

Effect of hydroxyl terminated polybutadiene number-averaged molecular weight on chemorheological behavior of polyurethane networking

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ABSTRACT

The time available for proper casting of the polyurethane (PU) system after isocyanate addition (called pot life) affects the macrodiol microstructure. In this research, the effect of molecular weight (\bar{M}_n) of hydroxyl terminated polybutadiene (HTPB) as an important macrodiol on the pot life of polyurethane system was rheologically investigated. The chemorheological behavior of polyurethane systems based on five different HTPBs with \bar{M}_n ranging from 2810 to 4450 g/mol and two common diisocyanates (TDI and IPDI) were studied in situ. The results showed that by increasing \bar{M}_n , the rotational viscosity as well as the constant reaction rate of urethane formation increases; whereas the pot life of the polyurethane system decreases. The pseudoplastic behavior of the samples showed the minimum rate constant/longest pot life at a critical molecular weight (M_c) of about 3100 g/mol, which may be due to physical chain entanglements. Rheomechanical spectrometry interestingly depicted that $\tan \delta$ originated-gel point occurs before the intersection of stored modulus (G') and loss modulus (G'') ($t_{gel} < t_{G'=G''}$). The kinetic model developed by Hsich showed excellent agreement with the cross-linking data of three polyurethane systems. **Polyolefins J (2023) 10: 191-204**

Keywords: HTPB; number-averaged molecular weight; pot life; gel time; dynamic rheological; polyurethane system.

INTRODUCTION

Wide use of hydroxyl terminated polybutadiene (HTPB), in the preparation of elastomers, adhesives, anti-corrosion coatings, electrical insulation, foams and as a polyurethane (PU) system of high-filled composites have led to many investigations to identify the behavior of this resin and improve its performance [1-4]. Till now, HTPB is the best choice for high-filled composites despite the availability of new energetic binders [5-7]. HTPB is characterized by low glass transition temperature and imparts unique properties such as hydrolytic stability,

low moisture permeability, resistance to aqueous acids and bases, adhesion to a variety of substrates, high solid loading, low temperature flexibility, electrical insulation properties, low embedment stress and high elongation with good elastic recovery. The performance of HTPB is greatly affected by its chain microstructures [1, 8].

The HTPB-based PU system may show suitable viscosity or fluidity at the end of mixing to facilitate casting. The parameters affecting pot life of the HTPB-based PU system include process parameters [9] (such

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as: mixing and casting temperature [10], curing ratio (NCO/OH) [11, 12], mixing shear rate and stirring time [13], application of nano and microparticles in slurry of composite system and feeding rate) [14, 15], and material parameters [16] (such as: curing agent [17-19], catalyst [6, 20], plasticizer [21] type and microstructural parameters of HTPB [22, 23]). During HTPB synthesis, the minimum changes in process parameters (temperature, pressure, catalyst, solvent, raw material and their ratio, etc.) lead to the formation of products with different microstructures [3, 24]. Relative isomer concentrations (cis/trans/vinyl), number and weight average molecular weight, molecular weight distribution (PDI), types of hydroxyl groups (G, H, and V), hydroxyl value (OH) and functionality distribution are the most important microstructural parameters of HTPB [3, 25]. These differences affect processability, pot life, curing behavior, mechanical properties, and aging of high-filled composites [26, 27].

The effect of HTPB number-averaged molecular weight (\bar{M}_n) on mechanical properties was investigated by Condon and Richardson. According to their research, the tensile strength of the HTPB-based PU elastomer, reduced by increase \bar{M}_n of HTPB, and this phenomenon is often intensified around $\bar{M}_n = 3000$ g/mol. Also, 100% modulus, stiffness and tear resistance decreased with increasing in \bar{M}_n similar to tensile strength. On the other hand, increasing the final elongation of HTPB elastomers increased linearly with increasing \bar{M}_n of HTPB [28-31].

Ono et al. investigated the effect of \bar{M}_n on the viscosity of HTPB-based PU elastomers. They found relationships between \bar{M}_n and viscosity at 30°C. It was understood that by increasing the viscosity of the high-filled composite slurry, the pot life of the polyurethane system decreases. Therefore, with increasing HTPB prepolymer \bar{M}_n , the pot life is reduced [28].

Sekkar investigated the pot life of the HTPB-based PU system, by using different curing agents including toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI), as well as examining different temperatures. In TDI and IPDI curing agents, due to the presence of different isomers in TDI and the presence of primary and secondary NCO in IPDI, in the viscosity-time plot separation and refraction were seen. TDI and IPDI-based polyurethane system showed two different rate constants (k_1 and k_2) which may attributed to the presence of two types of isocyanate group (NCO) with different reactivity [6,11]. Typically, curing of

elastomers is investigated by a dynamic time sweep, where the stored (G') and loss modulus (G'') modulus are monitored as a function of cure time at constant frequency. The G' and G'' vs time curve can then be fitted to an empirical kinetic model. The gel point of a cross-linking polymer is an important parameter, both from scientific and technological standpoints [32].

In the present study, in continuation of our previous study which showed that the \bar{M}_n may affect the pot life of the HTPB-based system and the curing reaction [3, 33], some HTPB prepolymer samples with different \bar{M}_n , along with two types of curing agents (TDI and IPDI with aromatic and cyclic aliphatic structure; respectively) at constant temperature of 40°C were rheologically investigated. The innovation of this work compared to other studies examines the effect of \bar{M}_n of HTPB polymer on in-situ chemorheological behavior of PU step polymerization in order to adjust the pot life of the system without any change in formulation ingredients or process parameters.

EXPERIMENTAL

Specifications of raw materials

Five types of HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E are supplied from the industry (Table 1) and used for the formulation of polyurethane systems.

TDI with purity of 98.95%, specific weight of 1.21 g/cm³ and refractive index (25°C) of 1.5667, IPDI with molecular weight of 222.3 g/mol, functionality of 2, NCO content of 37.56%, pH of 6.07 and density of 1.06 g/cm³, and dioctyl sebacate (DOS) with ester value of 99.46%, acidity (as Sebacic acid) of 0.036%, humidity of 0.09% and density of 0.9144 g/cm³ were supplied from Merck. Dibutyltin dilaurate (DBTDL) with the appearance of colorless liquid, molecular weight of 631.56 g/mol and density of 1.066 g/cm³ was supplied by Sigma Aldrich.

