

KINETIC POLYMERIZATION OF CASTOR OIL POLYURETHANES BY A RHEOLOGICAL METHOD AND NEURAL NETWORK

Joziel A. Cruz, Alexia Oberdiek, Otávio Bianchi and Sandro C. Amico

1 – Department of Materials Engineering, University of Rio Grande do Sul (UFRGS)- Porto Alegre - RS, Brazil
joziel.cruz@ufrgs.br

Abstract – This work presents the studies of kinetic polymerization of castor oil-based polyurethane using thermal analysis by isothermal of small amplitude oscillatory shear rheometry. The gelation time was determined by the crossover between modulus storage (G') and loss (G''). Arrhenius equation was used to plot a graph of $\ln(t_{gel})$ vs. $1/T$. The angular coefficient was obtained using a linear fit, and this was used to calculate the activation energy of polymerization. The experimental data were analyzed using neural network NN using Bayesian regularization. The activation energy measured for the castor oil-based polyurethane resin was 49.98 kJ/mol for experimental data and 50.41 kJ/mol for NN simulation. A high level of reliability of the predicted rheometry curves was obtained due to an excellent agreement between experimental and simulated results.

Keywords: Kinetics polymerization; Polyurethane; Castor oil; rheometry; Activation energy; Neural Network.

Introduction

Polyurethane-based systems are an extremely versatile material used in various applications that vary from linear polymers to thermosetting plastics [1]. The polyurethane (PU) structure is comprised of soft and hard blocks, and its properties can be tuned to satisfy particular material requirements. The soft segments, derived from a polyol, confer elastic characteristics to the polymer, whereas the hard is commonly formed by isocyanates and extenders [2].

The vegetable castor oil has been widely applied in the chemical industry as a raw material for paints, coatings, inks, and lubricants. It is also used as a biomaterial in implants and therapeutics agents, even in optics and electronic devices [3] It is considered appropriate for application in isocyanate reactions to produce polyurethane elastomers, millable, castables, adhesives, coatings, and foam. Some semirigid foams used as thermal insulation are produced through castor oil/polyether and toluene diisocyanate reactions. Castor oil, a non-food vegetable oil, contains hydroxyl groups (163 mg KOH/g). It is used to produce bio-based polyurethane because of its numerous advantages such as low toxicity and biodegradability and high purity [4]. Castor oil-based polyurethanes usually have a good balance of properties and resistance to hydrolytic degradation.

The cure mechanism and kinetics determine the network morphology, which dictates the cured product's physical and mechanical properties. Therefore, knowledge of the kinetic parameters of a reactive resin is essential for the design and processing of polymer and composite technologies. Many characterization methods have been used to monitor the kinetics of polymerization reactions[5]. One relevant parameter for the study of the curing process is the storage modulus (G'), which is proportional to the crosslinking density of the network being formed by chemical bonds [6].

There are many different methods and mathematical models for determining the kinetic characteristics of the polymerization process of polyurethane [7]. However, not all kinetics models can accurately describe the change in the kinetic function for each specific type of polymer. To simplify the simulation, it is proposed to use neural networks (NN), which are currently widely used for forecasting and approximation in many technical and humanitarian sciences fields.

Neural networks are self-learning systems that effectively build non-linear dependencies that more accurately describe sets of experimental data. The main advantage of neural network modeling is the training and synthesis of accumulated information based on a selection of experimental data [8].

In this context, the main purpose of this work is to obtain the activation energy (E_a) during polymerization of castor oil-based polyurethane using the dynamic rheology method and verify the possibility of using a neural network to predict the activation reaction energy.

Experimental

Polymeric diphenylmethane diisocyanate (MDI, purchased from Polysystem 31wt.% of free isocyanate). The castor oil (hydroxyl number 188, functionality 2.7, supplied by Alpha Quimica Ltda, Brazil) has a water removal process (for 8 hours at 100°C under vacuum) to polymerize. The polymerization kinetics of the castor oil polyurethane sample was studied from isothermal experiments in an oscillatory rheometer, at temperatures of 40, 50, 60, 70 and 80°C at an oscillation frequency of 1Hz, shear stress of 2Pas, parallel plates of 25 mm in diameter, distancing between 0.5 mm plates, in an Anton Paar Physica MCR 101 rheometer. The polymerization activation energy (E_a) was determined using the Arrhenius equation by performing the logarithm (Equation 1), assuming t_{gel} as the time in which the storage module G' is equal to the loss module, G'' [9]. Thus, a graph of $\ln(t_{gel})$ vs $1/T$ allows to obtain a straight line whose angular coefficient is equal to:

$$\ln(t_{gel}) = \ln(A) - \frac{-E_a}{RT} \quad (1)$$

Where A is the frequency factor (1/s), E_a is the activation energy of the cure reaction (kJ/mol), R is the universal gas constant (8.32 J/mol K), and T is the temperature (K). The graphic $\ln k$ versus $1/T$ shows a straight line where the activation energy and the frequency factor are obtained by the angular and linear coefficient of the straight line, respectively. A minimum of three isothermal experiments in different temperatures is necessary to obtain these parameters [9].

To analyze the rheological experimental data, the ANNs modeling was used. The method evaluated was Bayesian regularization, where the algorithm typically requires more time but can result in good generalization for difficult, small, or noisy datasets. Training stops according to adaptive weight minimization (regularization). The simulation was carried out in the MATLAB environment using the fitting neural network tools plugin, which will allow setting the number of neurons in the hidden layer and changing the percentage of training, test, and test samples.

