EFFECT OF ISOMER COMPOSITION OF HYDROXYL TERMINATED POLYBUTADIENE (HTPB) IN LOW SHEAR FLOW BEHAVIOR

Afni Restasari[1], Luthfia Hajar Abdillah, Retno Ardianingsih, Rika Suwana Budi
National Institute of Aeronautics and Space, Indonesia
[1]e-mail: afni.restasari@lapan.go.id

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ABSTRACT

HTPB is an ultimate component of matrix builder for high-filled composite materials. Flow behavior of HTPB in low shear is crucial in casting the composite. Considering the characteristics of hydrocarbon, this work aims to investigate the effect of microstructures composition of HTPB on its flow behavior. In this work, HTPBs with different compositions of 1,4-*cis*, 1,2-*vinyl* and 1,4-*trans* microstructures were used. Fourier-Transform Infra-Red spectroscopy (FT-IR) was used to determine the composition. It was calculated as a ratio of peak area at710, 910 and 970 cm^{-1} for 1,4-*cis*, 1,2-*vinyl*, 1,4-*trans* isomers respectively. Viscosity was measured using a rotational viscometer at various low shear rates. It is found that HTPB with high 1,2-*vinyl*/1,4-*trans* isomers shows shear thickening behaviour, distinguished significantly from Newtonian flow of the others. It is suggested that mechanism of shear thickening involves a certain configuration of 1,2-*vinyl* and 1,4-*trans* isomers that builds different degrees of flow resistance from one to other shear layers. The configuration and flow resistance change among layers as shear rate increases.

Keywords: *Microstructures, Viscosity, Hydroxyl Terminated Polybutadiene, Flow behaviour, Shear thickening.*

1 Introduction

Composite solid propellant is a kind of rocket fuel. It is made of solid and liquid content. Solid contents are energetic particles, such as Ammonium perchlorate and aluminum. While liquid content is a polymer. The polymer has responsibility in processing propellant slurry as well as in building a strong network to adsorb solid contents. It gives impact on mechanical and physical properties of solid propellant (Hartaya, *et al.,* 2017).

To improve specific impulse of propellant, liquid content that has high capability for loading solid is preferable. For this reason, elastomer Hydroxyl Terminated Polybutadiene (HTPB)-based polyurethane is commonly used as propellant binder (Dey, *et al.*, 2015).

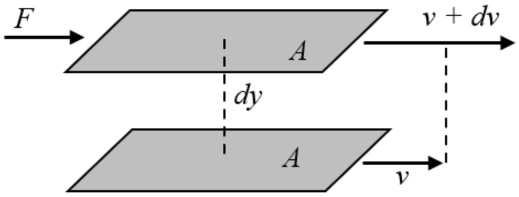


Figure 1-1: Illustration of viscosity of Newtonian fluid (Source: Onogi, 1982).

As a high-filled composite material, the processability of propellant becomes a significant issue. Propellant process involves mixing, casting and curing. An optimum process results in well-dispersed particles in propellant. It is important to prevent formation of void, pores, crazes and cracks. It is because the damage has a potential to induce failures in a motor rocket (Remakanthan, *et al.,* 2015). Parameters of this processability include viscosity, pot-life and flow behavior (Dombe, *et al.,* 2008), , (Tomasz, *et al.,* 2018). However, investigation about the origin of the flow behavior is still limited.