Test method

The pot life of the HTPB-based PU system was measured using Brookfield digital rotary viscometer (RV), LVDV models made in the United States using S63 and S64 spindles at 40°C [34]. For determination of molecular weight averages and molecular weight distributions (MWD), Tetrahydrofuran (THF) was selected as solution in size-exclusion chromatography (SEC) of 1100 GPC Agilent made by Perkin Elmer (United States) according to ASTM D6579-11 method

Table 1. Specifications of the HTPB samples.

Chemical and physical properties	Unit of measurement	Measurement Reference	HTPB type				
			HTPB-A	HTPB-B	HTPB-C	HTPB-D	HTPB-E
Viscosity (40°C)	Pa.s	Laboratory	5.28	5.46	3.6	3.7	-
Humidity	%	Technical Datasheet	0.067	0.068	0.066	0.067	-
Density (30°C)	g/cc	Laboratory	0.889	0.897	0.587	0.542	-
Number Average Molecular Weight (\bar{M}_n) (GPC)	g/mol	Laboratory	2810	3090	3751	4092	4450
Weight Average Molecular Weight (\bar{M}_w) (GPC)	g/mol	Laboratory	5536	6169	7545	9377	10290
Molecular weight distribution (M_w/M_n)	-	-	1.971	1.996	2.011	2.291	2.312
OH Value	mg KOH/g	Laboratory	38.2	60	62	69	102

[35]. In order to measure the hydroxyl value of samples, pyridine method was followed according to ASTM E222-10 [36] with an acetic anhydride-to-pyridine ratio 1:8 v/v. Dynamic chemorheological behavior of the HTPB-based PU system at 70°C temperature studied by rheomechanical spectrometer (RMS) rheometer of Anton Paar Physica MCR 301 made in Austria with parallel plates of 25 mm diameter, plate spacing of 0.5 mm and a 4 degree angle equipped with the system temperature control and N₂ gas generator. Using this device, at first a strain sweep test was done to determine the linear viscoelastic region at a constant frequency of 1 Hz and finally, dynamic tests in the time sweep mode at 70°C at three constant frequencies of 0.1, 1 and 10 Hz were performed. All

tests were performed under a nitrogen gas atmosphere to prevent oxidation. Rheological analysis was done at two steps. In the first step, static rheological tests were performed on five samples supplied from industry using RV reacting two curing agents of TDI and IPDI. In the second step, based on the result of the first step three samples and one curing agent (IPDI) were selected to investigate dynamic rheological tests using RMS.

Preparing polyurethane system

The PU system for five types of HTPB samples was prepared (Table 2) to evaluate the viscosity behavior versus time at 40°C. First, the viscosity of neat samples (without curing agent) was measured. Then,

Table 2. Formulation of PU systems.

sample code	Description	Weight (g)				
		HTPB	DOS	DBTDL	TDI	IPDI
HA-D	(HTPB-A)+DOS	34.200	5.224	-	-	-
HB-D	(HTPB-B)+DOS	34.200	5.224			
HC-D	(HTPB-C)+DOS	34.200	5.224			
HD-D	(HTPB-D)+DOS	34.200	5.224			
HE-D	(HTPB-E)+DOS	34.200	5.224			
S _A -T	(HTPB-A)+DOS+TDI	34.200	5.224	-	2.041	-
SB-T	(HTPB-B)+DOS+TDI	34.200	5.224	-	3.190	--
S _C -T	(HTPB-C)+DOS+TDI	34.200	5.224	-	3.292	--
S _D -T	(HTPB-D)+DOS+TDI	34.200	5.224	-	3.664	--
S _E -T	(HTPB-E)+DOS+TDI	34.200	5.224	-	5.415	--
S _A -I	(HTPB-A)+DOS+IPDI+DBTDL	34.200	5.224	0.014	--	4.066
S _B -I	(HTPB-B)+DOS+IPDI+DBTDL	34.200	5.224	0.014	--	2.289
S _C -I	(HTPB-C)+DOS+IPDI+ DBTDL	34.200	5.224	0.014	--	4.201
S _D -I	(HTPB-D)+DOS+IPDI+ DBTDL	34.200	5.224	0.014	--	4.675
S _E -I	(HTPB-E)+DOS+IPDI+ DBTDL	34.200	5.224	0.014	--	6.912

by adding the curing agent, viscosity of the samples was assessed. The HTPB-TDI-based PU system does not require a catalyst due to its reactivity and proper curing rate. Meanwhile, the HTPB-IPDI-based PU system needs DBTDL catalyst to show a reasonable kinetic. As the activation energy, enthalpy, progress and the rate of reaction were accelerated by the presence of the DBTDL catalyst [37].

According to the literature, the pot life values for the PU system based on HTPB are considered as 70,000 cP (\ln is equal to 11.15). Therefore, the viscosity measurement of all samples was performed up to 70,000 cP (as a criterion) [10, 11, 17, 38].

Curing ratio (R or NCO/OH) calculations

The ratio of the curing agent to the macrodiol (R) is one of the effective variables in the curing of urethane rubber, which can be calculated using Equation 1:

$$R = \frac{\text{mol}(NCO)}{\text{mol}(OH)} = \frac{\frac{m(NCO)}{M_{Eq}(NCO)}}{\frac{m(OH)}{M_{Eq}(OH)}} = \frac{m(NCO)}{m(OH)} \times \frac{M_{Eq}(OH)}{M_{Eq}(NCO)} \quad (1)$$

where, M_{Eq} is defined as the value of each substance (in grams or moles) whose efficiency in chemical reactions is equal to one gram of hydrogen and calculated based on Equation 2:

$$M_{Eq(OH)} = \frac{\bar{M}_n}{f(OH)} \quad (2)$$

Where, \bar{M}_n is the number average molecular weight of a polymer (determined by gel permeation chromatography (GPC) or Vapor phase osmometry (VPO) methods) and for non-polymeric materials such as a curing agent, the same molecular weight of the material is considered, f is also defined as a functionality for polymeric or non-polymeric material. This parameter is considered to be the number of NCO groups on the molecule, but differs for polymeric materials as chain length and the number of OH group varies. Equation 3 describes how f is calculated:

$$f(OH) = \frac{OH\text{value} \times M_n(OH)}{56100} \quad (3)$$

Where, OH-value is the value of hydroxyl present in one gram of resin (its unit is mg (KOH)/g (sample)) and is obtained by titration with standard potassium hydroxide solution (KOH). Functionality is a dimensionless number, and 56,100 is the molecular weight of potassium hydroxide in mg/mol [20, 39].

