

Extrusion Parameter · Co-rotating twin screw Extruder · Interaction between extrusion Parameters · Carbon black · Filler dispersion

The filler dispersion in a premixed compound prepared using an internal mixer was further improved by an intermeshing co-rotating twin screw extruder (TSE). The effects of the extrusion parameters (i.e., screw speed, barrel temperature and ribbon width) on the extrudate properties were investigated using response surface methodology (RSM). Significantly, the effect on the extrudate properties of any extrusion parameter depends on the level of the other parameters, called "interaction effect". Mooney viscosity can also be adjusted by simultaneously altering these extrusion parameters. RSM thus reveals a number of ways to adjust the extrudate properties in a minimised number of experiments.

Auswirkungen der Extrusionsparameter eines co-rotierenden Zweischnckenextruders und ihrer Wechselwirkungen auf die Eigenschaften von rußgefüllten Styrol-butadienkauschuken

Extrusionsparameter · co-rotierender Zweischnckenextruder · Wechselwirkungen zwischen Extrusionsparametern · Ruß · Füllstoffdispersion

Die Füllstoffdispersion eines im Innenmischer vorgemischten Compounds wird zusätzlich durch einen ineinandergreifenden co-rotierenden Zweischnckenextruder (TSE) verbessert. Der Effekt der Extrusionsparameter (z. B. Schneckengeschwindigkeit, Behältertemperatur und Streifenbreite) auf die Extrudateigenschaften wurden durch die Methode „Response Surface Methodology“ (RSM) untersucht. Die Auswirkungen eines jeden Extrusionsparameters auf die Extrudateigenschaften hängen besonders vom Niveau anderer Parameter ab, auch Wechselwirkungseffekt genannt. Die Mooney-Viskosität kann auch durch den simultanen Wechsel dieser Extrusionsparameter angepasst werden.

Figures and Tables: By a kind approval of the authors.

Effects of the Extrusion Parameters of a Co-Rotating Twin Screw Extruder and their Interactions on the Properties of Carbon Black filled Styrene-Butadiene Rubber

Introduction

Twin screw extruders (TSE), nowadays, are widely used in the rubber industries because of their high capabilities for continuous production and good filler dispersion [1-4]. Despite having these advantages, the TSE is usually not applied with direct compounding of rubber and fillers [4, 5]. Since high filler loadings are needed to achieve the sufficient reinforcement, the rubber and filler are usually pre-mixed before being fed into the TSE [4, 5]. Commonly, this is achieved by using an internal mixer [4, 5]. After undergoing the filler incorporation stage [6], the premix can be obtained as either granules or ribbons for further feeding into the TSE.

Regarding improvement of the filler dispersion, an alteration in the extrusion parameters plays an important role on the final state-of-mix [7]. This, then, determines the final properties of the extrudates [3-5, 8]. The independent parameters of the extrusion process are screw speed, feed rate (or throughput), barrel temperature and screw configuration [9, 10].

During extrusion, the stress generation, specific mixing energy and shear heating depends not only on the screw speed, but also on the throughput and the barrel temperature [9, 10]. Moreover, the residence time varies with alteration of the screw speed and/or throughput [11-15]. With regard to the extrudate properties, Uphus et al. [5] reported that the filler dispersion relies on the screw speed and/or the throughput. There is, sometimes, a non-linear dependence on these parameters [3-5, 8].

However, the influences of one parameter on the filler dispersion are not always unchanged when the levels of other parameters are altered. This is called an "interaction effect" [16, 17]. For example, the influence of the screw speed on improving the filler dispersion becomes less pronounced when the

compounds were extruded with higher feed rates [5]. Unfortunately, to date, the studies of the processing conditions on the extrusion process and the properties of the extrudate focus only on the variation of one parameter at a time. This may conceal some information when it is needed to adjust two or more extrusion parameters simultaneously. There is, then, a deficiency in the explanation of how the alteration of one parameter influences the effect of another parameter both during the extrusion process and in determining the final extrudate properties.

In previous work [18], the response surface methodology (RSM) (a statistical tool minimising the number of experiments [16, 17, 19]) was successfully used for the investigation of interactions between mixing parameters (and also the individual and non-linear effects of each parameter) on the changes in mixing behaviour when using an intermeshing-rotor internal mixer. This included the state-of-mix of the rubber compounds obtained.

Authors

Jirawat Narongthong, Bangkok,
Pongdhorn Sae-Oui, Pathumthani,
Chakrit Sirisinha, Nakhonpathom,
Thailand

Corresponding Author:
Chakrit Sirisinha,
Rubber Technology Research Centre,
Faculty of Science,
Mahidol University, Phutthamonthon
73170 Nakhonpathom, Thailand
TEL: +662 441 9816 Ext. 1142;
FAX: +662 441 0511;
E-Mail: chakrit.sir@mahidol.ac.th



KGK RUBBERPOINT

Discover more interesting articles
and news on the subject!

www.kgk-rubberpoint.de



Entdecken Sie weitere interessante
Artikel und News zum Thema!

In this work, the RSM was applied specifically to the rubber extrusion process. Since there are advantages of better distribution and dispersion when using co-rotating TSE, compared to the counter-rotating TSE [20], the intermeshing co-rotating TSE was used in this study. The premix of rubber and fillers was used as ribbon. The investigated extrusion parameters were screw speed, barrel temperature and ribbon width. In order to absolutely reveal the significant changes in extrudate properties when altering these parameters, the mild screw configuration was used. This was configured with forward conveying elements only [4, 5].

Experimental

Preparation of Premix-Ribbon

Materials and formulation used in the present work are listed in Table 1.

First, a dry blend of N330, ZnO, stearic acid, sulphur and 6PPD with raw SBR was charged into the mixing chamber of the internal mixer (HPV/ Pornviwat Engineering Ltd., Part., Thailand) using a fill factor of 0.85 and chamber temperature of 70°C. The mixing was conducted at rotor speeds of 30 rpm (front rotor) and 23 rpm (back rotor) for 4 minutes prior being discharged. The mix was homogenised using a two-roll mill (LRM 150W/ Labtech Engineering Co., Ltd., Thailand), and then cut into ribbon with a thickness of approximately 4 mm. The physico-mechanical properties of the premix are shown in Table 2.

Screw Configuration

The screw configuration used in this present work is illustrated in Figure 1. The details of the screw elements are given in Table 3.

Design of Experiment and Operation of Extrusion Process

The independent variables of the TSE investigated in this study were screw speed (X_1), barrel temperature (X_2) and ribbon width (X_3). The experiment was designed based on a RSM model of three-parameter variation. A detailed description of the point-by-point design features of this method is reported elsewhere [16, 17, 21, 22]. The experiments were conducted in 20 runs, as illustrated in Table 4.

