
Flow Properties and Melt Distortion in Molten Rubber Compounds under Capillary Extrusion: Effects of Vulcanizing Systems and Fillers

Somjate Patcharaphun^{1,†}, Yanichsa Sukniyom¹, Watcharapong Chookaew², and Narongrit Sombatsompop

¹Department of Materials Engineering, ²Department of Mechanical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand, 10900

³Polymer Processing and Flow (P-PROF) Group, School of Energy Environ and Materials, King's Mongkut University of Technology Thonburi, Bangkok, Thailand, 10140

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SUMMARY

This work aimed to make use of a rate-controlled capillary rheometer for investigating the effects of vulcanizing system using various fillers on the apparent viscosity and extrudate swelling of natural rubber (NR) compounds. The results suggested that the rubber compounds exhibited a pseudoplastic non-Newtonian behavior. At any given shear rates, the viscosities of rubber compound utilizing conventional (CV) and efficient vulcanizing (EV) systems were lower than that of non-sulfur (NS) system. This was due to the occurrence of premature crosslinking at the skin layer and subsequently led to the wall slip of rubber compound during the flow in capillary die. The irregular surface and the onset of smooth surface of rubber extrudate were evidently seen, especially for CV and EV systems. This could be associated with the amount of required energy to obtain the steady state flow in the die. The results also suggested that the swelling ratio of rubber extrudate ranged from 1.2 to 2.2 and the effect of filler type was more pronounced at high shear rates above 400 s⁻¹. In the case of silica filler (SiO₂) system, the severe irregularity of rubber extrudate was observed. The lower shear rate employed to obtain the smooth surface for rubber extrudate containing 30 phr of SiO₂ was possibly caused by high amount of PEG acting as an external lubricant which promoted the uniform slippage during the flow in capillary die.

Keywords: Rheological properties, Natural rubber, Melt distortion, Vulcanizing system, Filler type and content

†Corresponding author, e-mail: fengsjpc@ku.ac.th

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INTRODUCTION

Rheological property of molten polymers is vital for manufacturing process design. For example, a design of screw and die, and the optimized process conditions affect directly to a quality of products. Typically, the properties of polymers are a combination between the properties of elastic solid and viscous fluid. During processing, the viscous nature is dominant. The elastic, however, is still present. This results in many phenomena, such as, extrudate swell, sharkskin, and melt fracture. Extrudate swell and sharkskin are usually considered to be main factors to determine quality of the extrudates, for example, the dimension and surface of final products. Melt fracture is known as a parameter not only determine the product quality but also importantly control the production rate. Extrudate swell is defined as a cross-sectional area of extrudate is greater than that of the die. The general explanation for swelling is related to the recoverable elastic deformation developed during flow through the die. As the molecules flow through a die, they are subjected to a shear field. They deform elastically and at the die exit the elastic deformation is removed, the molecules recovering in part to their original shape.

Swelling is an important phenomenon in certain polymer processes, particularly pipes and profile extrusions, in which either inadequate swell or over-swelling can cause processing problems and defects in the finished product. Swelling behavior of rubber compounds is influenced by temperature, shear rate, filler, and molar mass [1-3]. It was found that the greater the shear rate, the higher the swelling ratio. Increasing the mastication time (corresponding to the decrease of molar mass) resulted in the decrease of extrudate swell. With respect to the effect of filler, it has been widely known that the reinforcing fillers in rubber compound, such as carbon black and silica (SiO_2), lowers the swell of rubber extrudate as compared to that of non-reinforcing filler i.e. calcium carbonate (CaCO_3) [4]. The elastic phenomena can be alleviated by processing temperature, shear rates, die designs, and also additives [5-7]. The surface irregularity of extrudate or surface melt fracture is known as sharkskin which is characterized by a series of ridges perpendicular to the flow direction, producing a rough surface varying from a loss of gloss to the texture of sharkskin. This phenomenon has also been identified by several studies [8, 11], particularly observed in polymer composite systems [12-14]. Previous work by Intawong et al. [15], a rotating-capillary die system was developed and employed to investigate the rheological properties of natural rubber (NR) compound in terms of apparent viscosity, extrudate swell ratio, and flow visualization in barrel. The rotating-capillary die system was coupled with rate-controlled capillary rheometer. In addition, recent work by Kaiyaded et al. [16] the die-rotating system was coupled with a single screw extruder in order to moderate entrance pressure drop and sharkskin for

