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Araştırma Makalesi / Research Article

Comparison of the Rheological Behavior of Iso- and Syndiotactic Polypropylenes

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Abstract

The rheological behavior of iso- and syndiotactic polypropylenes (iPP and sPP) for two different temperatures of 175 and 190˚C at atmospheric pressure is analyzed employing the Yahsi-Dinc-Tav (YDT) non-Newtonian viscosity model. The predicted viscosity with shear rates of 0.093 to 93.91 s^{-1} on PPs is compared with the corresponding estimations from the Cross-like model. The obtained results from the YDT model deviate from the reported experimental observations with 1.041% for iPP and 1.86% for sPP. From the zero shear viscosity correlation to temperature- and vacancy fraction-dependent thermo-occupancy function, $Y_h = Y_h(h, T)$, viscosity parameters were ascertained and associated with polymer tacticity. From the zero shear viscosity relation, an increase in $Y_h = Y_h(h, T)$ function and hole fraction loss results in increased viscosity. The dependence of the derivative of logarithm of viscosity (viscoholibility) on vacancy fraction, as a function of pressure and temperature, $h=h(P,T)$, procured from Simha-Somcynsky hole theory displays an exponentially decreasing behavior.

Keywords: Isotactic and syndiotactic polypropylenes, vacancy fraction, steric hidrance, viscoholibility, Simha–Somcynsky, tacticity.

İzo- ve Sindiyotaktik Polipropilenlerin Reolojik Davranışının Karşılaştırılması

Öz

Newtonyen olmayan Yahşi-Dinç-Tav (YDT) viskozite modeli kullanılarak, izotaktik ve sindiyotaktik polipropilenlerin (iPP ve sPP) atmosfer basıncında 175 ve 190˚C'lik iki farklı sıcaklık için reolojik davranışı analiz edilmiştir. PP'ler üzerinde 0.093 ila 93.91 s^{-1} kayma gerinimleri ile tahmin edilen kayma viskozitesi, Cross-benzeri modelden karşılık gelen tahminlerle karşılaştırılır. YDT modelinden elde edilen sonuçlar, iPP için %1.041 ve sPP için %1.86 ile, bildirilen deneysel gözlemlerden sapmaktadır. Sıcaklık ve boşluk kesri ile ilişkili ısıl-doluluk fonksiyonu, $Y_h = Y_h(h, T)$, ile sıfır kayma viskozite ilişkisinden, viskozite parametreleri belirlendi ve bu parametreler polimer taktisitesi ile ilişkilendirildi. Sıfır kayma viskozite ilişkisinden, Y_h fonksiyonundaki bir artış ve boşluk fraksiyonu kaybı viskozitenin artmasıyla sonuçlanır. Viskozite logaritmasının (viskoholabilite) türevinin, Simha-Somcynsky boşluk teorisinden sağlanan sıcaklığın ve basıncın fonksiyonu olan boşluk kesrine, h=h(P,T) bağlılığı, üstel azalan bir davranış sergiler.

Anahtar Kelimeler: İzotaktik and sindiyotaktik polipropilenler, boşluk kesri, sterik hidrans, viskoholibilite, Simha–Somcynsky, taktisite.

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1. Introduction

Shear viscosity concerned with non-Newtonian fluids is a very important factor to characterize the polymer molecular structure and define the transport properties of polymers since they are primarily used in many technical and industrial processes. It can be defined theoretically through the zero shear viscosity model including free volume effects in connection with pressure-volume-temperature (*PVT*) measurements. The alternating method to define shear viscosity is using viscosity measurements that can be applied to a shear viscosity model. However, while *PVT* measurements are easily produced under laboratory conditions, factors such as viscous heating and heat transfer that may arise during the experimental process for shear viscosity need to be considered for an accurate assessment for the notion of the shear viscosity. Because of these drawbacks in measuring, it is very favorable to utilize theoretical derivation.

Shear viscosity has been mostly described by Cross/Carreau models and their modified forms. Hieber and Chiang (Hieber and Chiang, 1992) evaluated the capability of the above formulations to fit steady-shear-viscosity experimental results for five commercially available generic polymers. They observed that the Cross model provided a preferable correspondence to the measurements. Kadijk and Van Den Brule (Kadijk and Vandenbrule, 1994) reported that the viscosity results for polypropylene obtained by fitting data to the generalized Cross/Carreau equation were less sensitive to measuring deviation than those obtained for polystyrene and acrylonitrile-butadienestyrene terpolymer. The paper handling by Sedlacek et al. (2005) deals with the description of the shear viscosity data of seven thermoplastic liquids by making use of the Carreau-Yasuda model. Dinc et al. (2014) utilized the same measurements of the thermoplastics (Sedlacek et al., 2005) to test the fitting performance of the YDT equation for both shear and elongational viscosities.