In coded units, the codes -1, 0 and +1 are, respectively, related to low, centre and high levels of each variable. The

1 Materials and formulation used in present work			
Materials		Grades/Suppliers	Content (phr)
Name	Abbr.		
Emulsion styrene-butadiene rubber 1723	SBR 1723	Low PCA oil content of 27.3% (or 37.5 phr)/ Styrene content of 23%/ BST Elastomers Co., Ltd. (Thailand)	137.5
Carbon black (N330)	N330	N330/ Thai Carbon Black Public Co., Ltd. (Thailand)	50
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	6PPD	Santoflex® 6PPD/ Flexsys (Belgium)	3
Sulphur	S	The Siam Chemicals Public Co., Ltd. (Thailand)	1.75
Stearic acid		ACID CHEM INTERNATIONAL SDN. BHD (Malaysia)	1
Zinc oxide	ZnO	White-seal/ Thai-Lysaght Co., Ltd. (Thailand)	3
N-tert-butyl-2-benzo thiazole sulfenamide	TBBS	Monflex PTE.Ltd. (Singapore)	1.38

2 The physico-mechanical properties of premix-ribbon			
Form	Property	Value	Characterisation
Compound	Mooney viscosity	85.0±1.7 MU	ISO 289-1
	Bound rubber content	4.39±1.20 %	Equation 2
	Payne effect	362.91±16.35 kPa	Rubber process analyser
Vulcanisate ^a	Filler dispersion	30.05±2.73 %	ASTM D7723
	Tensile modulus at 100% strain	1.49±0.06 MPa	ISO 37 (type 1)
	Tensile strength	17.04±0.80 MPa	ISO 37 (type 1)

^aProperty of the vulcanisate after passing the sequent processes of TBBS addition and cure, as will be described in section of operation of extrusion process.

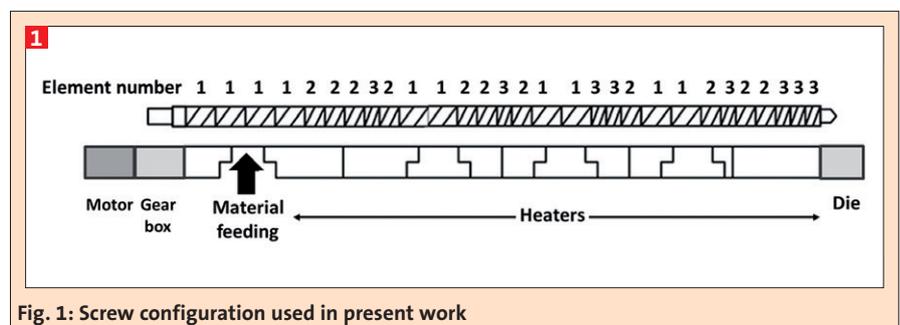


Fig. 1: Screw configuration used in present work

codes -1.682 and +1.682 are related to the extended levels of each variable [22]. The un-coded value of the variable at each level is shown in the parenthesis.

The regression equation for this design is expressed in Equation 1.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where, Y is the response. X_1 , X_2 and X_3 are screw speed, barrel temperature and ribbon width, respectively. β_p , β_{ij} and β_{ij} are linear, quadratic and interaction regression coefficients, respectively [16, 17, 21, 22].

For the extrusion process, the temperatures of heaters and die (see Figure 1) were set at X_2 . The premix-ribbon was continually put into the TSE (CTE D32L32, L/D ratio of 32, D=32 mm, Chareon Tut Co., Ltd., Thailand) at screw speed X_1 . Once the extrusion process becomes stable, the throughput and the residence time were evaluated.

In prepare the vulcanisate, 200g of the extrudate (an uncured compound after emerging from die lip) was taken for mixing with TBBS. This was conducted on two-roll mill at 70°C with nip gap of 2.3 mm, and was finished within 3 minutes. For the vulcanisation process, the uncured compounds were hot pressed at 160°C with t_{90} , as per ISO 6502.

Composite Characterisations

The Mooney viscosity (ML1+4 @100°C) of the extrudates was measured using a Mooney viscometer (ViscTech+, TechPro, USA) as per ISO 289-1.

The measurement of bound rubber content was performed by immersing approximately 1.0 g of the compound in 100 ml toluene for 7 days at room temperature. The insoluble fraction was filtered and dried at 70°C for 12 hrs. The bound rubber content was calculated by Equation 2 [18].

$$\text{Bound rubber content (\%)} = \frac{W_{fg} - W[m_f/(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100\%$$

where W_{fg} is the weight of carbon black-rubber gel, W is the weight of the original test specimen, m_f is the weight of filler in the compound, and m_p is the weight of polymer in the compound.

The molecular weight distributions (MWD) of raw SBR and SBR stored at 160°C for 12 minutes were characterised using gel permeation chromatography (GPC) with a refractive index detector (Waters, USA). Approximately 13 mg of rubber was dissolved in 5 ml tetrahydrofuran (THF) (HPLC grade, RCI-Labscan, Thailand) at room temperature for 12 hrs. Thereafter, the solution was filtered using 22 µm of mesh grid. The character-

3 Details of the screw elements used in present work (all are double-flight elements)

Element number	Manufacturer codes	Element type	Pumping direction	Screw lead (mm)	Pitch distance	Helix angle
1	CB 45/45 R	Conveying	Forward	45	20 mm	45°
2	CB 30/30 R	Conveying	Forward	45	15 mm	30°
3	CB 22.5/22.5 R	Conveying	Forward	22.5	10 mm	22.5°

4 RSM designed experiment. The actual value is shown in the parenthesis.

Run order	Design parameters		
	Screw speed; X_1 (rpm)	Barrel temperature; X_2 (°C)	Ribbon width; ^a X_3 (cm)
1	-1 (50)	-1 (90)	-1 (0.6)
2	+1 (130)	-1 (90)	-1 (0.6)
3	-1 (50)	+1 (120)	-1 (0.6)
4	+1 (130)	+1 (120)	-1 (0.6)
5	-1 (50)	-1 (90)	+1 (1.5)
6	+1 (130)	-1 (90)	+1 (1.5)
7	-1 (50)	+1 (120)	+1 (1.5)
8	+1 (130)	+1 (120)	+1 (1.5)
9	-1.682 (23)	0 (105)	0 (1.05)
10	+1.682 (157)	0 (105)	0 (1.05)
11	0 (90)	-1.682 (80)	0 (1.05)
12	0 (90)	+1.682 (130)	0 (1.05)
13	0 (90)	0 (105)	-1.682 (0.3)
14	0 (90)	0 (105)	+1.682 (1.8)
15	0 (90)	0 (105)	0 (1.05)
16	0 (90)	0 (105)	0 (1.05)
17	0 (90)	0 (105)	0 (1.05)
18	0 (90)	0 (105)	0 (1.05)
19	0 (90)	0 (105)	0 (1.05)
20	0 (90)	0 (105)	0 (1.05)