molten polypropylene (PP) and wood / polypropylene (WPP) composites. The results obtained from this investigation practically implied that the rotating die system could be used to minimize the fracture level of sharkskin for high filler loading WPP composites.

Melt fracture or distortion can appear as an irregularly shaped extrudates such as spiraling, uniform ripple, bambooning, and random fracture [6, 7]. Melt fracture has been investigated for a number of polymers [17-19], but based on the recent literatures, it has been found that most published works were focused on thermoplastics and their composites, especially polyolefins [18, 20]. Therefore, this work aimed to investigate the melt distortion and rheological properties of natural rubber compound using a rate-controlled capillary rheometer. The influences of shear rate and vulcanizing system with a wide range of fillers were of our interests. Several interesting correlations between the critical conditions for the onset of instability and smooth surface were approached and discussed.

EXPERIMENTAL

Raw Materials

Natural rubber (NR, STR5L) was supplied by Thai Rubber Latex Co., Ltd. (Bangkok, Thailand). The compound formulations, which include all the chemicals and their suppliers, for making natural rubber compounds are shown in **Table 1**.

Fillers

In this work, the non-reinforcing filler used was calcium carbonate (CaCO_3) and reinforcing fillers were silica (SiO_2) and carbon black (CB). The filler contents were varied from 0 to 30 phr. The specifications for all fillers are detailed below;

- Calcium carbonate (CaCO_3): The precipitated grade was supplied by Thai Poly Chemicals (Samutsakhon, Thailand) with an average particle size of 4-25 μm .
- Precipitated silica (PSi): The commercial grade silica (TOKUSIL233) was supplied by Tokuyama Siam Silica Co., Ltd. (Bangkok, Thailand). It had a pH of 6.5-7.5, bulk density 0.22-0.28 g/cm^3 and an average particle size of 10-40 nm.

Table 1. Compound formulations in part per hundred of rubber (phr)

Ingredient	Supplier	Content (phr)					
		NS	CV	EV	Carbon Black	SiO ₂	CaCO ₃
NR (STR5L)	Thai Rubber Latex Co., Ltd	100	100	100	100	100	100
ZnO	Microseen Co. Ltd	4	4	4	4	4	4
Stearic acid	Thai Poly Chemicals Co. Ltd	2	2	2	2	2	2
CB (N330)	Thai Poly Chemicals Co. Ltd	-	-	-	0/15/30	-	-
SiO ₂ (PSi)	Tokuyama Siam Silica Co. Ltd	-	-	-	-	0/15/30	-
CaCO ₃	Thai Poly Chemicals Co. Ltd	-	-	-	-	-	0/15/30
Sulfur	Microseen Co. Ltd.	-	2.4	0.8	2.4	2.4	2.4
PEG (4000)	Union Chemical 1986 Co. Ltd	-	-	-	-	0/0.9/1.8	-
CBS	Sunny World Co. Ltd	0.8	0.8	2.4	0.8	0.8	0.8
Aromatic Oil	Global Chemie Trading Co. Ltd	-	-	-	0/1/2	-	-

- Carbon black (CB): The carbon black N330 rubber grade was supplied by Thai Poly Chemicals (Samutsakhon, Thailand) with an average particle size of 26-30 nm.