All the polyurethane formulations prepared in this work are designed so that the curing ratio R (NCO/OH) = 1.

RESULTS AND DISCUSSION

Evaluating the molecular weight

The average molecular weight of hydroxyl-terminated polybutadiene samples was determined using the GPC method. As shown in Figure 1, the GPC chromatograms are shown for HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E samples. According to Figure 1, the HTPB-D and HTPB-E samples have relatively broad distribution of molecular weights (\bar{M}_w/\bar{M}_n) [27, 40, 41].

Pseudoplastic behavior of HTPB/DOS mixture

Rotational viscosity of HTPB/DOS mixture versus shear rate was obtained at 40°C (the resulting figures for the sake of brevity were omitted). The viscosity of the HTPB/DOS mixture decreases with shear rate increasing. This behavior reflects the pseudoplasticity nature of the mixture [10, 13], the same trend was observed for all HTPB samples. The HTPB-E sample with the largest molecular weight showed more viscose behavior than HTPB-B and HTPB-A. Therefore, the HTPB-E/DOS mixture has more rotational viscosity than the other mixture. The HTPB-A with the lowest molecular weight, showed the least rotational viscosity. The experimental results obey well the power law model (Equation 4):

$$\eta = Kx^m \quad (4)$$

where η , x , m and K are the viscosity, shear

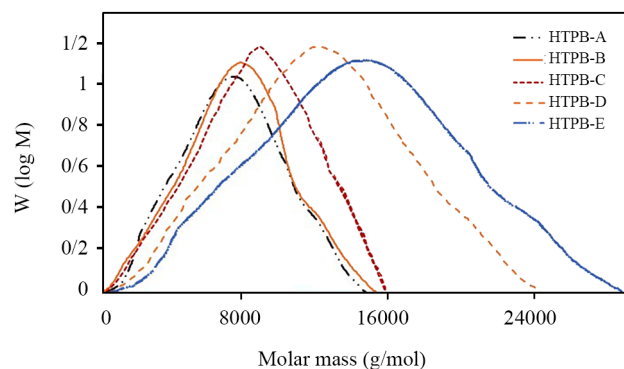


Figure 1. GPC chromatogram corresponds to the HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E samples.

rate, pseudoplasticity index and viscosity index, respectively. In Equation (4), for Newtonian fluids $m = 0$, in other words, the viscosity is independent of the shear rate. For dilatant fluids m is positive, while for pseudoplasticity fluids, m is between zero and -1 [7,10,42]. From the slope of viscosity vs. shear rate, pseudoplasticity index (m) and from the intercept, viscosity index (K) were determined. In order to easier description, the negative sign is removed from the value of the m and reported as percentage ($m\%$). Figure 2 describes the effect of \bar{M}_n on the pseudoplasticity index of the HTPB/DOS mixture as a non-Newtonian fluid. The values of the pseudoplasticity index varied between 79 and 100%, indicating pseudoplastic (shear-thinning) behavior [42].

The value, of pseudoplasticity index of HTPB/DOS mixtures do not change significantly with increase in \bar{M}_n of HTPB, but according to the values (m) it can be concluded that in general, all samples are pseudoplastic fluids. The value of the m for the HTPB-B/DOS mixture with molecular weight 3090 g/mol is significantly the largest one. This may be due to the effect of polymer chain entanglement in the critical molecular weight range (M_c) of HTPB [19, 29, 43]. Surprisingly, it was shown that the effect of \bar{M}_n , especially around the critical point, on the rheological behavior of the HTPB/DOS mixture can be very noticeable, which can change about 25% the pseudoplasticity index, and consequently, play an important role in solid loading of slurry mixture based on it. The relationship between the \bar{M}_n of HTPB/DOS mixture and viscosity (η) at constant shear rates (0.186, 0.265, 0.318, 0.424, 0.477 and 0.531 Hz) is almost linear (Figure 3).

Experimentally, the relationship between viscosity (η) and \bar{M}_n at shear rate of 0.186 Hz (for example) is $\log \eta = 3.953 + 7 \times 10^{-5} \bar{M}_n$. As can be seen from

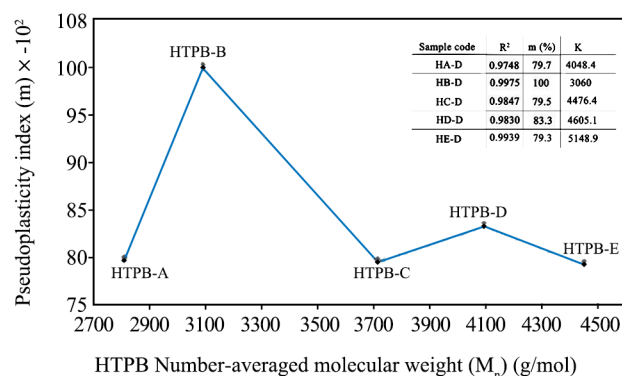


Figure 2. Changes in the pseudoplasticity index (m) of HTPB/DOS mixture versus n at temperature of 40°C.