^aAt constant thickness of approximately 4 mm

5 Physico-mechanical responses^a

Run	Extrusion process					Compound		Vulcanisate	
	Throughput (kg/hr)	Power change (kW)	Residence time (s)	Exit temp. (°C)	Die pressure (bar)	MV (MU)	BRC (%)	DI (%)	TS (MPa)
1	2.7	0.51	130	125	16	69.6	10.3	73.1	19.72
2	8.0	0.91	45	148	19	65.2	10.7	80.4	19.83
3	2.6	0.48	115	153	16	76.2	11.3	71.4	18.69
4	7.2	0.84	44	165	19	73.0	13.8	71.4	18.71
5	5.5	0.55	110	112	20	72.8	9.3	71.2	19.19
6	14.6	1.46	40	120	23	65.2	9.5	78.5	19.69
7	6.0	0.49	95	147	18	76.5	10.2	69.1	18.46
8	14.7	1.09	37	157	21	73.8	12.3	70.3	18.51
9	2.0	0.28	220	121	17	75.7	8.4	73.3	18.28
10	14.6	0.84	32	160	22	70.6	11.2	79.6	19.14
11	7.9	0.84	60	130	22	65.3	10.1	82.6	19.30
12	8.1	0.65	58	155	19	75.2	12.0	72.7	18.90
13	2.8	0.62	86	152	13	69.0	14.7	78.4	19.06
14	14.0	1.16	52	141	23	71.0	9.8	81.0	19.01
15	8.1	0.70	56	143	22	70.0	10.8	78.7	19.27
16	8.1	0.72	58	144	22	70.3	10.5	77.7	19.80
17	8.3	0.72	57	156	20	72.4	10.8	77.1	18.91
18	8.4	0.72	55	157	22	72.4	10.7	76.7	19.21
19	8.2	0.73	56	156	20	72.2	10.6	77.2	19.14
20	8.1	0.70	58	158	20	71.3	10.4	77.1	18.94

^a Mooney viscosity (MV); bound rubber content (BRC); dispersion index (DI); tensile strength (TS)

6 Coefficients (coeff.) and p-values of the reduced regression model (in coded units) of the responses: throughput, power change, residence time, exit temperature, die pressure, Mooney viscosity (MV), bound rubber content (BRC), dispersion index (DI) and tensile strength (TS)

Responses		Constant	Variables								
			X ₁	X ₂	X ₃	X ₁ ²	X ₂ ²	X ₃ ²	X ₁ X ₂	X ₁ X ₃	X ₂ X ₃
		β ₀	β ₁	β ₂	β ₃	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Throughput	Coeff.	7.991	3.59	-0.002	2.869					0.999	
	p-value	0.000	0.000	0.989	0.000					0.000	
Power change	Coeff.	0.7316	0.2334	-0.062	0.1286	-0.045		0.0720		0.0928	
	p-value	0.000	0.000	0.030	0.000	0.093		0.012		0.015	
Residence time	Coeff.	57.89	-43.95	-2.74	-7.99	22.43					
	p-value	0.000	0.000	0.400	0.023	0.000					
Exit temperature	Coeff.	150.40	.68	11.65	-5.38	-4.31	-3.60				
	p-value	0.000	0.001	0.000	0.019	0.046	0.088				
Die pressure	Coeff.	20.82	1.49	-0.662	2.11	-0.557		-1.09			
	p-value	0.000	0.000	0.041	0.000	0.071		0.002			
MV	Coeff.	70.86	-1.94	3.17	0.5581	0.7701			0.773		
	p-value	0.000	0.000	0.000	0.067	0.013			0.054		
BRC	Coeff.	11.12	0.7196	0.8064	-0.951	-0.373			0.4975		
	p-value	0.000	.003	0.001	0.000	0.075			0.078		
DI	Coeff.	76.72	1.93	-2.76	-0.21	-1.25			-1.68		
	p-value	0.004	0.017	0.002	0.773	0.093			0.094		
TS	Coeff.	19.18	0.155	-0.347	-0.086	-0.139					
	p-value	0.003	0.074	0.001	0.302	0.095					

X₁: screw speed; X₂: barrel temperature; X₃: ribbon width

risation was performed using a flow rate of 1 ml/min, THF as mobile phase and polystyrene as standard.

Dispersion index of the vulcanisates was measured using the dispersion grader (disperGRADER α view, Alpha Technologies, USA) according to ASTM D7723.

Tensile tests were performed with the universal mechanical tester (Instron model 5566, USA) according to ISO 37 (type 1).

Results and Discussion

Physico-Mechanical Properties

The physico-mechanical responses of both compound and final vulcanisate are shown in Table 5.

To establish the relationship between variables and responses, all of the test data were fitted to Equation 1, and analysed using Design Expert® statistical software (Version 11, USA). The insignificant terms, that is the ones with p-value higher than 0.1 (set significance level), were ignored. The main variables (X₁, X₂ and X₃) were maintained whether or not they had a p-value higher than the significance level (0.1). The responses were then re-fitted and analysed. The data analysis results are shown in Table 6.

Either main effect plots or 3-dimensional surface plots of the reduced model

of each response was also displayed using Design Expert®. These were drawn by using centre levels (90 rpm, 105°C and 1.05 mm ribbon width) as hold values for all drawings.

Influence of Extrusion Parameters on the Extrusion Process

In order to investigate the effects of the extrusion parameters on the extrusion process, the throughput (or the output rate of the extrusion process), the power change (the difference in power of the mixer when rotating with and without material loadings), residence time (in this case; the minimum time required to put the first tracker out from the die), the exit temperature (temperature of the extrudate compound at the die exit) and the die pressure were considered as responses. The results are shown in Figure 2.

Since there is no interaction between the extrusion parameters in their effect on the residence time, exit temperature and die pressure, the 2-dimensional main effect plots are used to present these response instead of the 3-dimensional surface plots. The discussion for these responses is given below.