Mixing and Compounding

Natural rubber (STR5L) was masticated with an internal mixer (KNEADER Machinery, KD10-30) at a temperature of 70°C for 3 min. The fillers and commercial grade of stearic acid, zinc oxide (ZnO), aromatic oil, and polyethylene glycol (PEG) were mixed into the masticated rubber using the two-roll mill (Kodair Seisakusho, R11-3FF) for 10 min in order to attain a homogeneous mixture of the rubber compound (aromatic oil and PEG were only employed in the case of CB and SiO₂ loadings, respectively). The rubber was then compounded with the amount of sulfur and accelerator (n-Cyclohexyl Benzothiazole-2-Sulphenamide, CBS) for about 3 min in accordance with the Non-Sulfur, Conventional and Efficient Vulcanizing systems (NS, CV and EV). Each batch was rolled and pressed between layers of polystyrene film

to produce a sheet of approximately 5 mm thickness. A hole punch (10 mm diameter) was used to cut the rubber sheet into the shape of a circular disc.

Instruments and Methodology

The Mooney viscometer (TECHPRO-visTECH model 123103) was utilized to determine the scorch time (t_{scorch}) and viscosity of the rubber compounds. The test temperature was set at 100°C and a large rotor was used, in accordance with standard test method ASTM D1646. The 90% cure time (t_{90}) of rubber compounds was analyzed by using a Moving Die Rheometer, MDR (TECHPRO-rheoTECH model 121105) in compliance with ASTM D2240. The rheological test was performed with a rate-controlled capillary rheometer in compliance with ASTM D5099-08 (Standard Test Methods for Rubber – Measurement of Processing Properties Using Capillary Rheometry). The length-to-diameter (L/D) ratio of a circular die was 15/1.5 mm/mm. The experimental procedures are commenced by heating the barrel to required temperature (the test temperature was set at 90°C). The rubber compound (circular disc shape) was loaded into the barrel and allowed to heat up to the barrel temperature for 20 min. The piston speeds were varied from 10.13 to 316.41 mm/min in order to generate the shear rate ($\dot{\gamma}$) from 40 to 1250 s⁻¹. A pressure sensor (Dynisco, Model PT460E-2CB-6, Franklin, MA) was located near the die entrance for the pressure drop (ΔP) measurement. The extrudate swelling ratio (B) of the NR compound was determined by calculating the ratio of the diameter of the extrudate to that of the die. The extrudate diameter based on the size of the extrudate diameter in the fully swollen state as shown in **Figure 1a**. A successful validation of this method was performed by means of a high-speed camera [15, 16]. In this work, a video-camera (SSC-DC398P with 752Hx582V pixel and 480TV lines) and a high resolution macro zoom lens (3x3 magnification) were utilized to visualize the extrudate leaving the die exit. The results were recorded in real time using a personal computer and the size of swollen extrudate was then measured by replaying the recorded flow. With this procedure, any error related to the cooling and gravity effect could be minimized. The details of experimental rig are schematically illustrated in **Figure 1b** (such as high speed data logger and operating control systems) can be found in previous work [15, 16]. It should be noted that the Bagley's and Rabinowitch corrections were not applied to the shear stress and shear rate data generated in this work, as these data were only used for the comparative purposes among processing parameters used. The results were reported in terms of apparent viscosity and swelling ratio given by the following equations, respectively:

$$\text{Apparent wall shear stress} = \tau_{\text{app}} = \frac{R(\Delta P)}{2L} \quad (1)$$

$$\text{Apparent wall shear rate} = \dot{\gamma}_{\text{app}} = \frac{4Q}{\pi R^3} \quad (2)$$

$$\text{Apparent viscosity} = \eta_{\text{app}} = \frac{\tau}{\dot{\gamma}} \quad (3)$$

$$\text{Swelling ratio} = B = \frac{D_{\text{Extrudate}}}{D_{\text{Die}}} \quad (4)$$

where R is the radius of the die, ΔP is the pressure drop along the die, L is the length of the die, Q is the volumetric flow rate along the capillary die, $D_{\text{Extrudate}}$ is the diameter of extrudate and D_{Die} is the diameter of capillary die, respectively.