The hole fraction influence on viscosity without directly quantifying it under pressure has become appealing academically. This may be due to the fact that the shear rate at which shear viscosity flattens to its limiting point is excessively low to be produced in rotational rheometers. Besides this difficulty, direct measuring for zero shear viscosity often requires a long duration of time. One way to obliquely determine zero shear viscosity is associating it with the structural properties of fluids, mostly free volume effects through the pressure-volume-temperature (*PVT*) measurements. To do so, a zero shear viscosity equation incorporating hole fraction parameter as a free volume measure is commonly practiced by many researchers. Utracki put into practice a modified version of the Doolittle equation (Doolittle, 1951, 1951b, 1952) to interpret the viscosity in connection with hole fraction obtained through Simha Somcynsky (SS) theory (Utracki, 1983a, 1983b, 1985, 1986; Utracki and Sedlacek, 2007). A modified version of Utracki's approach can be seen in Sedlacek et al. (2005). Yahsi (1998, 1999) derived a zero shear viscosity equation coupled with the SS model to make use of the hole fraction parameter. In order to correlate zero shear viscosity with unoccupied site fraction, applications for the model mentioned can be seen in Refs. Yahsi and Sahin (2004) for the branched/straight-chain alkanes, Sahin et al. (2006) for their mixtures and Sahin-Dinc et al. (2022) for some diesel fuels. In addition to the viscosity at zero shear, the viscosity at constant shear rate/stress, derived from the YDT model with reference to hole fraction is estimated for the special classes of polymers, so-called the thermoplastics including also some polyolefins [(PEs (LDPE, LLDPE, HDPE) and PP] along with PMMA, PC and PS (Dinc, 2014).

The paper aiming to determine the shear viscosity is curated in two parts including non-Newtonian viscosity modeling through the YDT model and correlating zero shear viscosity with hole fraction by virtue of the linear viscosity equation. At first, the non-Newtonian viscosity observations for two types of PPs at two tested temperatures at atmospheric pressure are fitted to the YDT model. Then, the zero shear viscosity equation developed by the YDT equation (Dinc et al., 2014; Sahin-Dinc, 2015; Sahin-Dinc et al., 2015) is used to link the linear viscosity of PPs in two tactic forms with thermooccupancy function including a vacancy fractional parameter determined through the Simha Somcynsky (SS) theory. The role of stereochemistry effects induced by chain tacticity on the rheological behavior of two stereoisomer forms of PPs, namely iPP and sPP, are elucidated in each part of the study.

2. Theories

2.1. An Epitome of the Hole Theory by Simha Somcynsky (SS)

The monumental SS theory (Simha and Somcynsky, 1969) serves a precise temperature (*T*), pressure (*P*), volume (*V*), and occupied fraction (*y*) relation:

$$\begin{aligned} \tilde{P}\tilde{V}\tilde{T}^{-1} &= (1-Q)^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[A(y\tilde{V})^{-2} - B] \\ \left[(s-1)/s + y^{-1}\ln(1-y)\right](s/3c) &= (Q-1/3)/(1-Q) \\ &\quad + (y/6\tilde{T})(y\tilde{V})^{-2}\left[2A - 3B(y\tilde{V})^{-2}\right] \end{aligned} \tag{1}$$

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ indicate the reduced quantities, reduced by P^*, V^* and T^*, respectively, and $y = 1-h$ is referred to as the occupied site fraction.

2.2. Yahsi-Dinc-Tav (YDT) Equation

In modeling viscosity determinations, the following equation is derived in respect of shear rate, $\dot{\gamma}$, and zero shear viscosity, η_0, (Dinc et al., 2014; Sahin-Dinc, 2015; Sahin-Dinc et al., 2015; Sahin-Dinc et al., 2019);

$$\eta = \frac{\eta_0}{1 + \frac{\theta_1}{\Gamma(q+1)}\left(\frac{\eta_0\dot{\gamma}}{\tau}\right)^q + \frac{\theta_2}{\Gamma(2q+1)}\left(\frac{\eta_0\dot{\gamma}}{\tau}\right)^{2q}} \tag{2}$$

where $\Gamma(q)$, a function of q corresponding to the power-law index, is the gamma function. The critical stress parameter is τ and θ with subscripts of 1 and 2 indicates the characteristic ratio measure.
In the denominator of Eq. (2), omitting the $2q$ power term, the equation turns out to be a Cross-like model (Dinc, 2014):

$$\eta = \frac{\eta_0}{1 + \frac{\theta_1}{\Gamma(q+1)}\left(\frac{\eta_0\dot{\gamma}}{\tau}\right)^q} \tag{3}$$

