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MATHEMATICAL MODELING OF FILLED POLYPROPYLENE BY MODIFIED CROSS MODEL

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Abstract: The aim of this paper is to develop a mathematical model to investigate the rheological characteristics of short fibre reinforced thermoplastics. The rheological properties of this polypropylene were investigated using a capillary rheometer. Rheological characteristics of the composite components influence the development of resultant microstructures; this in turn affects mechanical characteristics of composites. The main rheological characteristics of polymer materials are viscosity and shear rate. They are the ones with fibre ratio changed. From the viscosity of unfilled material and 10% filled material, we can calculate viscosity for other filled materials. This mathematical formula is discussed in this paper.
Keywords: viscosity, reinforced thermoplastics, polypropylene, rheology, mathematical model

INTRODUCTION

Recently, fibre-reinforced thermoplastic composites have found wide application in structural and non-structural applications because of their excellent mechanical properties. Structural parts a prepared by injection moulding, where moulds are manufactured by machining – milling and grinding. For this application currently new polymer composites are developed [1]. But choice of processing conditions depends primarily on the rheological response of polymers. The incorporation of fillers into the thermoplastic melt viscosity increases. The rheological properties of sisal [3] pineapple and [2] the fibers have been studied, but not mathematically described. The mathematical behaviour of rheology of short fibre reinforced thermoplastics by Power-Law has been studied [5]. Viscosity of the fiber-reinforced thermoplastic fibers is affected by the weight ratio of a length of fiber greater at a lower shear rate than at a higher shear rate.

RHEOLOGY

Absolute viscosity provides a measure of a fluid's internal resistance to flow. However, viscosity of a the polymer melt depends on the concentration and the size (molecular weight) of dissolved polymer. By measuring the viscosity of the solution, we should be able to get an idea of the molecular weight [7]. Figure 1 shows a unit volume of the liquid moving speed of the shear deformation. Liquid viscosity is the ratio of shear stress to the resulting deformation speed (or equivalently, ratio of shear stress needed

to move solution to a fixed strain rate given strain rate). Shear strain [4]:

$$\gamma = \frac{du}{dy} \qquad (1)$$

where u is displacement in the x direction. The strain rate is therefore:

$$\dot{\gamma} = \frac{d}{dt} \cdot \frac{du}{dy} = \frac{dv_x}{dy} \qquad (2)$$

where v_x is velocity in the x direction. The relations between viscosity (η), shear stress (τ), and shear rate ($\dot{\gamma}$) is:

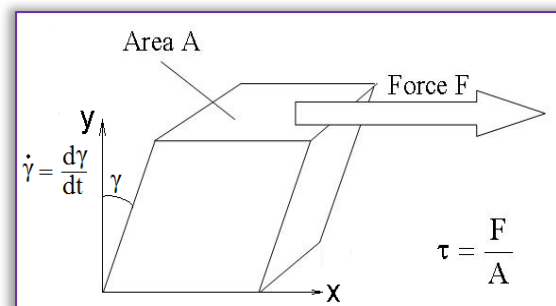$$\dot{\gamma} = \frac{\tau}{\eta} \qquad (3)$$

Figure 1. A volume unit of liquid moving at shear rate $\dot{\gamma}$ under the applied shear stress of τ

Newtonian fluid is one in which viscosity independents of shear rate. In other words, plot of shear stress versus shear strain rate is linear with a slope η. The Newtonian liquids, all of the energy passes through the molecules of sliding from each other. Liquids in which shear stress is proportional to the rate of strain are non-Newtonian flow. In the non-Newtonian fluids, relationship of shear stress /

strain rate is not linear. The viscosity varies with shear rate. Apparent viscosity is always defined by the relationship between shear stress and shear rate. Usually, the viscosity decreases at higher shear rates; This phenomenon is known as shear thinning. Real vs. shear forces shear rate to a non-Newtonian and Newtonian liquids are shown in Figure 2.
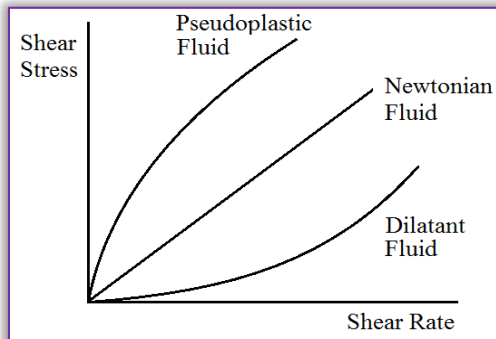