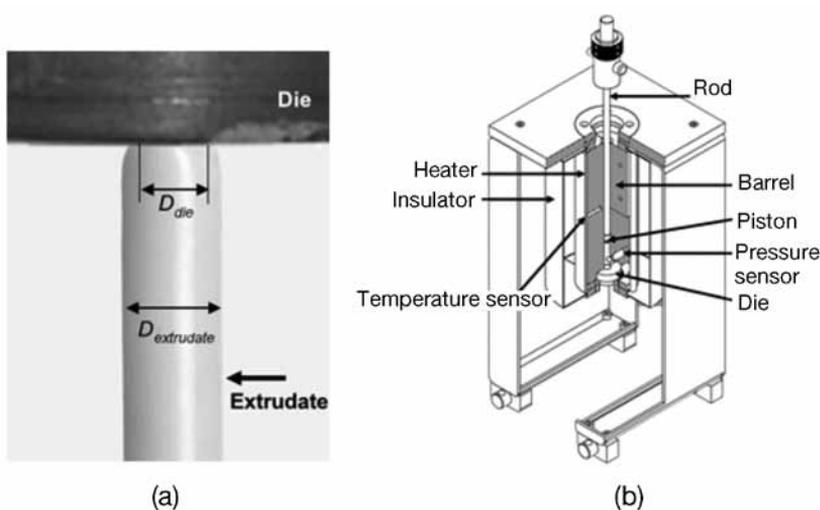


Figure 1. (a) Swelling of the rubber extrudate emerging from a capillary die and (b) schematic illustration of rate-controlled capillary rheometer used in this study

RESULTS AND DISCUSSIONS

Table 2 shows the Mooney viscosity, t_{scorch} , and t_{90} of rubber compounds for different curing systems. Generally, it can be seen that the effect of curing system had no significant effect on the changes in Mooney viscosity and scorch time. It was evident that the t_{90} of rubber compound vulcanized by EV

was shorter than that of CV system. This was attributed to the greater amount of accelerators (with respect to sulfur), which resulted in a more effective consumption of the sulfur as to attain the required degree of cure [21].

Table 2. Mooney viscosity, scorch and cure times of rubber compounds using various curing systems

Compound formulations	NS	EV	CV
Mooney viscosity	25.91	26.69	27.86
T_{scorch} (min)	-	7.63	7.90
T_{90} (min)	-	10.96	12.62

The effects of filler type and content on the Mooney viscosity, t_{scorch} , and t_{90} of rubber compounds using different curing systems are shown in **Table 3**. In the case of CaCO_3 , it can be noted that the adding CaCO_3 did not significantly affect the rheological nature of the NR compounds, whereas the addition of SiO_2 and CB caused a sharply increase in the Mooney viscosity, especially for SiO_2 at loading of 30 phr. This was due to the number of hydroxyl groups on the surface of SiO_2 , which resulted in strong filler-filler interactions and thus it can aggregate more tightly as compared to CB. This observation was also reported in previous works [22]. It can be seen that the t_{scorch} of all compounds, tended to decrease with the addition of fillers and the reduction of t_{scorch} was more pronounced in the rubber compounds with CB and SiO_2 loadings in comparison to CaCO_3 . This was due to the fact that the smaller particle size or the larger surface area of SiO_2 and CB, the greater the rubber-filler interactions [23-25] and impose extra resistance to flow as a higher restriction to the motion of rubber molecules. The decreases of t_{90} for CaCO_3 and CB systems were thought to be caused by the alkalinity of CaCO_3 as well as the surface treatment of commercial grade CaCO_3 with zinc oxide, which acts as an activator for the vulcanization reaction [21]. Furthermore, the reactive organic groups (such as phenolic, hydroxyl, quinone, carboxyl) and reactive hydrogen bonds, as well as free radicals on the surface of CB, can chemically react with the rubber molecules [21, 23], which has the potential to promote the kinetics of the crosslinking reaction. This phenomenon was also indicated by many studies [26, 27]. On the other hand, the rubber compound filled with SiO_2 had an increase in t_{90} which was probably associated with the adsorption of curatives (such as stearic acid and zinc oxide) by the silanol groups on the SiO_2 surface, although the application of PEG reduces the adsorption of accelerator or activator on the silica surface, however the amount of PEG used in this experiment may not be sufficient at such high SiO_2 loadings.