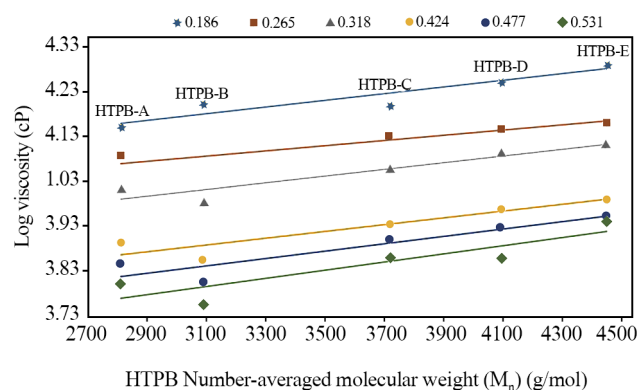


Figure 3. Changes in the viscosity (η) of HTPB/DOS mixture versus \bar{M}_n of HTPB at temperature of 40°C at different shear rates.

Figure 3, the viscosity increases approximately with the molecular weight increasing for all HTPB samples [23, 28, 29].

Viscometry of the PU system based on HTPB-TDI and HTPB-IPDI-DBTDL at 40°C

The viscosity changes of the polyurethane system based on different HTPB samples at different times and the constant temperature of 40°C are illustrated in Figure 4. Using laboratory data, as can be seen in Figure 4, viscosity increases exponentially versus time. The viscosity of the PU system increases with time as the urethane formation progresses. The increase in viscosity during the curing process can be related to an increase in molecular weight or chain branching [23, 25]. TDI has an aromatic structure and two isomers of 2,4 and 2,6 with a ratio of 80:20. As a result, increasing viscosity is expected to be observed in the plot, due to the *p*-NCO and the *o*-NCO groups, with different reactivity [10, 44].

According to Figure 4, among the five HTPB samples, the HTPB-E-based PU system shows a much faster increase than other samples to reach the pot

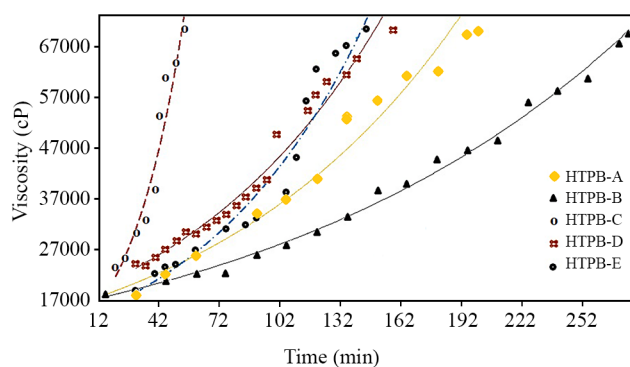


Figure 4. Viscosity (η) changes versus time for the PU system of HTPB-TDI at temperature 40°C.

life. This may be due to the higher molecular weight (4,450 g/mol) of HTPB-E than other specimens. Similarly, the rheological behavior and pot life of the HTPB-IPDI-DBTDL PU system at temperature 40°C in the presence of DBTDL catalyst at 0.03% was determined. IPDI has a cyclic asymmetrical molecular structure, with two isomers. As a result, similar to TDI, it is expected that there will be a two-step increase in viscosity in the plot, but due to the low reactivity of both groups of isocyanates in IPDI, almost linear behavior was observed in the viscosity increase diagram [17, 20, 45, 46].

The slope curve of the viscosity-time diagram for the HTPB-B-IPDI-DBTDL based PU system is less than that of other samples, because the curing time of the polyurethane system mixture is longer and it is more viscous than other systems. According to Figure 4, the sequence of pot life for HTPB-TDI/IPDI samples are as follows:

HTPB-B > HTPB-A > HTPB-C > HTPB-D > HTPB-E

The viscosity of HTPB-A-IPDI-DBTDL, after 200 min, increased from 23,552 cP in 30 min to 70,000 cP. This indicates that the pot life of the HTPB-A-IPDI PU system is about 200 min (70,000 cP, [11]) at temperature 40°C.

Effect of curing agent type on pot life at the temperature of 40°C

The pot life of the HTPB-TDI PU systems based on HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E in the absence of catalyst at the temperature of 40°C was 200, 277, 158, 145, and 54 min; respectively. The pot life of HTPB-IPDI-DBTDL PU systems based on HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E in the presence of catalyst, was 65, 135, 49, 35, and 28 min, respectively. The comparison of this research with related articles is given in Table 3. According to Table 3, the curing reaction of the HTPB-TDI PU system in

Table 3. Comparison of chemorheological parameters (pot life, experimental constants and exponential function) of HTPB-TDI and HTPB-IPDI-DBTDL system

Comparison	Curing agent type	sample code	Temperature (°C)	R	Catalyst content (%)	\bar{M}_n (g/mol)	Exponential function	R ²	Empirical Constants**		Pot life (min)
									a	b	
Present work	TDI	S _A -T	40°C	1.0	Without catalyst	2810	$\eta_A = 16200 e^{0.0079t}$	0.977	16200	0.0079	200
		S _B -T				3090	$\eta_B = 16442 e^{0.0053t}$	0.995	16442	0.0053	277
		S _C -T				3751	$\eta_C = 17728 e^{0.0093t}$	0.982	17728	0.0093	158
		S _D -T				4092	$\eta_D = 13080 e^{0.0118t}$	0.967	13080	0.0118	145
		S _E -T				4450	$\eta_E = 10685 e^{0.0356t}$	0.947	10685	0.0356	54
[47]	TDI	-	70°C	0.7	Without catalyst	2650	$\eta = 135.944 e^{0.0155t}$	-	135.944	0.0155	-
		-		0.8			$\eta = 165.069 e^{0.0166t}$	-	165.069	0.0166	-
		-		0.9			$\eta = 227.360 e^{0.01707t}$	-	227.360	0.01707	-
		-		1.0			$\eta = 286.975 e^{0.0169t}$	-	286.975	0.0169	-
		-		1.1			$\eta = 375.058 e^{0.01878t}$	-	375.058	0.01878	-
[10, 44]	TDI	-	40°C	1.0	Without catalyst	1.70*	$\eta = 6755.9 e^{0.0038t}$	0.98-0.99	6755.9	0.0038	285
		-	50°C				$\eta = 6028.5 e^{0.0042t}$	0.98-0.99	6028.5	0.0042	290
		-	60°C				$\eta = 4341.4 e^{0.0050t}$	0.98-0.99	4341.4	0.0050	300
Present work	IPDI	S _A -I	40°C	1.0	0.03	2810	$\eta_A = 7614 e^{0.0352t}$	0.947	7614	0.0352	65
		S _B -I				3090	$\eta_B = 19525 e^{0.0094t}$	0.973	19525	0.0094	135
		S _C -I				3751	$\eta_C = 12291 e^{0.0358t}$	0.995	12291	0.0358	49
		S _D -I				4092	$\eta_D = 9556.4 e^{0.0548t}$	0.954	9556.4	0.0548	35
		S _E -I				4450	$\eta_E = 14432 e^{0.0591t}$	0.949	14432	0.0591	28