Throughput

The throughput increases with increasing screw speed and/or ribbon width

(Figure 2a-a'). In the TSE, the throughput is equal to the feed rate because of self-wiping [23, 24]. These parameters also have a positive interaction effect on each other, Figure 2a' (see p-value of term X₁X₃ in Table 6). That is, more compound is obtained when using higher levels of one parameter with increasing level of another parameter. In other words, the slope of the throughput graph becomes steeper when using higher screw speeds and altering ribbon width. The resulting data analysis (Table 6) also shows that the barrel temperature does not significantly affect the throughput.

Power Change

The increases in screw speed and ribbon width also raise the magnitude of the power change (Figure 2b-b'). This is due mainly to the higher rate of compound mass being taken into the extruder at a time. This agrees well with the results of throughput (see Figure 2). These parameters show significant non-linear effects, but with different patterns. The power change increases in a convex up way with increasing screw speed, but in a concave up way with increasing ribbon width. At high screw speeds, the powers change increases only slightly because the very high shear heating causes the large decreases in the compound viscosi-

2

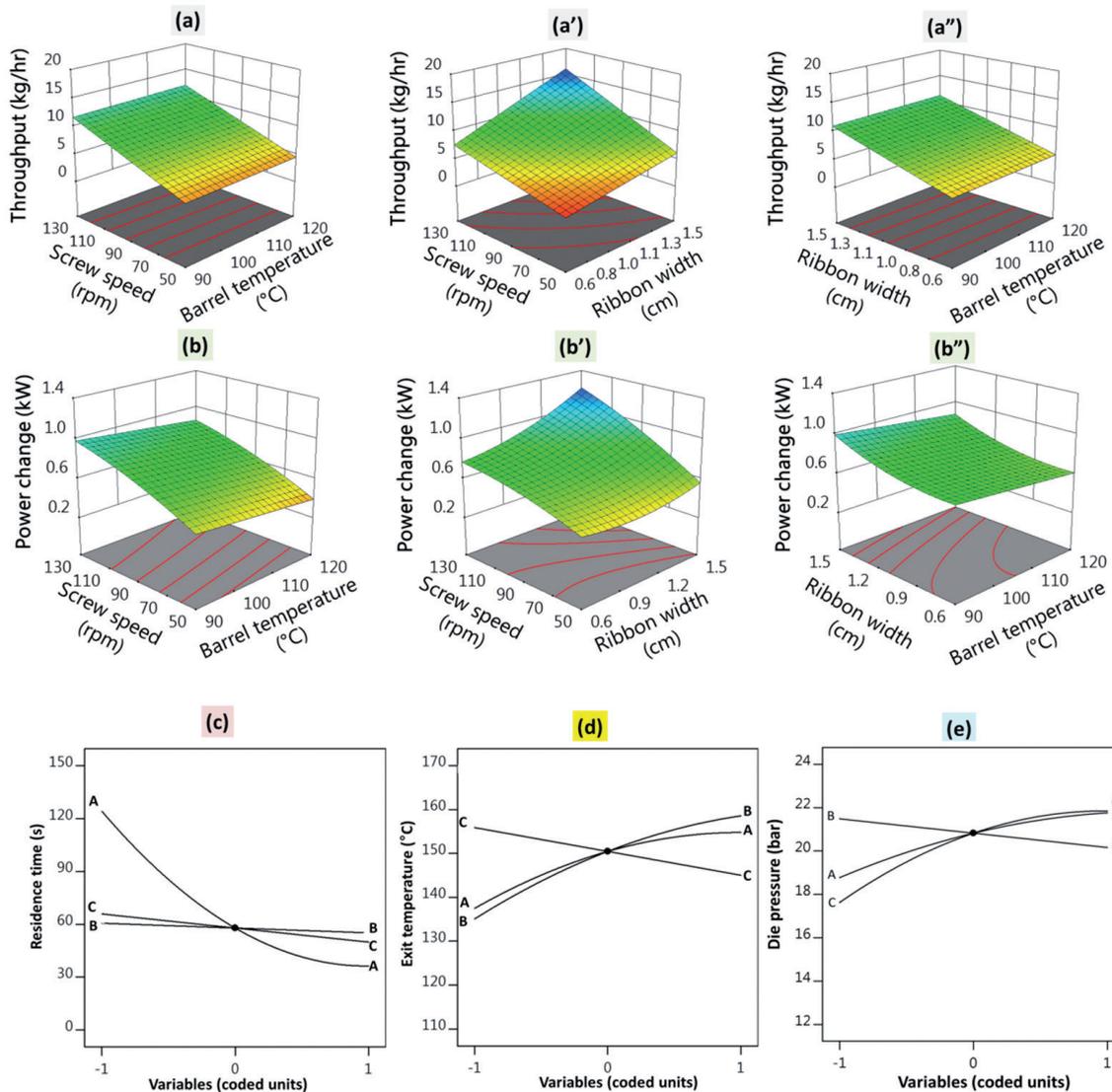


Fig. 2: 3-dimensional response surface plots of (a-a'') throughput and (b-b'') power change, and the main effect plots of (c) residence time, (d) exit temperature and (e) die pressure

ty and resulting stress generation. On the other hand, at high ribbon widths, the level of power change shifts non-linearly towards much higher values. This is because the higher feeding rate causes the compound (at low temperatures) to be more retained in the screw. So, higher power is required to pump the compound forwards.

The screw speed and ribbon width also have a significant positive interaction when affecting the power change (Figure 2b'). That is, the effect of the ribbon width on the power change becomes more pronounced at higher screw speeds, and vice versa. This is as discussed previously for throughput.

In contrast to screw speed and ribbon width, there is little difference in the ma-

gnitude of power change with altered barrel temperature (Figures 2b and b''). The compound is slightly softened by the higher temperatures, decreasing the stress (or power) required to push the compound forwards.

Residence Time

An increase in screw speed shows the greatest effect on the residence time. This increases the rate of pushing the material forwards, so decreasing the residence time, as reported previously [8, 10, 13, 20]. Evidently, with a linearly increasing screw speed, the residence time decrease non-linearly, concave up, towards an optimum-minimum. This is because the high screw speed not only decreases the compound viscosity, but also increases the

back-pressure at the die entrance. When these effects become dominant (at too high screw speeds), the pumping pressure is less pronounced. It becomes more difficult to get the compound through the die. As a consequence, the residence time then decreases only gradually.