The zero-shear viscosity expressed as the zeroth-order approximation of Eq. (2) is $\eta_0 = \eta^* e^{E_a/kT}$. Taking the logarithm of both sides of this equation with the substitution of activation energy, $E_a = a'q_z\Phi(1-h)/2h$, the following equation is obtained (Dinc et al., 2014):

$$\ln\eta_0 = \ln\eta^* + \alpha Y_h, \quad Y_h = \frac{1-h}{h}\frac{1}{T} \tag{4}$$

where the viscosity-intercept $\ln\eta^*$ corresponds to the extrapolated viscosity values when $Y_h = 0$ at high T and low P with maximum h. A measure of activation energy is denoted by α.

The parameters, η^* and α in Eq. (4) are ascertained to be:

$$\eta^* = \frac{\sqrt{2}N_A h_p}{\pi\kappa\upsilon} \text{ and } \alpha = a'\frac{q_z\Phi}{2k} \tag{5}$$

where κ denotes the transmission coefficient together with h_p and k symbolize Planck and Boltzmann constants, respectively. Molar segmental volume is specified by υ and Φ corresponds to the polymer segment-segment interaction potential energy. The activation energy proportionality constant is denoted by a'.

The word “viscoholibility” is coined of terms viscosity and vacancy fractional part stands for the derivative of Eq. (4) (Dinc et al., 2014):

$$\left.\frac{\partial \ln \eta_0}{\partial h}\right|_T = -\frac{\alpha}{h^2 T} \tag{6}$$

3. CALCULATIONS

3.1. *P**, *V**, and *T** Parameters in SS Theory

The polyolefin melts taken here into account are iPP and sPP. The molecular weight (MW) and the polydispersity index (PI) of iPP are 224 300 g/mol and 4.2, respectively. The MW for sPP is 181 300 g/mol and PI is 3.95.

In Ref. Rojo et al., (Rojo et al., 2006), the SS equations were employed to evaluate the characteristic pressure P^* in a complete range of pressure together with V^* and T^* at ambient pressure. The reducing parametric quantities, P^*, V^*, T^* of SS are reported by Rojo et al. (2006) as $V^* = 1.1883\ \mathrm{cm^3 g^{-1}}$, $T^* = 9009\ \mathrm{K}$, and $P^* = 555.2\ \mathrm{MPa}$ for iPP; $V^* = 1.1951\ \mathrm{cm^3 g^{-1}}$, $T^* = 9533\ \mathrm{K}$, and $P^* = 573.8\ \mathrm{MPa}$ for sPP. The quantities mentioned are utilized to determine the vacancy fraction through Eqs. (1), along with the viscosity prediction. In the current study, the structural flexibility parameter is employed as $3cs^{-1} = 1$

3.2. Shear Rate Dependence on Viscosity

The rheological observations for polypropylenes examined were published by Rojo et al. (2006) in the temperature and shear rate ranges 130-190°C and 0.093 to 93.91 s^{-1}, respectively at ambient pressure. The available sets of data are fitted to Eqs. (2) and (3) to acquire the zero level of shear viscosity, η_0, and the critical stress quantity, τ, at atmospheric pressure and for each temperature data set together with the fraction q as a power of shear rate. In order to have η_0 and τ, we apply nonlinear fitting presuming that q is employed as a dispensable parameter. The optimum q quantity is set at the minimum relative Mean Absolute Percentage Error (rMAPE) in viscosity ascribed to be:

$$\Delta\eta(\%) = \frac{100}{N}\sum_i \left| 1 - \frac{\eta_i^{calc}}{\eta_i^{\exp}} \right| \tag{7}$$

Table 1 lists η_0 and τ quantities at ambient pressure alongside with mean $\Delta\eta(\%)$, determined by Eq. (7) and correlation coefficient squared (the coefficient of determination), R^2. The values in parentheses are worked out via Eq. (3) while the rest with Eq. (2). The YDT and Cross-like models reveal $\Delta\eta(\%)$ for both polymers less than %2.1 and %3.6 at ambient pressure, respectively. Hence, the YDT model fits the viscosity data with a better conformance at ambient pressure compared to the Cross-like model. In addition, the influence of tacticity or stereoregularity/stereoirregularity in the viscosity of iPP and sPP is in good agreement with measured data for iPP and sPP.