* M_w/M_n

** Calculated using Equation 5 based on fitting data presented in Figure 4.

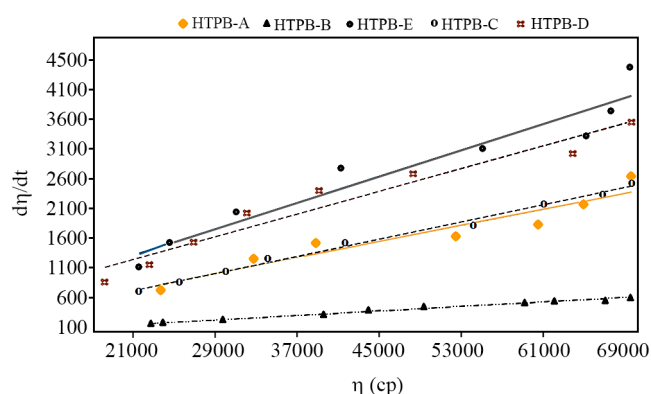
Table 4. Comparison of the effect of viscosity changes on the rate constant of the HTPB-TDI and HTPB-IPDI-DBTDL systems.

Comparison	Curing agent type	sample code	Temperature (°C)	R	\bar{M}_n (g/mol)	Linear function	R ²	Rate constant × 10 ² (min ⁻¹)
Present work	TDI	S _A -T	40°C	1.0	2810	y = 0.0083x - 13.777	0.9627	0.83
		S _B -T			3090	y = 0.0054x - 2.5106	0.9949	0.54
		S _C -T			3751	y = 0.0093x + 1.6078	0.9721	0.93
		S _D -T			4092	y = 0.0109x + 35.008	0.9583	1.09
		S _E -T			4450	y = 0.0332x + 101.05	0.9387	3.32
[47,48]	-	-	60°C	1.0	2930	y = 0.0245x + 0.7266	0.9971	2.45
		-			3290	y = 0.0189x - 0.0438	0.9981	1.86
		-			3510	y = 0.0146x - 0.8205	0.9972	1.42
		-			4480	y = 0.0073x - 0.4584	0.9970	0.71
Present work	IPDI	S _A -K	40°C	1.0	2810	y = 0.033x + 91.445	0.9330	3.30
		S _B -K			3090	y = 0.0093x + 2.9918	0.9844	0.93
		S _C -K			3751	y = 0.0354x + 17.293	0.9943	3.54
		S _D -K			4092	y = 0.0467x + 306.36	0.9429	4.67
		S _E -K			4450	y = 0.054x + 224.81	0.9249	5.40

the Sekkar's study showed two stages (at temperature of 30°C). In the first stage, the viscosity goes up to 130 min, and in the second stage, it continues from 130 up to 350 min [6, 11, 45]. The longer pot life in the articles compared to this work may be due to the lower amount of catalyst and temperature. For example in the Sekkar's work [6], the HTPB-IPDI-DBTDL catalyst with lower DBTDL catalyst content (0.0322 phr vs. 0.03% of this work) and at lower temperature (25°C vs. 40°C of this work) showed longer pot life (about 275 min vs. 135 min) by the assumption of similar HTPB molecular weight (at around 3000 g/mol).

Curing rate constant of the PU system based on HTPB

The changes in viscosity versus time for different types of HTPB are shown at constant temperatures of 40°C in Figure 4. According to Figure 4, the viscosity of networking polyurethane increases with time as

**Figure 5.** dn/dt changes versus viscosity for PU system of HTPB-IPDI-DBTDL at temperature of 40°C.

the urethane formation progresses. A mathematical relationship between viscosity and time can be obtained by fitting the data to an exponential function by the least-squares method. In Equation 5, a and b are experimental constants which are presented in Table 4:

$$\eta = ae^{bt} \quad (5)$$

From Equation 5, the rate of viscosity build up (dn/dt) at different intervals can be calculated by placing in the derivative equation for all HTPB-based PU systems and plotted against viscosity (η) (Figure 5). The good linearity of the diagrams in Figure 5 indicates that the viscosity build up for the HTPB-based PU system is a first-order reaction. As the rate of increase in viscosity (dn/dt) depends on the curing reaction amount at a time (t), it can be used as a criterion to measure the concentration of the curing reaction components [47, 48]. Therefore, the slope of viscosity increase rate (dn/dt) against the viscosity (η) can be considered as a criterion for determining the rate constant (k) increase based on viscosity (Table 4).

Effect of molecular weight on constant rate of PU networking

Five HTPB samples at the temperature of 40°C reacted with TDI and IPDI at a stoichiometry ratio of $R = 1.0$. According to Table 4, the values of the rate constant were determined by increasing the viscosity of the curing reaction with TDI and IPDI, and its relationship with \bar{M}_n of HTPB samples was evaluated. Figure 6 examines the effect of \bar{M}_n of the HTPB samples on the rate constants of PU networking in HTPB-based

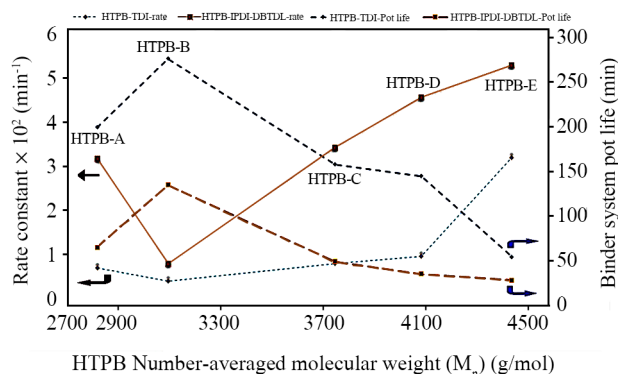


Figure 6. Rate constant and pot life changes versus the number average molecular weight (\bar{M}_n) of HTPB prepolymers for the HTPB-TDI, HTPB-IPDI-DBTDL-based system at 40°C.