Flow behavior is concerned about viscosity. Viscosity is a resistance of fluid to flow. It is illustrated in Figure 1-1 where two liquid surfaces move in parallel. The medium is a flowing viscous liquid. Surfaces move with force F, area A and distance dy. An ideal viscous liquid is liquid that flows when any force, other than hydrostatic pressure, acts. The deformation of the liquid does not recover even if the force is removed. Assuming that the flow velocity is large, $dv/dy = D$ is the velocity gradient and $F/A = \sigma$ is shear stress. D is equal to shear rate, γ. For Newtonian fluid, viscosity, η, is governed by using Eq. (1-1) (Onogi, 1982).

$$\sigma/\mathrm{D} = \sigma/\gamma = \eta \qquad (1\text{-}1)$$

$$\eta = \mathrm{k}.\ \gamma^{n-1} \qquad (1\text{-}2)$$

For Newtonian fluid, viscosity is independent of shear rate. While, for shear thinning or quasi-viscous flow, viscosity decreases with increasing shear rate. For shear thickening, structural viscosity increases with increasing shear rate. Both types of fluid follow Power Law model in Eq. (1-2) where k is consistency index and n is flow behavior index. Shear thinning is indicated by $n > 1$. Shear thickening is indicated by $n < 1$ (Onogi, 1982).

Propellant slurry is reported to have flow behavior that depends on the kind of liquid content. Glycidyl azide polymer (GAP)-based propellant shows almost Newtonian flow (Manu, 2009). While HTPB-based propellant shows shear thinning (Abdillah, *et al.,* 2020), (Ardianingsih & Kumoro, 2019), (Restasari, *et al.,* 2018). It has been reported that the ideal value of n for HTPB-based propellant is 0.8 – 1 for vacuum top casting and 0.6 - 1 for pressure casting (Dombe, *et al.,* 2008). To obtain those values, controlling the flow index of HTPB is crucial. The control needs a sufficient understanding about the origin of HTPB flow behaviour

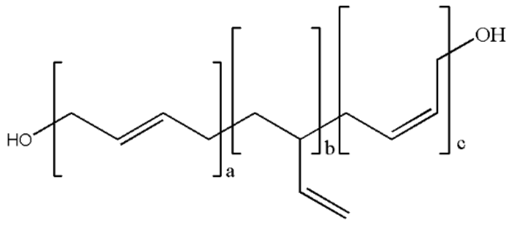
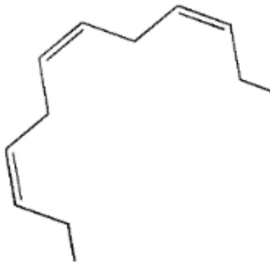


Figure 1-2: Microstructures of HTPB with 1,4-*trans* (a), 1,4-*cis* (b) and 1,2-*vinyl* (c) isomers (Source: Dey et al., 2015).



(a) Spring-like structure of 1,4-*cis* isomer

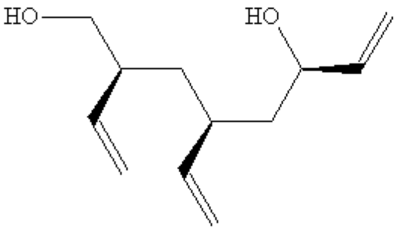
(b) Rod-like structure of 1,4-*trans* isomer

Figure 1-3:Assumption of 1,4-*cis* and 1,4-*trans* isomers of HTPB (Source: Dey, Sikder, & Athar, 2017).

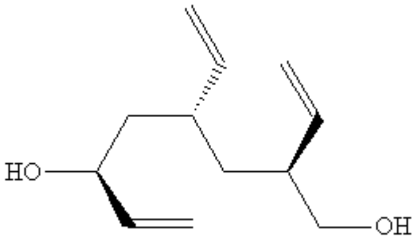
HTPB consists of hydroxyl groups and hydrocarbon chain. In HTPB-based polyurethane binder, hydroxyl groups of HTPB act as hard segment builder. While a long hydrocarbon chain is soft segment builder (Dey, *et al.,* 2015), (Rosita, 2016), (Wibowo, 2015).