Table 1. Rheological parameters determined by Eq. (2) at two temperatures at ambient pressure. The values in parenthesis were obtained from Eq. (3).

Polymer	T(K)	q	η_0(Pa□s)	τ(Pa)	$\Delta\eta$ (%)	R^2
iPP	448		1192.63	2755.3	1.20	0.9997
		0.550	(1164.66)	(1691.9)	(1.34)	(0.9997)
	463	(0.626)	848.862	2629.6	0.92	0.9999
			(829.653)	(1613.5)	(0.92)	(0.9999)
sPP	448	0.580	11077.0	13807.9	1.60	0.9999
		(0.72)	(10811.2)	(4330.5)	(2.63)	(0.9999)
	463		6935.85	14964.2	2.12	0.9993
			(6760.76)	(4763.6)	(3.59)	(0.9993)

Logarithmic shear viscosity vs logarithmic shear rate for PPs at two temperatures and atmospheric pressure is graphed in Figure 1 to overtly demonstrate the access of the viscosity to its limiting at both low and high shear rate values. The graph illustrates that the viscosity of PPs approaches its limiting value where it is nearly constant at the lowest shear rates, so-called the Newtonian region. The curves turn out to be straight lines evoking power-law behavior at the highest shear rates where they are appearing to be nearly converged with each other. sPP displays about 10 times higher viscosity than iPP. The substantially enhanced viscosity of sPP compared to iPP might be attributed to the difference in the conformations of iPP and sPP arising from the alternating-trans conformation of the sPP chain that couldn’t be destroyed in the polymer melt completely (Eckstein et al., 1997). The alternating location of the methyl groups effectively brings on the trans configuration of the backbone and may induce a steric hindrance (Madkour and Soldera, 2001). This results in a significantly extended and expanded chain conformation (Jones et al., 2002) and a larger chain dimension of sPP in the liquid state in comparison with the isotactic analog. sPP chain becomes bulkier and restrains its segmental motion. As a sequence of this, sPP is more stable, more rigid, stiffer, and as a consequence more viscous.