PU system (primary vertical axis).

According to Figure 6, the rate constant of HTPB-based PU networking (left vertical axis) shows a decreasing behavior before $\bar{M}_{n, \text{HTPB}}$ of less than 3,100 g/mol. However, at $\bar{M}_{n, \text{HTPB}}$ of higher than 3,100 g/mol, the rate constant increases significantly. For example, for a PU system based on HTPB-E-TDI, with $\bar{M}_{n, \text{HTPB}} = 4,450$ g/mol, the rate constant value is $k = 3.32$. Therefore, it can be stated that with an increase in the \bar{M}_n of HTPB, the PU networking rate of the PU system based on HTPB increases. Moreover, for both TDI and IPDI curing agents the least rate constants were observed at $\bar{M}_{n, \text{HTPB}}$ of around 3,100 g/mol. This may indicate that at this critical \bar{M}_n , physical entanglements may obstruct PU networking.

Effect of \bar{M}_n on the pot life of the HTPB-based PU system

Pot life changes related to the HTPB-A, HTPB-B, HTPB-C, HTPB-D and HTPB-E samples were investigated. Figure 6 (right vertical axis) shows the changes in pot life versus \bar{M}_n of the samples for the HTPB-based PU system at the temperature of 40°C. The HTPB-E based PU system, which has the highest \bar{M}_n and initial viscosity compared to the other four samples, has the lowest relative pot life (28, 54 min). HTPB-A, with a lower initial viscosity than other samples, has a pot life of 200 min for the HTPB-A-TDI system, and 65 min for the HTPB-A-IPDI system. The pot life is 277 min for the HTPB-B-TDI system and 135 min for the HTPB-B-IPDI system. In general, with the increase in \bar{M}_n (hydroxyl value decreases [28]), the pot life decreases, which may be due to the increase in the initial viscosity.

According to Figure 6 (secondary axis), when \bar{M}_n is about 3000-3200 g/mol, the HTPB-based PU system

has the longest pot life (135, 277 min). Entanglement threshold or entanglement molecular weight (M_c) for HTPB may be considered around $M_c = 1,600$ g/mol [19, 43, 49], and the critical molecular weight value will be $M_c = 3,200$ g/mol ($M_c = 2M_e$ [50]). Therefore, it can be stated that about the \bar{M}_n of 3000-3200 g/mol, chain entanglements may disorder PU networking reaction. Chain entanglement becomes more important at molecular weights higher than 3000 g/mol [29, 51]. Therefore, for \bar{M}_n of about 3000-3200 g/mol, the HTPB-based PU system shows the longest pot life [29, 51]. A critical limit for the effect of microstructural parameters on the final properties of composites based on HTPB is presented by Manjari at around 3300 g/mol [52] and the physical properties of elastomer based on HTPB is reported by Ono at around \bar{M}_n of 3000 g/mol [28].

Dynamic rheological study of PU system based on HTPB

Viscoelastic tests are valuable and interpretable when performed within a linear viscoelastic range [53]. To determine the linear viscoelastic range of HTPB resin with different \bar{M}_n , HTPB-E resin sample (highest \bar{M}_n) was used, which considered the angular frequency in the strain sweep test, at constant frequency (1 Hz) and temperature (70°C). The value of the strain at which G'' and G' decrease is considered to be the final limit of the linear range. The linear viscoelastic region was determined to be 1-50%, and until this range is reached, there is no significant change in the structure of the sample.

The purpose of the time sweep test was to obtain the gel time of HTPB-based PU systems by examining the dynamic viscosity of the HTPB-based PU system and comparing it with the pot life obtained via static viscosity measured by the Brookfield viscometer. Rheological parameters including storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) are plotted against the networking time at constant temperature (70°C), frequency (0.1, 1 and 10 Hz) and strain range (<50%).

PU system based on HTPB-IPDI-DBTDL: Time sweep test

For the isothermal network reaction in gel-like samples (HTPB-based PU system), the gel time (t_{gel}) occurs when the reaction reaches the gel point. From the results of the mechanical-dynamic modulus for PU system, Winter and Chambon proposed a criterion for determining the gel point, at which the PU system gel time, the intersection of the storage modulus (G')

and the loss modulus (G'') ($G' = G''$), is obtained [54]. The ratio of the viscous modulus (G'') to the elastic modulus (G') called the loss factor ($\tan\delta$) (Equation 6), is a method for evaluating the viscoelastic behavior of the sample.

$$\tan \delta(t) = \frac{G''(t)}{G'(t)} \quad (6)$$

When the loss factor is less than 1, the elastic behavior is predominant, while the loss factor values above 1 indicate the viscous behavior. Since the loss factor, $\tan \delta$, at the gel point is independent of the angular frequency, the single point through which the $\tan \delta$ curves pass at different frequencies indicates the gel time (t_{gel}) [32, 55, 56].

HTPB-A-IPDI-DBTDL PU system

Figure 7 shows the time sweep test for HTPB-A based PU system at constant temperature of 70°C and three different angular frequencies (0.1, 1 and 10 Hz). In this figure, the storage and loss moduli (G' and G'') and $\tan \delta$ are plotted against networking time.

According to Figure 7, the storage and loss moduli (G' and G'') have increased at the beginning of the PU networking, which tend to show a plateau after a while. At the constant temperature of 70°C, according to Winter and Chambon, the gel point value $t_{G'=G''}$ [54] for PU systems based on HTPB-A-IPDI-DBTDL at three different frequencies are 98, 120, and >120 min; respectively. Moreover, in terms of the intersection of $\tan \delta$ at three different frequencies, t_{gel} of PU system based on HTPB-A-IPDI-DBTDL at the temperature of 70°C was found to be around 88 min.