The effect of vulcanizing system on the apparent viscosity of rubber compounds at the test temperature of 90°C is shown in **Figure 2**. Generally, it was evident

that all the rubber compounds exhibited a pseudoplastic non-Newtonian behavior, in that the apparent viscosity dramatically decreased with shear rates from 40 to 500 s⁻¹. Further increasing shear rate from 500 to 1250 s⁻¹ did not cause any significant changes in the viscosity of rubber compound. Considering the changes in apparent viscosity of rubber compound using different curing systems, one would expect to obtain the similar (or virtually the same) viscosity, since the test temperature of 90°C was much lower than the curing temperature of the rubber compound. However, from the results obtained in this work, the viscosity at any given shear rates of rubber compound using EV system was lowest as compared to the highest of NS system. This was probably attributed to the shear heating during the flow in the capillary die, especially at the die wall where the shearing stresses were relatively high. This phenomenon could lead to an occurrence of premature crosslinking at the skin layer of rubber extrudate. The premature crosslinking was expected to be high for the EV system since the vulcanization reaction accelerated. The premature crosslinking can then result in a wall slip phenomenon of rubber extrudate as schematically illustrated in **Figure 3**. When comparing the apparent viscosities of rubber compound using CV and EV systems, it was observed that the viscosity of rubber compound using EV system was lower than that of CV system. This was due to the higher crosslinking

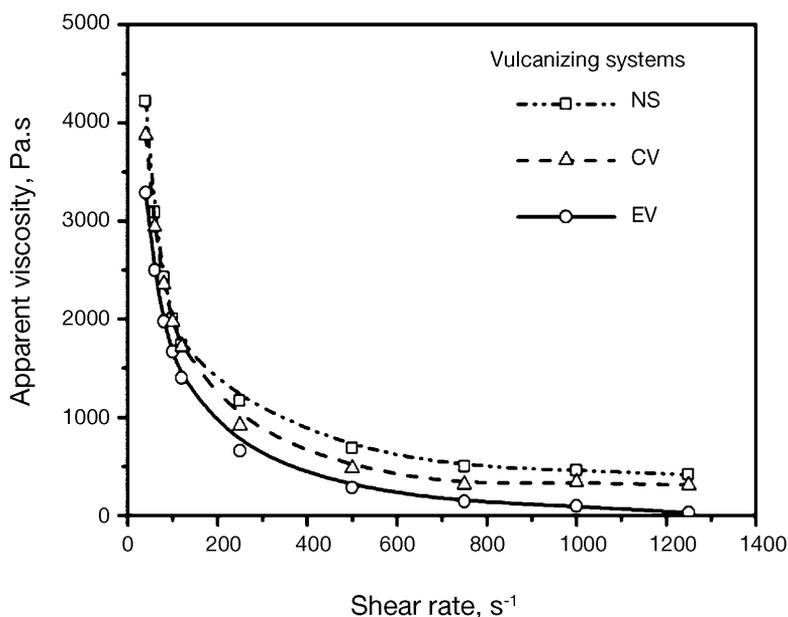


Figure 2. Plots of apparent viscosity versus shear rate for rubber compound vulcanized by various curing systems using the capillary die with L/D of 15/1.5