Soft segment of an elastomer is reported to affect glass transition temperature (T_g) that strongly affects mechanical properties (Kida, *et al.,* 2020). For HTPB, it consists of 1,4-*cis*, 1,4-*trans* and 1,2-*vinyl* isomers described in Figure 1-2. It is reported that the percentage of 1,4-*cis* isomer affects the elasticity (Zhang, *et al.*, 2019), 1,4-*trans* isomer build the tensile strength and 1,2-*vinyl* isomer has role in governing viscosity of propellant. Effects of 1,4-*cis* and 1,4-*trans* isomers are assumed to be originated from its spring-like and rod-like shape respectively (Dey, *et al.*, 2015, 2017). It is described in Figure 1-3. The 1,2-*vinyl* isomer effect is from its anchor-like pendant structure. The structure has stereoregularity including atactic, isotactic and syndiotactic, described in Fig. 1-4 (Dey, *et al.*, 2015, 2017).

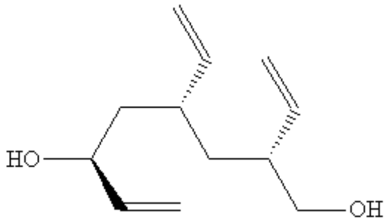
Viscosity is related to fluid resistance. It is correlated not only with the structure of isomers but also friction of isomers. The friction is measured as monomeric friction coefficient, ξ_0. With assumption that isomers in HTPB is similar with polybutadiene, it is reported that value of ξ_0 for 1,4-*cis* and 1,4-*trans* isomers are same. It is log ξ_0 = -6.75 dynes-sec/cm at 25 ℃ and different from 1,2-*vinyl* isomer. The value is ξ_0 = -4.11 dynes-sec/cm (Ferry, 1980). With the difference value of ξ_0, viscosity of HTPB can be assumed as viscosity of polymer mixture and approached by Rouse theory.



(a) Isotactic



(b) Syndiotactic



(c) Atactic

Figure 1-4: Stereoregularity of 1,2-*vinyl* isomer of HTPB (Source: Dey, *et al.*, 2015).

Based on Rouse theory, viscosity of polymer mixture is a sum of viscosity of the components multiplied by its free volume and friction factor. Friction factor is friction coefficient of mixture divided by friction coefficient of component. The approach is strengthening by difference value of free volume, ν, which is space in a solid or a liquid that is not occupied by polymer molecules. Value of log ν of polybutadiene at 25 ℃ and *G'* = 108 dyne/cm^2 for 1,4-*cis* and 1,4-*trans* isomers are same, 6.1. While for 1,2-*vinyl* isomer, it is 3.9 (Ferry, 1980).

With an approach towards Rouse theory, it is hypothesized that composition of 1,4-*cis*, 1,4-*trans* and 1,2-*vinyl* isomers has an important role in governing flow behaviour of HTPB. Therefore, this research aims to investigate the effect of microstructures composition of HTPB on flow behavior of HTPB.

2 Methodology

2.1. Sample Preparation

In this study, three types of HTPBs were used, named HTPB A, B and C. The specifications include average molecular weight of 2300 – 3500 g/mole, hydroxyl value of 0.81 – 1.0 mmole/g, polydispersity of 1 - 2.5 and hydroxyl number of 47.1 mm KOH/g. HTPB A and B were produced by Dalian Chlorate, Ltd, while HTPB C was produced by Hanwha. HTPB A samples was taken from a fresh opened package, while HTPB B had been stored for 2 years.

2.2. Experimental

To investigate flow behavior, viscosity of each HTPB was measured accurately at room temperature using Brookfield Viscometer with rotational spindle. The rotational speed of 0.17, 0.2 and 0.33 rps were applied to represent low shear regions. Low shear region was chosen to represent shear rate region of mixing and casting that is conducted in range of 0.1 – 10 rps (Green, 2004). Flow index that represents flow behavior was determined by fitting graph of η *vs* γ to Eq. (1-2). While zero shear viscosity or ZSV (η_0) that represents structure of fluid was determined by fitting graph of log η *vs* log (γ+1) to Eq. (2-1) (Goh & Wan Nik, 2018).