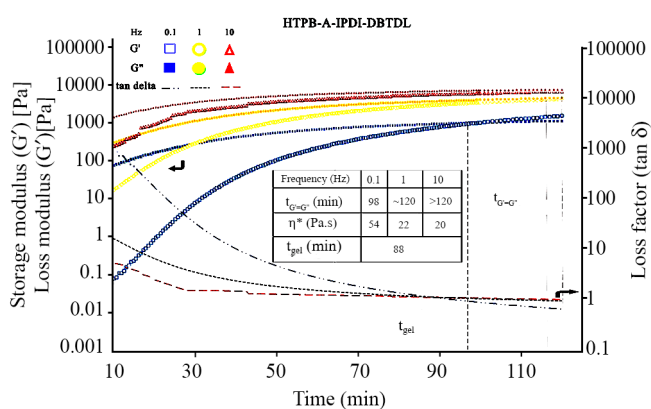


Figure 7. Changes in storage and loss moduli (G' and G'') and $\tan \delta$ versus networking time for PU system based on HTPB-A-IPDI-DBTDL at 70°C at three different angular frequencies (0.1, 1 and 10 Hz).

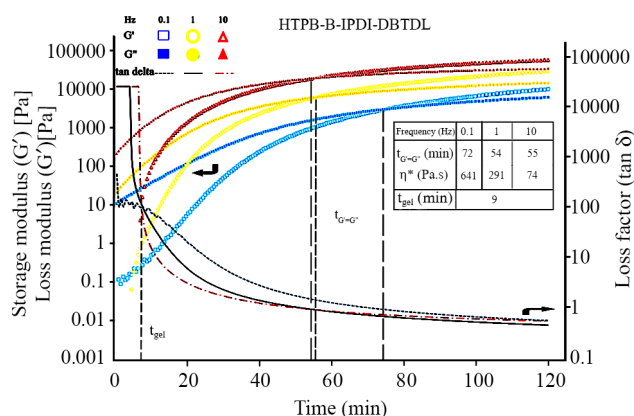


Figure 8. Changes in storage and loss moduli (G' and G'') and $\tan \delta$ versus networking time for PU system based on HTPB-B-IPDI-DBTDL at 70°C and three different angular frequencies (0.1, 1 and 10 Hz).

HTPB-B-IPDI-DBTDL PU system

Figure 8 shows the time sweep test for HTPB-B based PU systems at the constant temperature of 70°C and three different angular frequencies (0.1, 1 and 10 Hz). Similar to storage modulus (G'), the loss modulus (G'') increases at the beginning of the PU networking, which decreases after a while. At the beginning of the reaction, G' is smaller than G'' and over time becomes equal to and even larger than it. According to Figure 8, the storage and loss moduli (G' and G'') show a sooner intersection point in comparison to the HTPB-A sample at all frequencies. At the constant temperature of 70°C, according to Winter and Chambon, the gel point value $t_{G'=G''}$ [54] for PU systems based on HTPB-B-IPDI-DBTDL at three different frequencies is 72, 54 and 55 min, respectively. Moreover, in terms of the intersection of $\tan \delta$ at three different frequencies, t_{gel} of PU system based on HTPB-B-IPDI-DBTDL at the

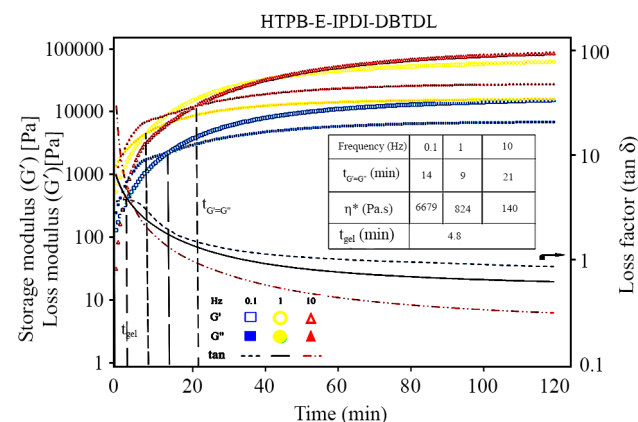


Figure 9. Changes in storage and loss moduli (G' and G'') and $\tan \delta$ versus cure time for polyurethane system based on HTPB-E-IPDI-DBTDL at 70°C and three different angular frequencies (0.1, 1 and 10 Hz).

temperature of 70°C was found to be around 9 min.

HTPB-E-IPDI-DBTDL PU system

Figure 9 shows the time sweep test for the HTPB-E based PU system at the constant temperature of 70°C and three different angular frequencies (0.1, 1 and 10 Hz). According to Figure 9, HTPB-E shows a sooner intersection point of storage and loss moduli (G' and G'') in comparison to HTPB-A and HTPB-B samples at all frequencies. At the constant temperature of 70°C, according to Winter and Chambon, the gel point value $t_{G'=G''}$ [54] for PU systems based on HTPB-E-IPDI-DBTDL at three different frequencies is 14, 9 and 21 min, respectively. Moreover, in terms of the $\tan \delta$ intersection at three different frequencies, t_{gel} of PU system based on HTPB-E-IPDI-DBTDL at the temperature of 70°C is found to be about 5 min.

As expected, by increase in \overline{M}_n of the HTPB samples in the HTPB-based PU system a systematic change in the loss factor ($\tan \delta$) and a decrease in the gel time (t_{gel}) occurred. Considering the differences between two methods for gel point determination, it can be understood that for the PU system based on HTPB-A (with the lowest \overline{M}_n) two methods have similar results. But for two other samples, HTPB-B and HTPB-E (with highest \overline{M}_n) two methods have very different results.