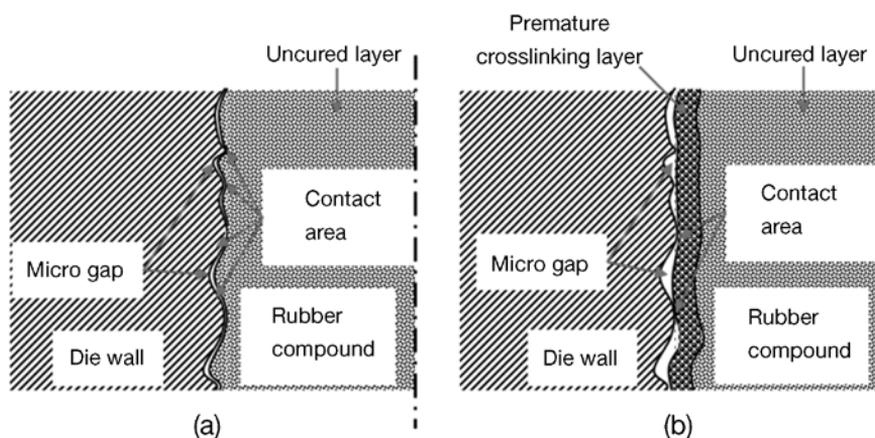


Figure 3. Schematic illustrations of the wall slip phenomena occurring during the flow in capillary die; (a) NS system and (b) CV and EV curing systems

occurred at the skin layer for the EV system, as a result of a thicker cured layer in comparison to the CV system, and thus, increased the wall slippage level of rubber extrudate during the flow in capillary die. It should be noted that the premature crosslinking effect was the key explanation for viscosity differences in **Figure 2**, since the pressure drop values used for the shear stress and viscosity data were obtained using a pressure transducer located near the die entrance. Therefore, any slippages of the extrudate due to the premature crosslinking as described in **Figure 3** could be detected.

Figure 4 depicts the effect of curing system on the appearance of rubber extrudate. At very low shear rate (40 s^{-1}) for all the cases, slight irregularities were observed on the surface of rubber extrudate. Further increasing the shear rate from 100 to 1250 s^{-1} , perfectly smooth surface of extrudate was observed in the rubber compounding without the presence of elemental sulfur (NS). This was a result of the shear thinning behavior of rubber compound in that the melt viscosity decreased with increasing shear rate due to the disentanglement and the enhanced mobility of polymer molecules. However, this was not the case for CV and EV systems where a more irregular surface or melt instability was observed with increasing shear rate. One of the reasons for the elastic turbulence at high shear rate could be attributed to the non-uniform slippage of the melt at the die wall [6-7]. Furthermore, the onset of smooth surface of rubber extrudate using CV and EV systems were clearly evident at the shear rate of 1000 and 1250 s^{-1} , respectively. The explanation for this may be associated with the type of sulfur linkage occurred at the skin layer of rubber extrudate. In CV system, where a high level of sulfur and a

correspondingly low level of accelerator, provided high amount of polysulfidic crosslinks (S-S linkages) which had a lower bond dissociation energy (230 kJ/mol) as compared to mono- and disulfidic crosslinks (C-S-C linkages) obtained by EV system (314 kJ/mol) [28]. Therefore, it can be expected that the amount of energy generated by increasing shear rate (1000 s^{-1}) for breaking the S-S bonds in order to obtain the steady-state flow in the die (by increasing the mobility of rubber molecules) were lower than that of C-S bonds (at shear rate of 1250 s^{-1}).