An increase in ribbon width results in a decreased residence time. In this study, the throughput is not kept constant during varying ribbon width, but varies as a response. When the ribbon width makes more compound mass being fed at a time (see throughput), there is a higher pressure to push the compound throughout the die (see die pressure, Figure 2e) [11, 12]. In addition, with higher compound feedings, the compound viscosity is barely reduced by the softening effect of the

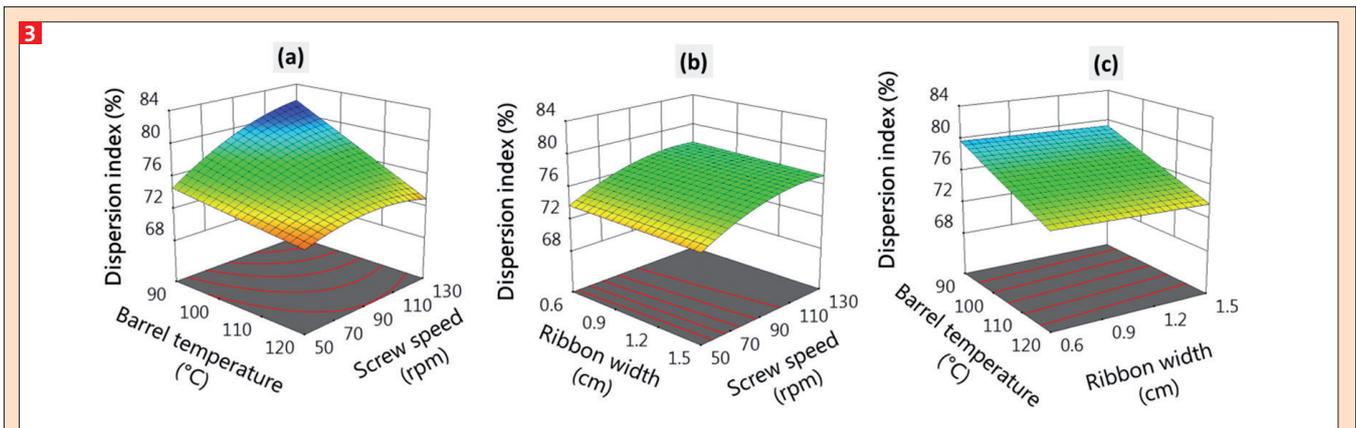


Fig. 3: 3-dimensional response surface plots of the dispersion index.

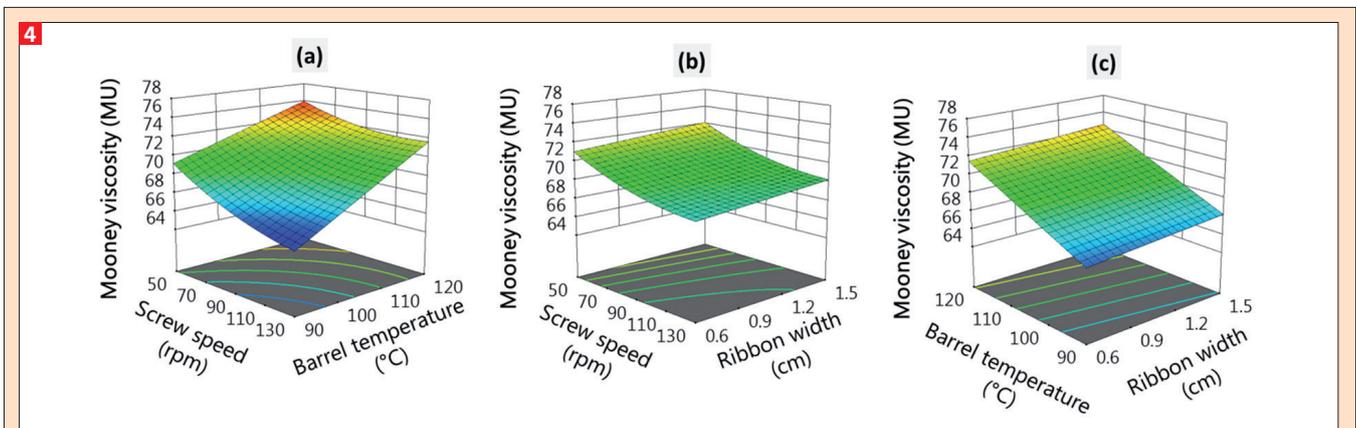


Fig. 4: 3-dimensional response surface plots of Mooney viscosity.

barrel temperature (see exit temperature, Figure 2d). These, together, generate a higher pumping pressure, pushing the compound forwards more rapidly.

The barrel temperature has the least effect on the residence time (see p-value in Table 6).

Exit temperature

Evidently, the exit temperature is higher than the set barrel temperature (between 90-130°C, see Table 4) under any given mixing conditions.

The exit temperature increases with increasing screw speed because the higher screw rotation generates higher shear stress and so greater viscous energy dissipation, as reported previously [3, 5, 10, 25, 26]. However, at very high screw speeds, the exit temperature increases only gradually. That is because the higher stress simultaneously causes a decrease in the compound viscosity. This non-linear effect is similar to the way that the screw speed acts on the power change (Figure 2b-b”).

Even though the increased ribbon width increases the power change (Figure

2b’-b”), the higher ribbon widths lower the exit temperature. This is attributed to the reduced residence time. This result also implies that the higher power change is caused only by the higher mass of fed compound, by a requirement to generate higher shear stress.

As expected, an increase in barrel temperature significantly increases the compound temperature, due mainly to heat conduction [10]. However, the effect of the barrel temperature increasing compound temperature becomes less pronounced at too high barrel temperatures. That is because the higher temperature lowers stress generation, as stated previously in section of power change. In this way, the dependence of exit temperature on barrel temperature departs from linearity.

Die Pressure

Figure 2e shows that the barrel temperature reduces the die pressure in a linear fashion by softening the compound [10, 27]. This agrees well with the increased exit temperature. The die pressure increases with increasing screw speed and/or

ribbon width, because of the increased feed rate (or throughput) [1, 20]. This increases the filling magnitude at the die entrance, thus generating higher pumping pressure. The die pressure might decrease with increasing screw speed if the feed rate (or throughput) is kept constant, due to the decreased compound viscosity [1, 20]. However, this effect is minimised in this case due mainly to the dominant effect of throughput.

Moreover, the increase in die pressure becomes smaller, or drops off from the linearity, at very high screw speeds or ribbon widths. This is because a high back pressure is generated at the die entrance [15]. That, in turn, slightly decreases the compound viscosity and increases the compound temperature. Then, the die pressure does not increase much further.

Filler Dispersion

The level of filler dispersion was investigated via the dispersion index. The results are shown in Figure 3.

Only the screw speed affects the dispersion index in a non-linear fashion.