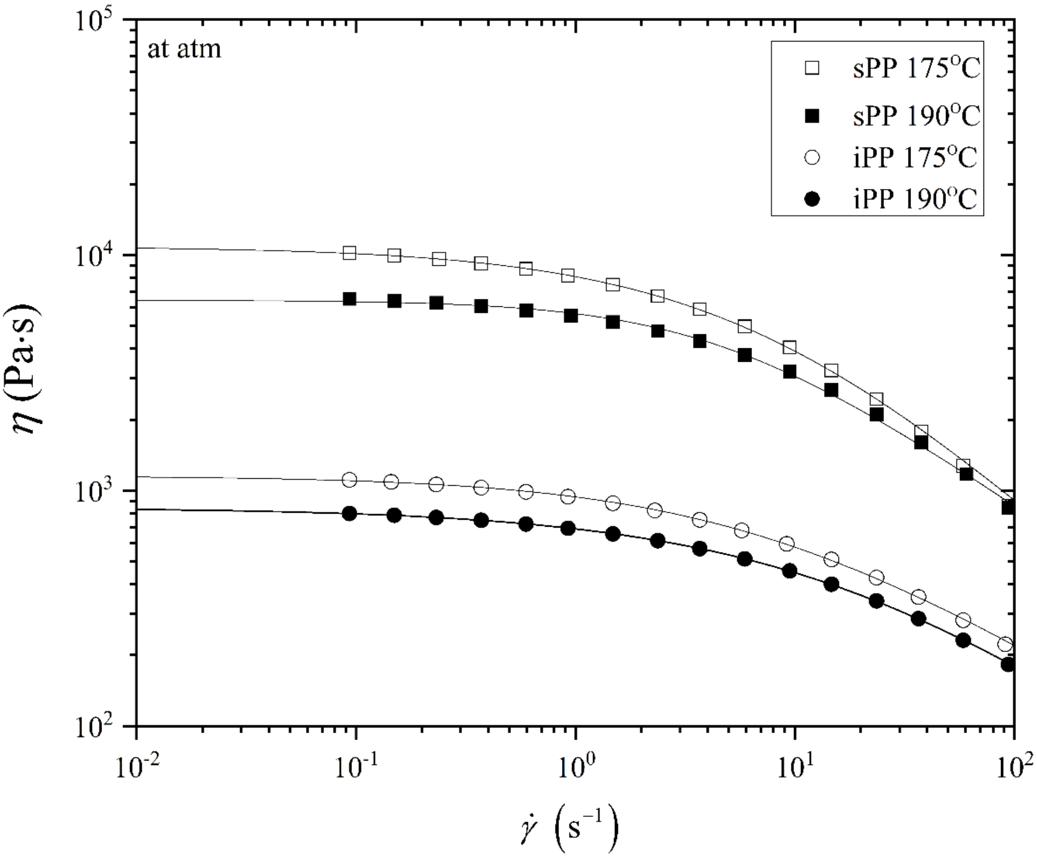

Figure 1. The logarithm of η vs $\dot{\gamma}$ of PPs with two temperatures at ambient pressure. Solid lines correspond to data fitting through Eq. (2).

3.3. Hole Fraction-Zero Shear Viscosity Dependence

The viscosity values at zero-shear are digitized from Figure 3 in Ref. Rojo et al. (2006) with four and five temperature values for iPP and sPP, respectively. The zero-shear viscosity findings predicted by Eq. (2) in Table 1 are not used to correlate with the thermo-occupancy function, Y_h, because we have them only at two temperature references. The zero-shear viscosity observations are inserted into Eq. (4) where the vacancy fraction is worked out by adopting Eqs. (1). The quantities, $\ln\eta^*$ and α in Eq. (4) are reported in Table 2 with R^2 and $\Delta\eta(\%)$ for iPP and sPP. The average percentage deviations of viscosity data at zero shear for the tested temperatures and at atmospheric pressure are % 0.39 for iPP and %0.38 for sPP. The relative mean average percentage error in zero shear viscosity (rMAPE), $\Delta\eta_0(\%)$, is computed from the following expression:

$$\Delta\eta_0(\%)=\frac{100}{N}\sum_i\left|1-\frac{\eta_i^{calc}}{\eta_i^{\exp}}\right| \tag{8}$$

Table 2. Viscosity parameters of Eq. (4) (vacancy fraction dependence to viscosity) together with data fit statistics.

Polymer	$\ln\eta^*$	α	a' ($\times10^4$)	κ	$\Delta\eta_0$ (%)	R^2
iPP	3.76	166.58	0.13	0.091	0.39	0.99998
sPP	5.33	175.40	0.16	0.019	0.38	0.99998

To elucidate the logarithmic viscosity-thermooccupancy behavior, $\ln\eta$ vs Y_h is plotted in Figure 2 with the lines standing for the optimum approximation of the observations for the individual polymers. Through the line, the temperature drops as going higher. At the down part of the lines the temperature rises. As going lower part of the line, increased temperature gives rise to the amount of nanovoids. In addition, as going lower temperatures, the hole fraction decrement, produce less movement of molecules, peculiarly the polymers with more extended chain length and more expanded chain (Jones et al., 2002). The figure presents that sPP is a more viscous sample as expected. The figure also shows that at a given temperature at atmospheric pressure the logarithmic viscosity has a linear dependency on thermo-occupancy function.