Figure 2. A schematic graph of shear stress to the shear rate for a Newtonian liquid Newton

The higher viscosity η of the polymer is generated by the higher resistance to flow of the melt. Otherwise, i.e. less resistance. The curves of viscosity of most thermoplastics exhibit the same dependence on shear rates, as shown in Figure 3.
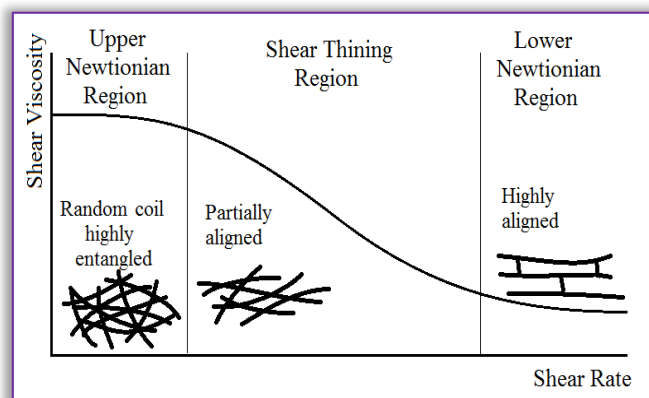

Figure 3. Characteristic viscosity curve of thermoplastics (log-log plot)

At low shear rates, the viscosity is almost constant. This is usually referred to as the upper Newtonian area. The polymer chains are evenly accordance with increasing shear rate so that the viscosity be reduced accordingly. This is called thixotropic region. When all the polymer chains fully with the shear viscosity becomes virtually insensitive to shear rate. This is called the Lower Newtonian region. The upper region and Newtonian shear thinning region is observed in the majority of polymers. The lower the Newton region is not completely clear in most thermoplastics, as shown in the molecular degradation of the ultra-high shear rates.

EXPERIMENTAL MATERIALS AND MEASUREMENT

In this case, the ratio of polypropylene with another fiber, and 0, was 10, 20, 30 and 40%. The thermoplastic is dried in an oven heraus T6 at 80°C for 4 hours. Measurement of the melt rheological properties of the model have been carried out LCR7001 Dynisco a capillary rheometer at a different speed of the piston from 0.9 up to 648 mm.min⁻¹. The diameter of the nozzle is 0.7 mm. The sample was placed inside the extrusion barrel assembly and forced into the nozzle, with the piston in a predetermined piston speed. Measuring conditions were maintained the same in all experiments, and the shear viscosity at various shear rates were obtained on a single charge of material. The measurements carried out at 230°C for each material.

The shear stress at different piston speeds are calculated using the formula:

$$\tau = \frac{F}{4A_P(l_c/d_c)} \tag{4}$$

RESULTS

Measured apparent viscosity vs. function of shear rate with varying proportions of glass fibers, at 230°C, shown in Figure 4. These curves are typical of pseudoplastic materials. They exhibit a decrease in viscosity with increasing shear rate. The behavior of measured curves can be described by the modified Cross equation:

$$\eta = \frac{\eta_0}{1+\left(\frac{\eta_0 \cdot \dot{\gamma}}{\tau^*}\right)^{1-n}} \tag{5}$$

where n is a power index and η_0 zero shear rate. This model is similar to cross. It also describes the dependence of the shear assessment across the top region of Newtonian and shear-thinning region. However, it is generally more suitable for thermoplastics with a broad molecular weight distribution (BMWD). Commercially available grade are usually made with BMWD, so this model is widely used in conventional databases simulation software. The model is exponential (EXP) and the temperature dependence is also known as a Cross-Exp model.

