for this blend was obtained at 190 °C, 60 rpm, 5.44 min.

Conclusion

The blending conditions from droplet breakup theory are 190 °C, 56.5 rpm, 3.47 ÷ 5.47 min. And the blending conditions resulting in optimum mechanical properties were found to be 190 °C, 60 rpm, 5.44 min. The preliminary data on materials properties and drop diameter evaluation (desirable morphology) show how to control operating conditions.

Acknowledgements: I sincerely appreciate the assistance and help suggestion of Dr. Thao Vo Huu. I would also like to thank my mother, Dao Nguyen Thi, for her love and encouragement.

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