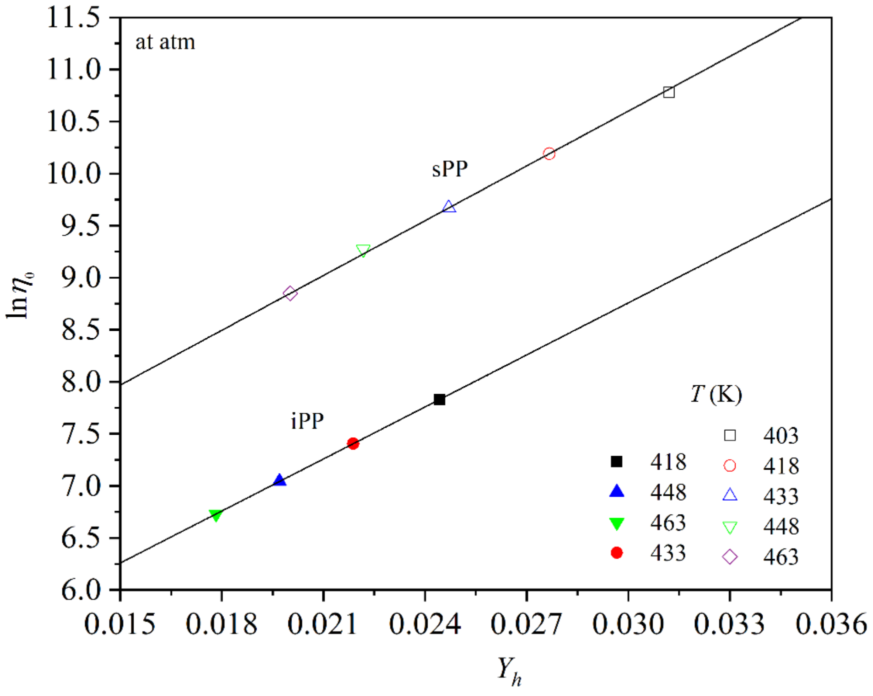

Figure 2. $\ln\eta_0$ vs Y_h with the solid lines calculated by Eq. (4).

Above, each slope of the line indicates the measure of activation energy coefficient, α , in the Kelvin scale, explicitly observed using Eq. (4). The magnitudes of parameters α and a' go up with raising viscosity while they drop as going lower viscous materials, namely from sPP to iPP as demonstrated in Figure 2. sPP has greater α and a' values relative to the isotactic analog. We can explain that this difference arises with stereoregular/stereoirregular formation of sPP and iPP in the back-bone as tacticity, respectively. The reason for higher viscous sPP melt can be described by trans configuration of the chain and the steric hindrance induced by the alternating position between methyl (CH_2) pendant groups on the alternating neighboring chiral carbon atoms (Eckstein et al., 1997; Loos et al., 1996; Madkour and Soldera, 2001). The conformational difference of sPP due to the elongated trans configuration and steric hindrance leads to a larger chain dimension that is referred to the chain with both a larger chain diameter and longer chain length. The extended/expanded chain of sPP is characterized by a higher end-to-end distance, a measure of the characteristic ratio, sweeps out a greater volume (Madkour and Soldera, 2001; Panagiotis-Nikolaos et al., 2018). Therefore the extended coil will encounter the greater number of other chains with which it might entangle (Fetters et al., 1994) and retrains the segmental motion. The steric hindrance and higher characteristic ratio which are directly related to the viscosity lead to the chain being, respectively, more rigid and stiff with close meanings (Jones et al., 2002; Panagiotis-Nikolaos et al., 2018). A corollary of a rigid and stiff chain, sPP becomes more stable and viscous. In addition, the larger chain dimension also refers to the higher segment length and segment number that accompanied with the enhanced viscosity. In this study sPP with a higher segment length (Jones et al., 2002) has an increased viscosity with respect to the counterpart iPP. Besides, the stiffer the backbones are, the more intermolecular contacts occur. The higher intermolecular contacts results in enhanced density. From the open literature from which the author obtained the data (Rojo et al., 2006), it is reported that sPP with a lower specific volume is slightly denser than iPP (at $200\,^{\circ}\mathrm{C}$ and ambient pressure, $\rho_{iso} = 0.700$ g/cc and $\rho_{syndio} = 0.717$ g/cc). However, it is expected that an augment in the coil dimension is accompanied by a less efficient intra- and inter-molecular interaction with decreased density (Amer et al., 2015; Fetters et al., 1994; Müller, 2008; Wang and Nies, 1998) or vice versa. Although the denser sPP chain with lower hole fraction, as a kind of free volume fraction, is characterized by higher viscosity, higher density will not always induces higher viscosity. Lower free volume is also attributed to higher toughness of sPP due to the increased chain packing (Huang et al., 2015).

Further, sPP is a semicrystalline material and exhibits a low degree of crystallinity compared to iPP. Because isotacticity degree is deliberated as the basic parameter that has an impact on the crystallinity of polymers (Amer et al., 2015; Xu et al., 2019). In other words, with some exclusions, higher crystallinity accompanied by higher density and stiffness (Amer et al., 2015). Normally, low crystallinity results in decreased viscosity. In one of our study (Sahin-Dinc et al., 2015) we found that the semicrystalline sPS has high viscosity compared to the less isotactic and amorphous analog aPS. In this study, contrary to the expectation, the enhanced viscosity might not be ascribed to the isotacticity and crystallinity.