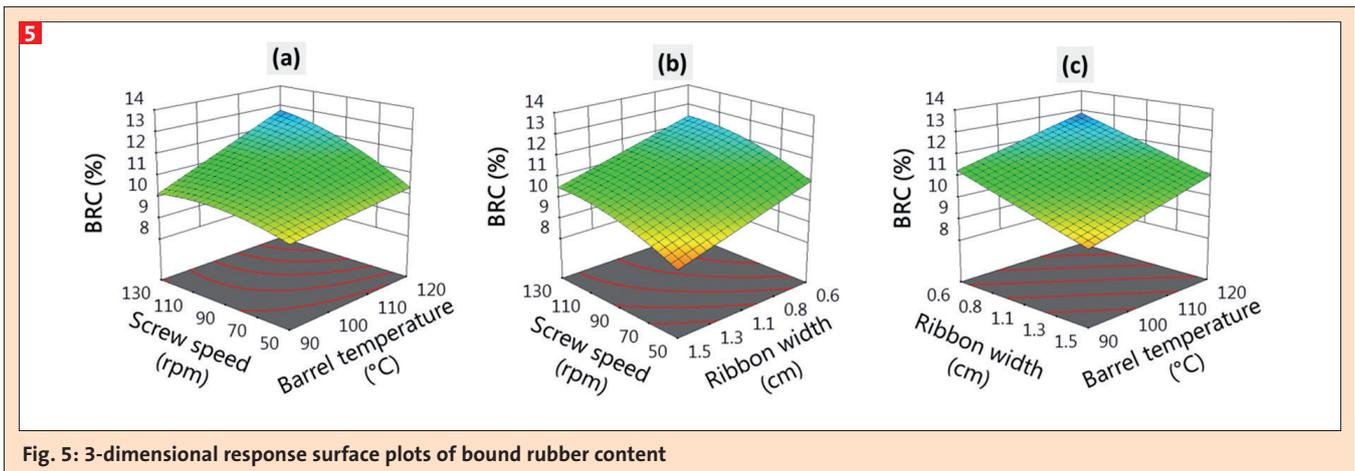


Fig. 5: 3-dimensional response surface plots of bound rubber content

With increasing screw speed, the dispersion index increases, convex up, towards an optimum-maximum, as evidenced in Figures 3a and 3b. The deviation from the linearity is because the rise in screw speed increases not only the stress generation, but also the compound temperature (see Figure 2d) [5]. The latter causes a reduction of the compound viscosity, which, in turn, reduces the effect of the generated stress. This effect agrees well with the power change (Figure 2b-b'). However, at higher barrel temperatures, the effect of the screw speed on the dispersion index becomes less pronounced (shallower slope of the plots in Figure 3a), indicating a significant negative interaction effect between the screw speed and barrel temperature (see the coefficients in Table 6). This is because the higher barrel temperature decreases the compound viscosity. This, then, lowers the stress generation, and so the state-of-mix.

In contrast to screw speed, an increase in barrel temperature shows a linear negative effect on the decrease in dispersion index. This is due to the temperature softening effect decreasing the generated shear stress (see power change). However, it does not mean that the increase in barrel temperature makes the compound reach a final poor state-of-mix, since the lowest dispersion index of the extrudate (approximately 69%, Table 5) is much higher than that of premix-ribbon (30.05±2.73 %, see Table 2). However, it does mean that the higher barrel temperature presents a greater resistance to the achievement of an improved state-of-mix. The variations in other parameters (screw speed and ribbon width) hardly help to improve the state-of-mix. In the case of ribbon width, the resulting data analysis in Table 6 reveals that the ribbon width has the lowest effect, and

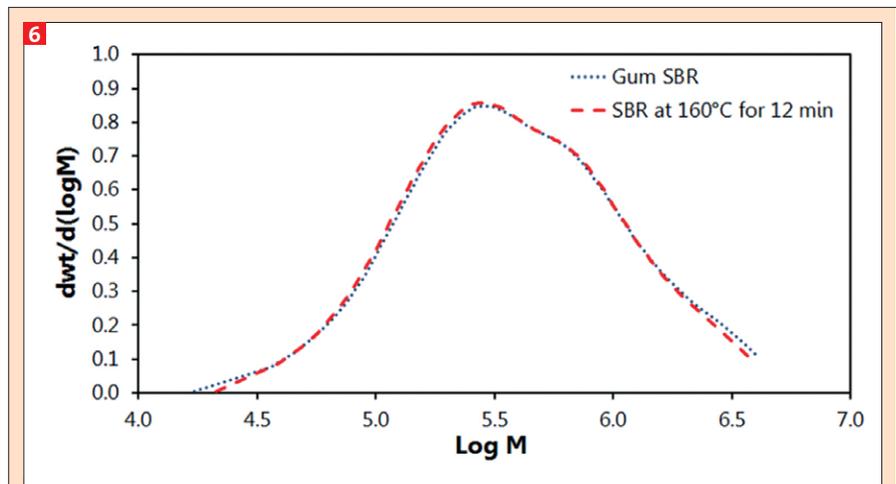


Fig. 6: Molecular weight distributions of raw SBR and SBR stored at 160°C for 12 minutes.

so barely affects the dispersion index. That is because, even though an increased ribbon width increases the power change (in relation to the increased shear stress), it decreases the residence time. The compound remains only a short time in the TSE.

Significantly, Table 5 and Figure 3 show that the alterations in these extrusion parameters from mild to severe conditions cause an improvement of the filler dispersion up to 180%, which is calculated based on the dispersion index of premix-ribbon (30.05% dispersi-on, Table 2).

These results emphasise an efficient improvement in the filler dispersion in the co-rotating TSE, especially when using a mild screw configuration.

Mooney Viscosity

The Mooney viscosity of the uncured rubber compounds was used to investigate the effect of extrusion parameters on the disruption of filler-filler networks. The coefficients listed in Table 6 show

that variation in the screw speed has the greatest influence on the resulting Mooney viscosity, followed by the effect of the barrel temperature. As evidenced by the graphs (Figure 4), the change in Mooney viscosity is mainly controlled by the screw speed and barrel temperature, rather than by the ribbon width. The red zone (poor state-of-mix) appears when using a very low screw speed or a very high barrel temperature (Figure 4a).

Moreover, both the tabulated coefficients (Table 6) and the surface plots show that, with increasing screw speed, the Mooney viscosity decreases non-linearly, concave up, towards an optimum-minimum. However, with higher barrel temperatures, the effect of the screw speed on decreasing the Mooney viscosity becomes less pronounced. This indicates a significant negative interaction between the screw speed and the barrel temperature.