Inclusion of fibers increases the viscosity of polymer systems, and with an increasing fiber content. It is found that prevail at lower shear rates, where the fibers and the polymer molecules are not fully oriented increase in viscosity.

Results measured by capillary rheometer were obtained to discuss the rheological behavior of mixtures. The study showed that the viscosity of the glass fiber reinforced polypropylene, in the molten state, is dependent on the shear rate, and the different fiber content by weight. Chart analysis shows that raw PP is less viscous than reinforced polypropylene. The results in Figure 4 show that increasing the viscosity of the PP reinforced with a fiber material.

Effect of particular fillers on the viscosity is given in the following mathematical formula:

$$\eta = \eta_M + (C \cdot \psi + 1) \tag{6}$$

In Modified Cross model case:

$$\eta = \frac{\eta_0}{1+\left(\frac{\eta_0 \cdot \dot{\gamma}}{\tau^*}\right)^{1-n}} + (C \cdot \psi + 1) \qquad (7)$$
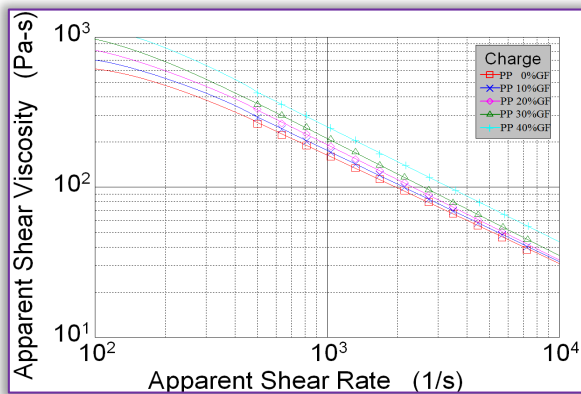

Figure 4. Graphical comparison of measured viscosity
and regression viscosity curves at 230°C

In this case:

$$\eta = \frac{1875}{1+\left(\frac{1875 \cdot \dot{\gamma}}{89\,373}\right)^{1-0.232}} + (0.0132 \cdot \psi + 1) \qquad (8)$$

Values n and $\dot{\gamma}$ were calculated by the first and last points of unfilled material by Modified Cross equation. Variable ψ takes the values 0, 10, 20, 30 and 40 in our case.

Tables 1 to 5 show measured viscosity, calculated viscosity by equation 8 and ratio of these viscosities.

Table 1. Measured and calculated viscosity
of composites at 0 % glass fibres

Point	Sh.rate (1/sec)	Apparent viscosity (Pa·s)		Difference of viscosities
		Measured	Calculated	
1	500	265.33	264.81	-0.20%
2	637.5	224.82	225.15	+0.15%
3	812.8	190.06	190.72	+0.35%
4	1036.3	160.37	161.05	+0.42%
5	1321.3	135.2	135.62	+0.31%
6	1684.7	113.74	113.94	+0.17%
7	2147.9	95.44	95.54	+0.10%
8	2738.6	79.97	79.97	+0.00%
9	3491.7	66.87	66.84	-0.04%
10	4451.9	55.86	55.80	-0.10%
11	5676.2	46.51	46.54	+0.07%
12	7237.1	38.48	38.78	+0.78%

Table 2. Measured and calculated viscosity
of composites at 10 % glass fibres

Point	Sh.rate (1/sec)	Apparent viscosity (Pa·s)		Difference of viscosities
		Measured	Calculated	
1	500	291.96	299.76	+2.60%
2	637.5	245.46	254.87	+3.69%
3	812.8	204.42	215.90	+5.32%
4	1036.3	171.71	182.31	+5.81%
5	1321.3	143.03	153.52	+6.83%
6	1684.7	121.95	128.98	+5.45%
7	2147.9	100.88	108.15	+6.72%
8	2738.6	84.08	90.52	+7.12%
9	3491.7	69.94	75.66	+7.57%
10	4451.9	58.02	63.17	+8.15%
11	5676.2	48.25	52.68	+8.42%
12	7237.1	40.25	43.90	+8.32%