$$\log\eta \;=\; n\,log\,(\gamma+1) \;+\; log\,\eta 0 \qquad (2\text{-}1)$$

In order to identify microstructure contents, each HTPB was carefully subjected to Fourier-Transform Infrared Spectroscopy (FT-IR) (Shimadzu IR PRESTIGE-21) 3 times. The wavelength range covered 650 – 1010 cm^{-1}. The spectra of peak of 710, 910 and 970 cm^{-1} were defined accurately for 1,4-*cis*, 1,2-*vinyl* and 1,4-*trans* isomers, respectively. The compositions were determined as the ratio of peak area (Wibowo, *et al.*, 2019).

3 Result and Analysis

Figure 3-1 shows the plotting of viscosity of HTPB A, B and C in function of shear rate. It can be stated clearly that the behaviour of HTPB A is extremely different from HTPB B and C. HTPB A has a strong shear dependent. Its viscosity is 3 times increased in increasing shear rate from 0,17 - 0.3 rps. While, the flow of HTPB B and C are almost independent of shear. To measure the strength of shear dependence, determined flow indexes are presented in Table 3-1. In addition, Figure 3-1 also shows different viscosity at starting point of 0.17 rps. It indicates different zero shear viscosity that is analysed in Figure 3-2 and Table 3-2.

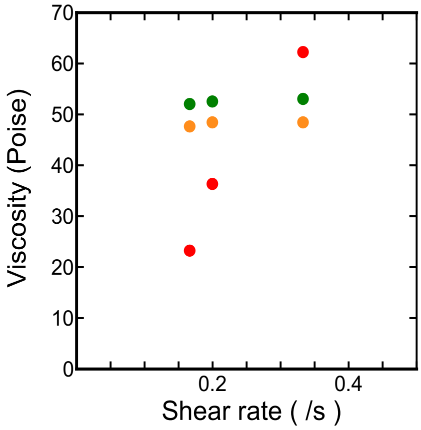


Figure 3-1: Viscosity (η) of HTPB A (red circle), B (green circle) and C (orange triangle) in function of shear rate (γ).

According to Table 3-1, the shear dependence of HTPB A is confirmed to be a shear thickening behavior with flow index of 2.343. This shear thickening is reported as the property of shock absorber polymer (Malvern Instruments Worldwide, 2016). The property is identical with HTPB. The behavior is also reported for paint, sand-rich material, kernel oil and coconut oil (Adewale, *et al.*, 2017), (Green, 2004), (Jeong, 2019). Those liquids have hydrocarbon chains similar with HTPB. HTPB B and C are confirmed to have almost Newtonian behavior with flow index of 1.0255 and 1.0188, respectively. An almost Newtonian HTPB has been also reported with flow index of 1.0474 (Restasari, *et al.*, 2018).