The evaluation for the peculiar behavior of sPP is that the larger chain dimension, as a result of steric hindrance due to the alternating trans configuration, induce the higher viscosity whether or not sPP is denser or less crystalline with respect to the counterpart iPP. Consequently, the more viscous material with more activation energy results in larger α and a' in magnitudes.

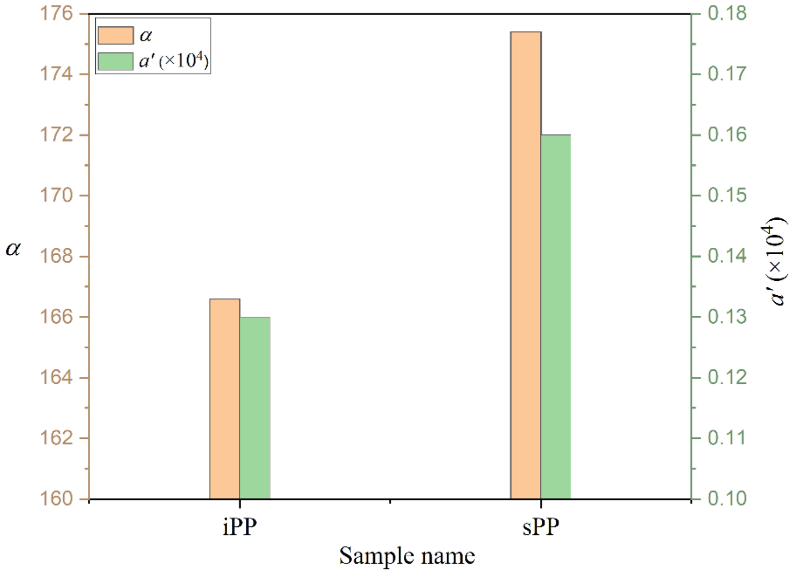

Figure 3. The material dependence of α and a' ascertained by Eq. (4).

The transmission coefficient, κ and $\ln\eta^*$, incoming from the linear viscosity equation (Eq. (4)) are inversely related to each other as seen in Figure 4. The maximum hole fraction values at ambient pressure and higher temperature, the viscosity equals to $\ln\eta^*$ from Eq. (4). The parameter κ gets higher at this condition due to the availability of hole fraction. iPP has higher κ but lower $\ln\eta^*$ values compared to sPP since sPP is more viscous depending on trans-configuration conformation that can't be destructed in the liquid state thoroughly.

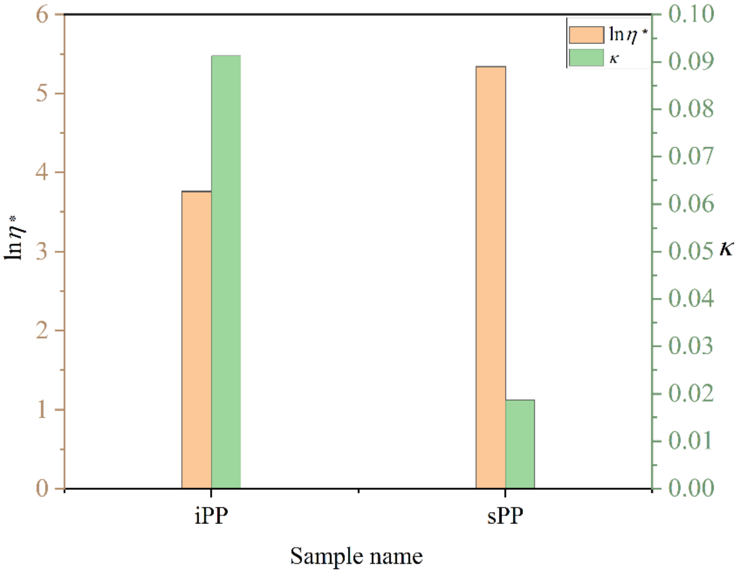

Figure 4. The material dependence of $\ln\eta^*$ and κ, ascertained by Eq. (4).

The graphical summary of the differentiation of logarithm of zero shear viscosity (viscoholibility), vs hole fraction in Figure 5, presents the viscosity change with reference to *h*, at constant *T* while the fraction *h* varies through the abscissa axis. The viscoholibility over the structure-related parameter, $-\alpha$, defined in Eq. (6), coincides with the whole data, on the ordinate axis. The viscoholibility times temperature, *T* on the vertical axis in Figure 6 demonstrates a smoother graph.