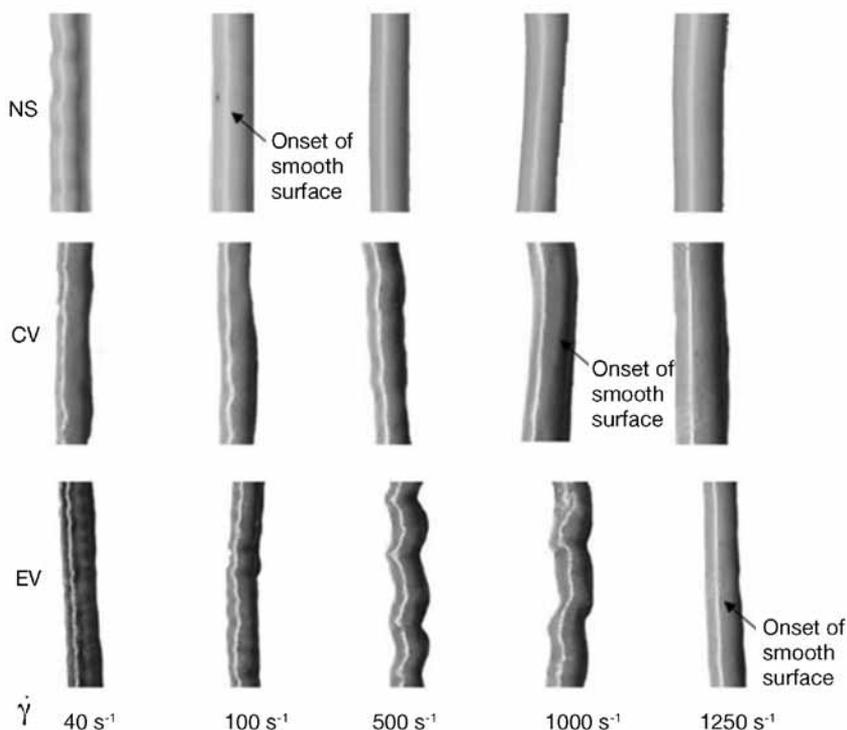


Figure 4. Direct observation of rubber extrudates using NS, CV, and EV systems at various shear rates

In this work, the different types of filler were loaded into rubber compound using CV system at the concentration ranging from 0 to 30 phr. Generally, the viscosity of rubber compound increased with the increase of filler concentration, this being more pronounced in the case of silica [22]. **Figure 5** shows the plots of swelling ratio versus the apparent shear rate at the test temperature of 90°C for the rubber compound containing CaCO_3 and CB contents. It can be seen that

the swelling ratio of the rubber, regardless of vulcanizing system, ranged from 1.2 to 2.2. The higher the filler loading the lower the swelling as expected. In the case of SiO_2 loadings, the irregularity of rubber extrudate was found during the experiment. Thus, the swelling ratio of rubber compounding with SiO_2 was