Table 3-1: Flow index of HTPB

No	HTPB	Flow index	R^2
1	A	2.343	0.9549
2	B	1.0255	0.9289
3	C	1.0188	0.4947

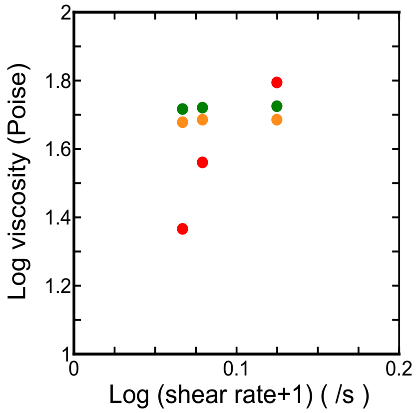


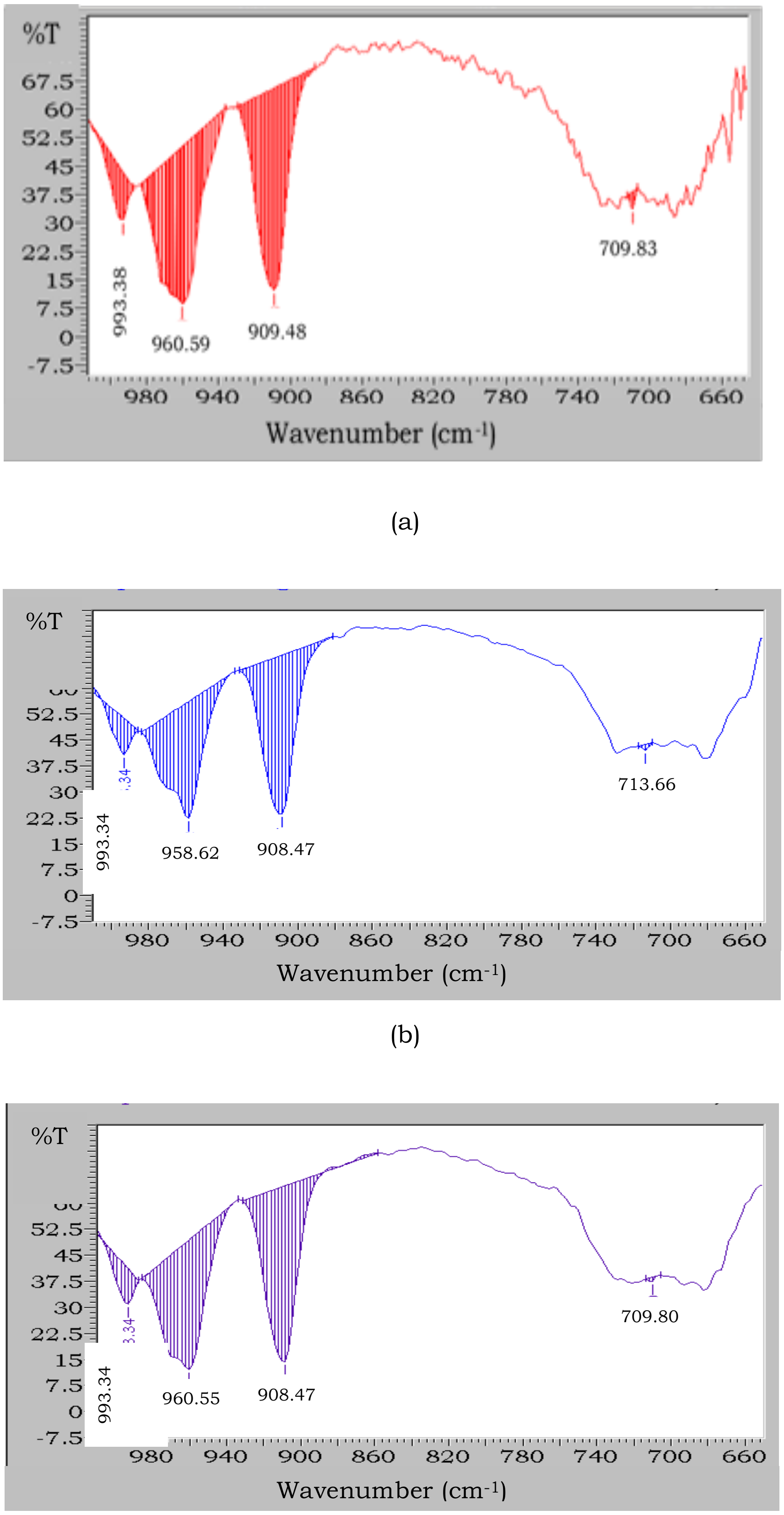
Figure 3-2: Logarithmic function of generalized viscosity model of HTPB A (red circle), B (green circle) and C (orange triangle).