The least effect is found for the ribbon width. Because of this lowest effect, the plots of the Mooney viscosity as func-

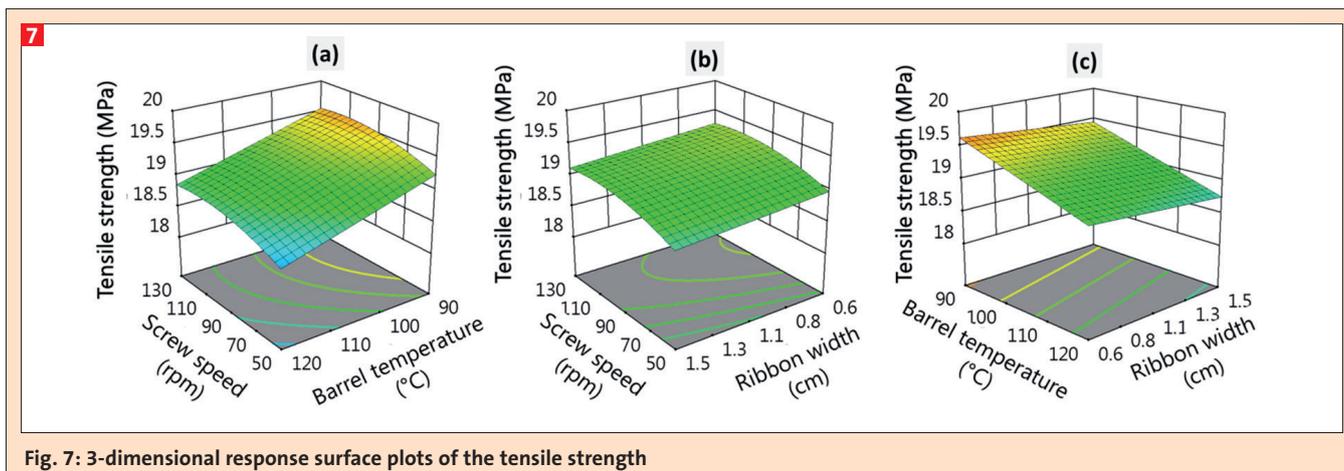


Fig. 7: 3-dimensional response surface plots of the tensile strength

tions of screw speed and barrel temperature are not distorted when varying the levels of ribbon width.

All the above results agree well with the increased dispersion index (Figure 3), which relates to the breakdown of the filler-filler networks. As the filler dispersion increases, the filler agglomerates breakdown to the dispersed aggregates, reducing the proportion of filler-filler networks. That, in turn, releases more the trapped rubber molecules to be the matrix. So, a lower Mooney viscosity is the result.

The highest Mooney viscosity after extrusion is between 76-77 MU (see Table 5). That is much lower than that of the master batch (85.0 ± 1.7 MU, Table 2). This indicates that, even extruding with inefficient conditions (high barrel temperature, low screw speed and high ribbon width), the shear stress generated by the screw configured with all conveying elements can significantly affect the extrudate, giving an approximately 10% drop in Mooney viscosity. On the other hand, using high intensities of these extrusion parameters (high screw speed, low barrel temperature and low ribbon width), the Mooney viscosity is much reduced to as low as 65 MU. This is approximately a 25% drop in the Mooney viscosity.

Rubber-Filler Interaction

The bound rubber contents of uncured rubber compounds were considered in order to investigate the effect of extrusion parameters on the formation of the rubber-filler physical interaction. The results are shown in Figure 5.

In this case, with increasing screw speed, the bound rubber content increases, convex up, towards an optimum-maximum. It also increases linearly with decreasing ribbon width. These effects

agree well with the increased dispersion index, as discussed previously (Figure 3). As the filler dispersion increases, the large agglomerates are more broken-down to the smaller aggregates. That increases the rubber-filler interface, allowing more rubber molecules to be adsorbed on the filler surfaces [28, 29]. That, then, results in a higher bound rubber content, indicating greater rubber-filler interaction [30].

The effect of the barrel temperature on the bound rubber content opposes to that acting on the dispersion index and the Mooney viscosity. In this case, the increase in barrel temperature shows a positive linear effect, increasing bound rubber content at any given screw speeds and/or the ribbon widths. That is because, at a given filler loading, the bound rubber content increases not only with increasing state-of-mix, but also with increasing temperature and storage time, as described in [31]. In this case, the barrel temperature shows a strong effect on the compound temperature, as discussed in the section of exit temperature (Figure 2d). So, the temperature, rather than the state-of-mix, has the dominant effect on the formation of bound rubber. This effect is in accordance with the chain mobility [31, 32]. The higher temperatures, during extrusion and after exiting the die, facilitate faster movement of the rubber molecules to approach and be adsorbed on the filler surface. So, the higher compound temperatures make the large rubber molecules (or larger chain segments) move into position as fast and as efficiently as the small bound rubber segments [30-32].

There is a possibility that other effects that might cause an apparent increase in the bound rubber content. These might be occluded rubber and the formation of gels of SBR-molecules. The gels would be

entangled networks of rubber molecules in which the entanglement points may be tight physical, or even chemical, attachments. They can be caused by the higher barrel temperatures. Then, some occluded rubbers and SBR gel may not be completely extracted from the cages of the non-dispersed agglomerates, so increasing the apparent bound rubber content. However, neither is the cases, as confirmed by i) bound rubber content of premix and ii) the molecular weight distributions of the SBR before and after storing at 160°C for 12 minutes (Figure 6). This is discussed below.

If the occluded rubber cannot be extracted from the non-dispersed agglomerates, the bound rubber content of the premix should be higher than the extrudate since it has a lot of occluded rubber. However, the bound rubber content of the premix-ribbon is only $4.39 \pm 1.20\%$ (see Table 2).

Considering the possibility of a gelation effect, Figure 6 reveals that molecular weight distributions of the SBR before and after storing at 160°C for 12 minutes are not different, suggesting that there is no gelation of the SBR in the mixing process under the given time and temperature. The very slight shift of the curve extremes to lower values might be caused from the thermal degradation of the SBR molecules.

The ribbon width shows a linear negative effect on the bound rubber content. This is accorded to the filler dispersion and the exit temperature as they decrease with increasing ribbon width.

A significant interaction effect on the bound rubber content is found between screw speed and barrel temperature. This is a positive interaction, even though these two parameters show a negative one in their affecting the dis-

persion index (Figure 3). This indicates that, at higher screw speeds where the filler dispersion is high, the increase in the barrel temperature accelerates bound rubber to reach an equilibrium state more rapidly.

Tensile Properties

The tensile strength of the vulcanisates increases with increasing screw speed and has a non-linear convex-up relationship. Where the chemical crosslink density is considered to be invariant (see Table 1), the tensile strength is the resulting combination of the increased filler dispersion and rubber-filler interaction. The greater amount of rubber-filler interfaces, in conjunction with the higher rubber-filler interactions, makes the composite better able to withstand higher mechanical loads. So, the effect of screw speed on the tensile strength agrees well with that on the other properties, i.e., dispersion index, Mooney viscosity and bound rubber content, as discussed above.