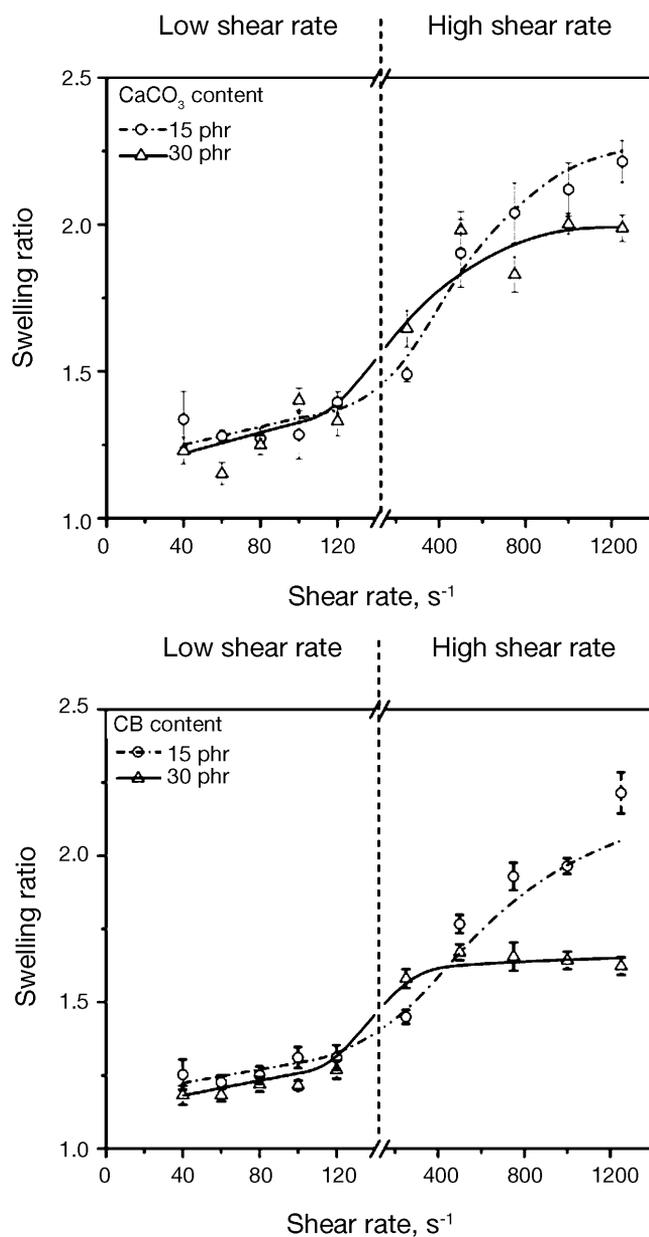


Figure 5. Swelling ratio versus apparent shear rate of rubber compound filled with different filler type and content

been proposed that the influence of the polymer/filler interface on extrudate swell was significant in rubber compounding with CB, due to the presence of a rubber-CB transient network which can easily be disrupted by a certain amount of stress. This network was expected to decrease the extrudate swell because of the increase in energy dissipation [29].

Figure 6 shows the extrudate morphologies of rubber compound containing 15 and 30 phr of silica filler at different shear rates. At the initial stage (40 s^{-1}), the surface irregularity of rubber extrudate was observed and this may be a result of strong agglomeration of silica filler [22, 23]. The onset of smooth surface in rubber extrudate containing 15 phr of silica was found at the higher shear rate (500 s^{-1}) as compared to those obtained at the lower shear rate (100 s^{-1}) for rubber compound filled with 30 phr of silica. This is probably caused by concurrent effects from (i) high amount of PEG, comparative to the diluted amount of rubber part for the compound with 30 phr silica which can be act as lubricant [30], and (ii) the shear heating effect. These two effects promoted the uniform slippage during the flow in capillary die and yielded the smooth extrudates. The gloss extrudate distortion at shear rates ($1,000$ or $1,250 \text{ s}^{-1}$) were seen as a result of the excess shearing stresses above the critical shearing stress values as one would expect.

CONCLUSIONS

In this work, the influences of vulcanizing systems and fillers on the rheological properties and melt fracture of natural rubber compounds were investigated using a rate-controlled capillary rheometer. The results suggested that the rubber compounds exhibited a pseudoplastic non-Newtonian behavior in that the apparent viscosity dramatically decreased with the increase of shear rate. It was evident that rubber compound using EV system showed the lowest apparent viscosity as compared to those obtained by CV and NS systems, respectively. This was due to the occurrence of premature crosslinking at the skin layer and subsequently resulted in the wall slip phenomenon. The irregular surface and the onset of smooth surface for rubber extrudate using CV and EV systems were clearly evident. The swelling ratio of the rubber, regardless of vulcanizing system, ranged from 1.2 to 2.2, and the effect of filler type was more pronounced at high shear rates above 400 s^{-1} . The results also suggested that the swelling ratio of rubber extrudate loaded with CB was lower than that with CaCO_3 , especially at the high shear rates. In the case of SiO_2 system, the irregularity of rubber extrudate was found for all loadings used, and then followed by the smooth surface for rubber extrudate due to shear heating effect and high PEG loading acting as external lubricant to promote the uniform slippage during the flow.

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