Table 3. Measured and calculated viscosity
of composites at 20 % glass fibres

Point	Sh.rate (1/sec)	Apparent viscosity (Pa·s)		Difference of viscosities
		Measured	Calculated	
1	500	333.17	334.72	+0.46%
2	637.5	267.7	284.59	+5.93%
3	812.8	226.78	241.08	+5.93%
4	1036.3	187.88	203.57	+7.71%
5	1321.3	154.32	171.42	+9.98%
6	1684.7	129.41	144.02	+10.14%
7	2147.9	107.57	120.76	+10.92%
8	2738.6	89.29	101.08	+11.66%
9	3491.7	74.26	84.49	+12.11%
10	4451.9	61.32	70.54	+13.06%
11	5676.2	50.63	58.83	+13.93%
12	7237.1	42.8	49.02	+12.69%

Table 4. Measured and calculated viscosity
of composites at 30 % glass fibres

Point	Sh.rate (1/sec)	Apparent viscosity (Pa·s)		Difference of viscosities
		Measured	Calculated	
1	500	355.18	369.67	+3.92%
2	637.5	301.19	314.31	+4.17%
3	812.8	250.78	266.25	+5.81%
4	1036.3	209.13	224.83	+6.98%
5	1321.3	171.99	189.33	+9.16%
6	1684.7	140.69	159.06	+11.55%
7	2147.9	117.27	133.37	+12.07%
8	2738.6	96.08	111.63	+13.93%
9	3491.7	78.92	93.31	+15.42%
10	4451.9	65.13	77.90	+16.39%
11	5676.2	54.45	64.97	+16.19%
12	7237.1	45.15	54.14	+16.61%

Table 5. Measured and calculated viscosity
of composites at 40 % glass fibres

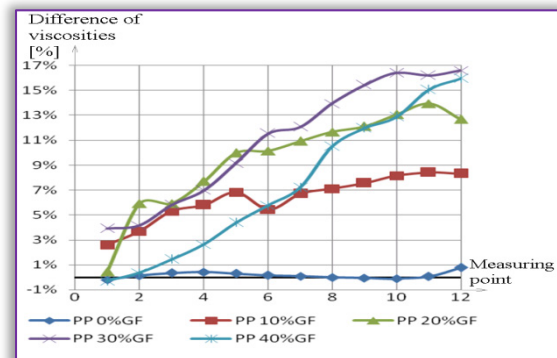| Point	Sh.rate (1/sec)	Apparent viscosity (Pa·s)		Difference of viscosities
		Measured	Calculated	
1	500	405.8	404.63	-0.29%
2	637.5	342.72	344.02	+0.38%
3	812.8	287.18	291.43	+1.46%
4	1036.3	239.55	246.09	+2.66%
5	1321.3	198.14	207.23	+4.39%
6	1684.7	164.01	174.10	+5.79%
7	2147.9	135.47	145.98	+7.20%
8	2738.6	109.37	122.19	+10.49%
9	3491.7	89.9	102.13	+11.98%
10	4451.9	74.3	85.27	+12.86%
11	5676.2	60.4	71.11	+15.07%
12	7237.1	49.81	59.26	+15.95%

Figure 5. Comparison of measured and calculated
viscosity ratio at different materials

CONCLUSION

In this paper, a rheological model for viscoelastic materials was modified in order to predict rheological properties and then compared with experimental results on polypropylene. The predictive results indicated that the developed model well supports the determination of rheological characteristics of the investigated material, such as viscosity and shear stress. All results were obtained from capillary rheometer.

Coefficients n and η_0 were calculated from unfilled material using the Modified Cross model. C was calculated from the filling material coefficient. This enabled to construct the function of the calculation using shear rate and fibre weight fraction.

The measured and calculated viscosities were compared for all materials. Their mutual ratio is shown in Figure 5. This implies that all the values differ by less than ±10%.Using the Power Law model, the values differed by less than ± 10% (different 20%) [5].

However using Modified Cross model the values differed by less than -0.29% and +16.61% (different 16.90%). This means that use of the Modified Cross model gives more accurate values (against Power Law model) comparable to the measured values.

Acknowledgment

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