Table 3-2: Zero shear viscosity of HTPB

No	HTPB	Zero shear viscosity (Poise)	R^2
1	A	9.16	0.9294
2	B	51.12	0.8981
3	C	47.23	0.4398

To analyze zero shear viscosity (ZSV), generalized viscosity model (Eq. (2-1)) is used. The plots are described in Figure 3-2 and determined values of ZSV are presented in Table 3-2. It shows various values of ZSV. The lowest is possessed by HTPB A while the highest is possessed by HTPB B. As ZSV has a positive correlation with molecular weight of polymer (Ferry, 1980), it indicates that the lowest average molecular weight is possessed by HTPB A and the highest average molecular weight is possessed by HTPB B. Considering the origin of the samples, storage period is reasonable for the difference. HTPB is reported to have an increase in molecular weight during storage (Wibowo, *et al.*, 2020).

Results of FTIR spectra are shown in Figure 3-3. For all kinds of HTPB, bending wagging vibration of the CH groups of 1,4-*cis* isomer is shown by a small peak at 710 cm^{-1}. Out-of-plane wagging vibrations of the CH_2 groups, located near 1,2-*vinyl* isomer, is shown by an obvious peak at 910 cm^{-1}. 1,2-*vinyl* isomer is also detected by peak at 990 cm^{-1}. The wavelengths are the same as previous reports (Li, *et al.,* 2019), (Wibowo, *et al.,* 2020). While, for out-of-plane wagging vibrations of CH groups near 1,4-*trans* isomer, the peak is shown broad and clear at 960 cm^{-1} and slightly different from the previous report. This difference is related to different chemical environments (Sone, 2016), (Wibowo, *et al.,* 2020).



(a)

(b)

(c)

Figure 3-3:FT-IR Spectra for microstructures of (a) HTPB A, (b) HTPB B and (c) HTPB C.

Table 3-3: Microstructures Compositions of HTPB

HTPB	**Microstructures Contents (%)**		
	1,4-*cis*	**1,2-*vinyl***	**1,4-*trans***
A	0.1299	0.5254	0.3447
B	0.2374	0.4119	0.3507
C	0.0529	0.4019	0.5453

Microstructures contents are shown in Table 3-3. It is shown that 1,2-*vinyl* isomer is more dominant in HTPB A. However, for B and C, 1,2-*vinyl* isomers are similar. In previous report, HTPB with high 1,2-*vinyl* isomer content has high viscosity. However, in this research, viscosity of HTPB is more sensitive towards molecular weight than 1,2-*vinyl* isomer content (Dey, *et al.,* 2017), (Ferry, 1980), (Restasari, *et al,* 2015), (Wibowo, *et al.,* 2020). Considering different storage period, it has been reported that aged HTPB has less 1,2-*vinyl* isomer content (Akbaş, *et al.*, 1994).

Regarding flow behavior, in Table 3-1, HTPB B and C have similar *n*. While in Figure 3-4, 1,2-*vinyl*/1,4-*trans* isomers of HTPB B and C is similar. While, *n* and 1,2-*vinyl*/1,4-*trans* isomers of HTPB A is the highest of all. Therefore, it is suggested that flow behavior comes from 1,2-*vinyl*/1,4-*trans* isomers. It is supported by different values of coefficient friction and free volume between 1,2-*vinyl* and 1,4-*trans* isomers that allow different behavior for different composition of 1,2-*vinyl*/1,4-*trans* isomers (Ferry, 1980).

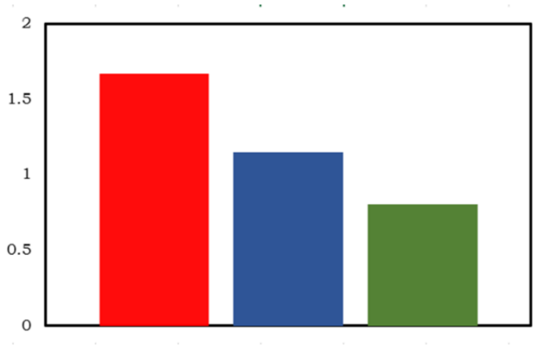


Figure 3-4: Ratio of 1,2-*vinyl*/1,4-*trans* isomers of HTPB A (red), B (blue), C (green).