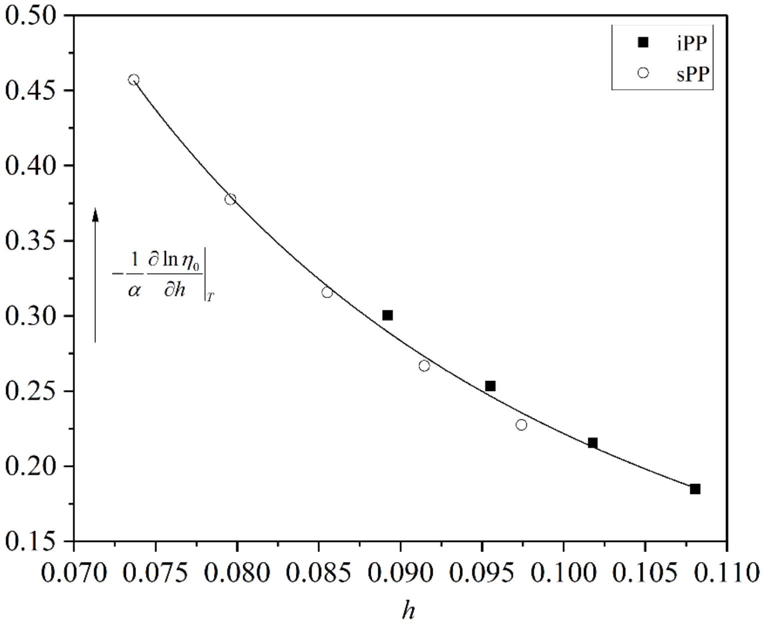

Figure 5. $\left(-1/\alpha\right)\left(\partial\ln\eta_0/\partial h\right)\Big|_T$ vs *h* dependence via Eq. (6) for the polypropylenes under study.

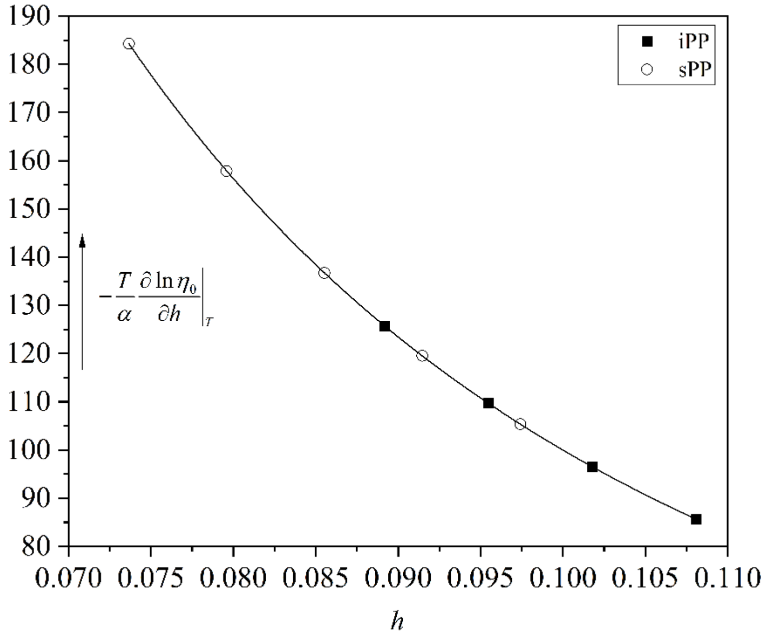

Figure 6. Dependence of $(-T/\alpha)(\partial \ln \eta_0/\partial h)\big|_T$ vs *h* dependence via Eq. (6) for the polymers under study.

4. Conclusions and Recommendations

The YDT equation organized to define the non-Newtonian viscosity of polypropylenes can favorably fit the shear viscosity measurements of PPs at ambient pressure. The zero shear viscosity established from the YDT model at zero shear has a direct relation with temperature- and hole fraction (defined by SS theory) dependent thermooccupancy function. The magnitudes of the parameters in the zero shear viscosity model namely activation energy and transmission coefficient change with polymer conformation and structure that is affected by tacticity. The viscoholibility of PPs in two tactic forms of iPP and sPP goes down with hole fraction which is a measure of structural defects. It is shown that the steric hindrance resulting from the alternating positions of methyl side groups has effects on the materials to be more viscous, rigid, and stiffer. An interesting future work could be on predicting other thermophysical properties such as thermal conductivity for different families of liquids including nanofluids or ionic fluids with a similar approach followed in the present study.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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