With increasing barrel temperatures, the tensile strength is reduced, even though the bound rubber content increases. On the other hand, the tensile strength is increased when the state-of-mix is augmented, such as at low barrel temperatures (see dispersion index, Figure 3). This suggests that, in use, the product of high rubber-filler interactions associated with poor filler dispersion cannot withstand the higher mechanical loadings. That is due mainly to the low number of rubber-filler interfaces. However, the higher barrel temperature does not make the extrudate unusable since the tensile strength of cured-extrudates (in the range of 18.28-19.83 MPa, see Table 5) is significantly higher than those of cured-premix (17.04±0.80 MPa, see also Table 2).

The variation in ribbon width shows a negligible effect on the resulting tensile strength because it has only a slight influence on the filler dispersion and the bound rubber formation.

As evidenced by the statistical p-values, there is no significant interaction between the parameters affecting the tensile strength.

Conclusions

With linearly increasing screw speed, the residence time decreases non-linearly (concave up) while the compound temperature and the die pressure increase in a convex up manners. The increase in screw

speed increases throughput and power consumption. The net result is the increase in state-of-mix, convex-up, towards an optimum-maximum. The increase in barrel temperature affects the extrusion process via the softening effect, decreasing compound viscosity, and so the generated stress. Even though the higher barrel temperature increases the rubber-filler interaction, the poor mechanical properties are resulted, because of the low improvement of filler dispersion. The variation in ribbon width mainly affects the extrusion process, i.e., increasing throughput and power change, but has little effect on the compound and vulcanisate properties.

The effect of screw speed on the state-of-mix (or filler dispersion) has a negative interaction with the barrel temperature, according to the limit of stress generation. When one parameter decreases the compound viscosity (either by softening or by increasing magnitude of filler-filler network disruption), the other parameters cannot affect the state-of-mix much further.

In use, tensile strength related to the overall reinforcement efficiency depends on the filler dispersion (major) and the rubber-filler interactions (minor). However, a higher rubber-filler interaction promoted by a higher compound temperature, but without sufficient filler dispersion cannot withstand higher mechanical loads.

Acknowledgements

This work was financially supported by the Thailand Research Fund (TRF) through the Research and Researchers for Industries (RRI) and CHAREON TUT Co., Ltd. (Grant PHD58I0011). The authors acknowledge with pleasure the assistance of Prof. Alastair M. North.

References

[1] A. Lewandowski, Challenges of Modern Technology **2** (1) (2011) 36.
 [2] J. W. G. Mani, German Institute of Rubber Technology (DIK) (2010) 130.
 [3] S. Luther, M. Bogun, R. H. Schuster, U. Göl, KGK **59** (9) (2006) 473.
 [4] M. Bogun, S. Luther, R. Schuster, U. Göl, H. Radosch, KGK **57** (12) (2004) 633.
 [5] R. Uphus, O. Skibba, R. Schuster, U. Göl, KGK **53** (5) (2000) 279.
 [6] G. R. Cotten, Rubber Chemistry and Technology **57** (1) (1984) 118.
 [7] C. Sirisinha, W. Sittichokchuchai, J. Appl. Polym. Sci. **76** (10) (2000) 1542.
 [8] J. W. G. Mani, S. Luther, R. H. Schuster, U. Göl,

KGK **60** (2007) 303.
 [9] A. Lewandowski, K. J. Wilczyński, A. Nastaj, K. Wilczyński, Polym. Eng. Sci. **55** (12) (2015) 2838-48.
 [10] O. S. Carneiro, C. J. A., V. B., J. Appl. Polym. Sci. **78** (7) (2000) 1419.
 [11] A. Poulesquen, B. Vergnes, Polym. Eng. Sci. **43** (12) (2003) 1841.
 [12] T. Villmow, B. Kretzschmar, P. Pötschke, Compos. Sci. Technol. **70** (14) (2010) 2045.
 [13] R. Baron, P. Vauchel, R. Kaas, A. Arhaliass, J. Legrand, Chem. Eng. Sci. **65** (10) (2010) 3313.
 [14] G. E. Gasner, D. Bigio, C. Marks, F. Magnus, C. Kiehl, Polym. Eng. Sci. **39** (2) (1999) 286.
 [15] A. Eitzlmayr, G. Koscher, G. Reynolds, Z. Huang, J. Booth, P. Shering, J. Khinast, Int. J. Pharm. **474** (1) (2014) 157.
 [16] M. Balachandran, S. Devanathan, R. Muralakrishnan, S. S. Bhagawan, Mater. Design **35** (2012) 854.
 [17] R. Rajan, S. Varghese, M. Balachandran, K. E. George, Rubber Chem. Technol. **89** (2) (2016) 211.
 [18] J. Narongthong, P. Sae-Oui, C. Sirisinha, Rubber Chem. Technol. **90** (3) (2018) 521.
 [19] R. H. Myers, D. C. Montgomery, C. M. Anderson-Cook, Wiley (2011).
 [20] P. G. Lafleur, B. Vergnes, Chichester: UK (2014) 109.
 [21] M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villar, L. A. Escalera, Talanta **76** (5) (2008) 965.
 [22] T. R. Kukreja, D. Kumar, K. Prasad, R. C. Chauhan, S. Choe, P. P. Kundu, Eur. Polym. J. **38** (7) (2002) 1417.
 [23] S. Moradi, N. G. Ebrahimi, N. Granpayeh, M. K. Moravveg, Open Mechanical Engineering Journal **2** (2018) 93.
 [24] M. H. Hong, Q. Jiang, J. L. White, Int. Polym. Proc. **23** (1) (2008) 88.
 [25] A. Amash, M. Bogun, U. Göl, M. Schmitt, Plast. Rubber Compos. **30** (9) (2001) 401.
 [26] B. Chen, L. Zhu, F. Zhang, Y. Qiu, Academic Press: Boston (2017) 821.
 [27] J. L. White, E. K. Kim, Hanser Publications (2010).
 [28] E. Dannenberg, Rubber Chem. Technol. **59** (3) (1986) 512.
 [29] J. L. Leblanc, J. Appl. Polym. Sci. **78** (8) (2000) 1541.
 [30] G. R. Cotten, Rubber Chem. Technol. **48** (4) (1975) 548.
 [31] J. L. Leblanc, Prog. Polym. Sci. **27** (4) (2002) 627.
 [32] J. L. Leblanc, J. Appl. Polym. Sci. **66** (12) (1997) 2257.