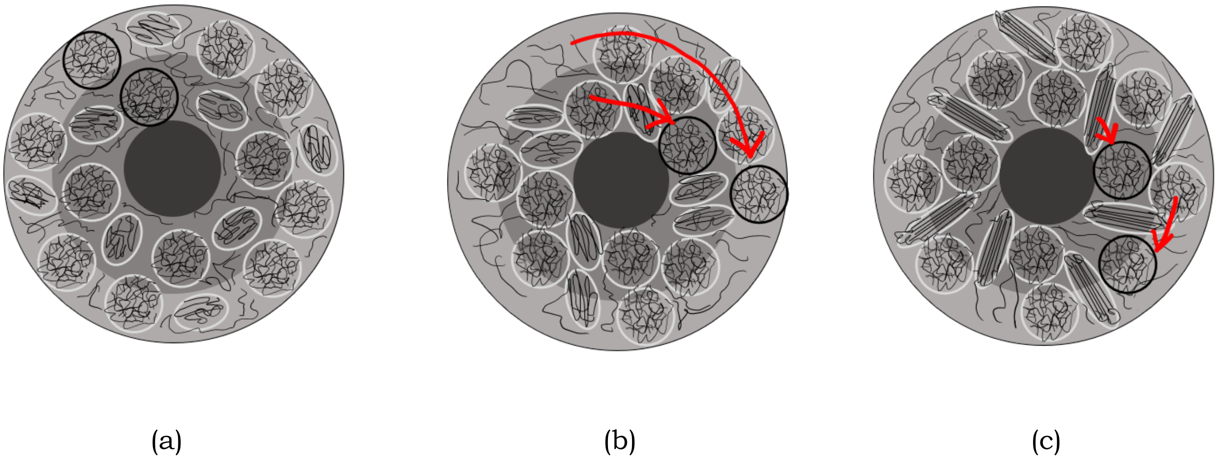

(a)
(b)
(c)

Figure 3-5. Illustration of Group A (1,2-*vinyl*-rich chain groups), sphere, and Group B (1,4-*trans*-rich chain groups), ellipsoid shape, in zero shear (a), under low shear rate (b) and high shear rate (c) of rotational shear.

In order to explain correlation between microstructures and flow behavior, illustration about motion of HTPB chain during rotational shear in viscosity measurement is given in Figure 3-5. It is shown that 1,2-*vinyl*-rich chain groups (Group A) and 1,4-*trans*-rich chain groups (Group B) flow under rotational shear with increasing shear rate. A wall slip is suggested to be occurred and divides area into 2 regions as also reported by Jeong *et al* (Jeong, 2019). Two regions are dark grey (Area 1) and light grey (Area 2). Area 1 is higher shear rate area, near spindle While Area 2 is the lower shear rate area, far from spindle.

In Figure 3-5, Group A and B are described by two different shapes. Group A is sphere because the pendant structure of 1,2-*vinyl* isomer is entangled and entraps to each other. It is assumed to build a big spherical knot. While Group B is ellipsoid. It describes relaxation of rod-like 1,4-*trans* chains. Moreover, it is assumed that Group A is heavier than Group B because Group A has higher friction coefficient. That friction allows Group A to hold more chain than Group B (Dey, *et al.*, 2017). In figure 3-5, two geometrical shapes, 1 of Group A and 1 of Group B, have bold lines as markers for motion.