Comparing the results of pot life obtained based on rotational viscometry and gel point obtained based on rheomechanical spectrometry shows that in spite of presenting an optimum level for pot life in the PU system based on the HTPB-B sample with critical \overline{M}_n , but for the gel point, no optimal level was observed in this sample. In other words, it seems that the effect of physical entanglement was more important in pot life determination than gel point happening. Moreover, it can be concluded that the trends of both pot life and gel point decreased by increasing \overline{M}_n . Also, changes in complex viscosity and rotational viscosity with increasing \overline{M}_n showed a similar increasing trend.

Complexity viscosity (η^*) changes: effect of HTPB molecular weight

Figure 10 shows the change of η^* as a function of time at different frequencies (0.1 to 10 Hz) for the HTPB-A-IPDI-DBTDL polyurethane system at a cure temperature of 70°C, which is considered as an example. Other samples showed similar behavior to the HTPB-A system and are omitted for brevity.

Using dynamic analysis, the complex viscosity gives a good estimate of the viscosity during the curing

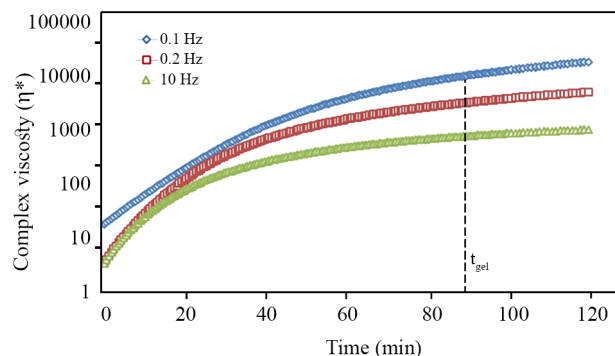


Figure 10. Complex viscosity (η^*) versus cure time for HTPB-A-IPDI-DBTDL PU system at 70°C at different angular frequencies (from 0.1 to 10 Hz).

reaction up to the gel point. The viscosity index and characteristics show that the molecular changes due to the effects of the reaction cause a significant change in the rheological behavior. It can be seen from Figure 10 that in the lower level of the gel time (t_{gel}), the frequency in the early stages of curing has less effect on the complex viscosity. After about 20 minutes, the frequency changes become more significant, which increases the complex viscosity as the frequency decreases. PU systems based on HTPB-A-IPDI-DBTDL showed the lowest and HTPB-E-IPDI-DBTDL samples showed the highest complexity viscosity (η^*), due to changes in \overline{M}_n of HTPB.

Rheological-kinetic networking model of HTPB-based PU system

A kinetic model developed by Hsich and co-workers, which has proved to be operative in describing the curing behavior of filled elastomeric systems [57, 58], was used to describe the evolution of rheological properties in the networking system. In this model, changes of dynamic properties, such as elastic modulus (G') are interpreted during cross-linking in terms of mean square fluctuations of thermodynamic ordering parameters (Equation 7):

$$\alpha = \frac{(G'_t - G'_0)}{(G'_\infty - G'_0)} = \exp \left[- \left(\frac{t - t_0}{\tau} \right)^\beta \right] \quad (7)$$

where in, (α) is the rheological degree of conversion which can be evaluated at different constant temperatures from the time dependence of storage modulus (G') or loss modulus (G''), G'_t is the value of the storage modulus at time t ; G'_0 and G'_∞ are the values of the storage modulus at the beginning of the experiment and at the eventually cross-linked polymer and β and τ are fitting parameters, which

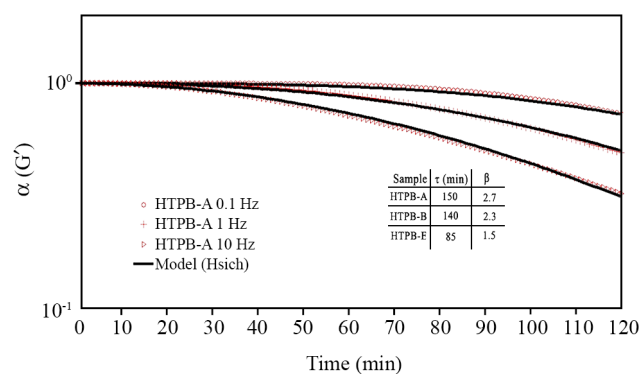


Figure 11. Rheological degree of conversion, α , as a function of curing time for polyurethane system based on HTPB-A-IPDI-DBTDL at three constant angular frequencies of 0.1, 1 and 10 Hz and temperature 70°C.

τ being interpreted as a characteristic relaxation time associated with the chemical reaction. Figure 11 shows the rheological degree of conversion (α) (calculated from Equation 7) as a function of curing time for the polyurethane system based on HTPB-A-IPDI-DBTDL at three constant frequencies of 0.1, 1 and 10 Hz. Obviously, the degree of conversion is constant before the onset of the cross-linking process (around 20 min) and then increases strongly as curing time progresses [32]. This model was used to fit the data, and a typical fit at 70°C is shown in Figure 11. It was found good agreement between experimental data and the model predictions. Cross-linking data for different types of polyurethane systems based on HTPB-IPDI-DBTDL with dissimilar molecular weights were fitted using the Hsich model and the values of the fitting parameters, τ and β are tabulated in Figure 11.

CONCLUSION

In this study, the effect of the HTPB \bar{M}_n on the chemorheological behavior of HTPB-based PU system was investigated using TDI and IPDI curing agents. The results showed that by increase in the number average molecular weight, the pot life decreases. The PU system with the highest \bar{M}_n showed the shortest pot life. At a critical molecular weight ($M_c = 3000\text{--}3200$ g/mol), the physical chain entanglements may disorder PU networking reaction and have the longest pot life. At the stoichiometric ratio of $R = 1.0$, the intersection point of G' and G'' does not correspond to the gel point as expected, but for the HTPB-E based PU system it was found that the crossing point ($t_{G'=G''}$)

is about twice t_{gel} (crossing point of $\tan \delta$ at different frequencies). The PU system based on HTPB-A-IPDI-DBTDL showed the lowest and the HTPB-E-IPDI-DBTDL sample showed the highest complex viscosity (η^*), due to changes in molecular weight of the prepolymer sample. Therefore, by increasing the molecular weight of HTPB, the complex viscosity of PU system increases.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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