As shear rate increases, shown in Fig. 3-5b, the geometrical shape of Group B can change. Shape of Group B changes to be more ellipsoid oriented towards flow direction. This orientation is affected by several factors. First, low friction and high free volume of 1,4-*trans* isomer make it easier to be oriented. Second, the structure of 1,4-*trans* isomer allows a neat arrangement of several 1,4-*trans* isomers combined together. Third, high stability of 1,4-*trans* isomer structure with heat of hydrogenation of 4 kJ/mole, less than 1,4-*cis* and 1,2-*vinyl* isomers, makes 1,4-*trans* tend to maintain its rod-like structure. Fourth, the stiffness of 1,4-*trans* isomer makes it difficult to be relaxed, once oriented. This stiffness is proven by the value of Young Modulus. At 4 K, Young modulus of 1,4-*trans*-polybutadiene is 9.4 x 10^{10} dyne/cm^2, while 1,4-*cis*-polybutadiene is 8.7 x 10^{10} dyne/cm^2. Fifth, difficulties to be relaxed is supported with low temperature conditions (Ferry, 1980), (Li & Matsuba, 2017), (Prine, 2018), (Sridhar & Vernerey, 2018).

Different from Group B, Group A is illustrated to maintain its shape. However, in increase of shear rate, centrifuge force increase and it draws Group A to the center of rotation. As a consequence, Group A moves from Area 2 to Area 1. Thus, Area 1 becomes more crowded and has more resistance to flow. Group A is also possible to block flow in Area 2, for example, when a sphere in Area 1 meets a sphere in Area 2.

Centrifuge force also draws an ellipsoid Group B. The motion governs a slope with a certain angle of which 1 edge is in Area1 and another edge is in Area 2. The edge that is in Area 2 inhibits flow in Area 2. However, there are still enough areas of free flow in Area 2 than Area 1.

As shear rate is more increased, described in Figure 3-5c, centrifuge force is stronger. This force induces three phenomena. First, Group A is stronger drawn to the center so that flow resistance in Area 1 is more governed. Second, because the tendency of Group A to be crowded in Area 1, it forces ellipsoid Group B to increase its slope and build a configuration that more inhibits flow in Area 2. Third, stronger centrifuge force strengthens all five factors mentioned that makes Group B more oriented. This high oriented structure increases the stiffness of Group B. Stiffness can be represented as Young Modulus. It is reported that effective Young Modulus increases in the onset of shear thickening (Berret, *et al.*, 2001).

Based on the above illustration, microstructures of HTPB affects shear thickening through 3-steps mechanism. First, 1,2-*vinyl* and 1,4-*trans* isomers govern a certain configuration. Second, as shear rate increases, the configuration governs different flow resistances from one flow layer to the others. Third, as shear rate increases, both configuration and flow resistance of each layer changes. Although there is a report that extended chains in increasing shear rate flow, such as 1,4-*trans* in this case, reduce the viscosity (Dunstan, 2019), the causes of flow behaviour of HTPB are dominated by configuration of microstructures. Regarding Newtonian flow of HTPB B and C that have more 1,4-*trans* isomer content, its lower ratio of 1,2-*vinyl*/1,4-*trans* isomers governs a compact configuration in each shear layer. As shear rate increases, the configuration hardly allows any changes in flow resistance for each layer and in configuration itself.

4 Conclusions

In this work, investigation about effect of microstructures composition of HTPBs on its flow behaviour at low shear is conducted. The viscosity of three kinds of HTPBs with different compositions at various shear rates were measured by using rotational viscometer. It is found that HTPB with high 1,2-*vinyl*/1,4-*trans* isomers ratio performs shear thickening. With consideration of its physical properties, qualitative models of flow of those microstructures under increasing shear rate are illustrated. It is strongly suggested that 1,2-*vinyl* and 1,4-*trans* isomers govern certain configuration that induces different degree of flow resistances among shear layers. These interlayer flow resistances are changes with increasing shear rate.

This work strengthens the importance in considering HTPB microstructures in order to obtain desired flow behavior whether of HTPB itself or its particle composite slurry. Moreover, about storage period, molecular weight and microstructures composition of HTPB are sensitive towards storage condition. Therefore, an improvement in storage condition of HTPB is advised.

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Contributorship Statements

AR is the main contributor. LHA and RA checked data analysis. RSB and AR discussed the qualitative model.

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