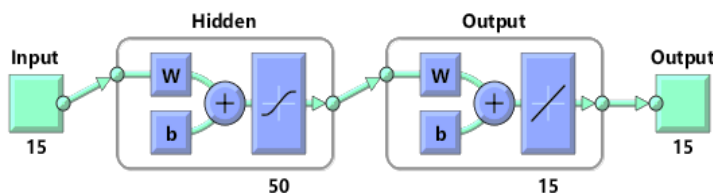


Figure 1: Block diagram of a neural network

The number of neurons in the hidden layer was set in the amount of 50 pieces. The training set was 70%, the validation and testing was 15%, with 11, 2, and 2 samples respectively Fig. 1. The neural network was trained using the “with the teacher” algorithms. Three vectors were specified - input values (INPUTS), target output values (OUTPUTS), and test. The experimental array of data with modulus G' and G'' in 5 temperatures was used as an input vector.

Results and Discussion

Viscosity increase is the most common method to identify the gel point, one of the essential rheological parameters in processing a crosslinked polymer. Strictly, the gel point is where the viscosity takes on an infinite value [10]. However, it is not possible to measure this accurately. One method is to apply a small amplitude oscillatory shear during polymer cure using an oscillatory rheometer. Initially, the loss modulus G'' (pseudo viscous liquid) is high, while the storage modulus G' is still negligible. Subsequently, as the degree of conversion increases, G'' increases and G' increases sharply until it crosses and exceeds G'' presenting a pseudo solid elastic behavior [11].

According to ASTM D7750, in this type of test with small amplitude oscillatory shear, the gel time can be interpreted as the crossover point between G' and G'' ($\tan \delta = 1.0$). Fig 2 shows the results of the storage modulus (G') and loss modulus (G'') during the polymerization of castor oil polyurethane as a function of time at temperatures of 40,50,60,70 and 80°C studied in the oscillatory rheometer.

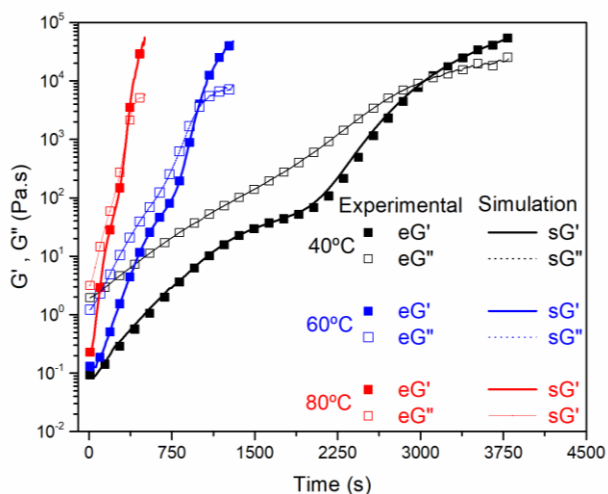


Figure 2: Curves of G' and G'' modulus experimental (rheological method) and simulation (neural network).

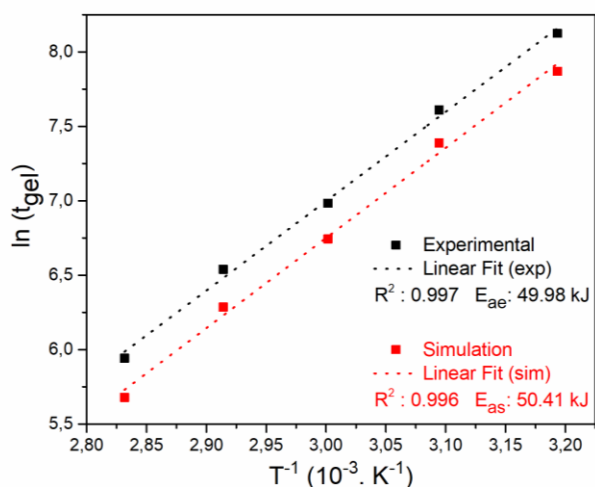


Figure 3: $\ln(t_{gel})$ versus $1/T$ used to obtain the activation energy during polymerization of polyurethane

The symbol dots represent the experimental results, while the solid lines are the fits derived from the NN mathematical approach for each isothermal. For better visualization of the graph, the curves G' and G'' of temperature 50 and 70°C will not be required in Fig 2.

Table 1: Modulus (G', G'') and gel time experimental and simulation networks neurais of castor oil polyurethane polymerization.

Temperature (°C)	Experimental		Simulation - NN	
	$G' = G''$ (Pa.s)	t_{gel} (s)	$G' = G''$ (Pa.s)	t_{gel} (s)
40	10713	3105	10218	3042
50	4540	1855	4602	1879
60	3339	991	3337	986
70	1582	636	1503	624
80	1221	350	1221	340

Drastic structural changes occurred in the samples, which became solid-like viscoelastic polymers by intermolecular and intramolecular cross-linking [4]. From the Fig. 2 is possible see, that temperature has significant impact on the reaction rate of the polymerization process. The curves of G' and G'' crossed over at a time point, which greatly differed at different curing temperatures, according to Table 1 results.

As the reaction polymerization temperature rise, the time until the crossover of modules G' and G'' (t_{gel}) decreases. This occurs because there is a greater probability of $-NCO$ and $-OH$ groups reacting due to increased mobility and effective collisions. The increase in the reaction temperature increases the monomer entropy, and consequently, the reaction rate is increased, as shown in Fig. 2[13].

Based on the data assigned in Table 1, the natural logarithm of the t_{gel} for the polymerization of castor oil polyurethane was found, and the graph was plotted as a function of the inverse of the absolute temperature ($1/T$), as shown in Fig. 3. From the linear fits, the polymerization activation energy value is determined using an Arrhenius equation (Eq. 1). Generally, chemical reactions present activation energy from 30 to 100 kJ/mol [14].

The E_a of the castor oil-based polyurethane experimental found was 49.98 kJ/mol and 50.41kJ/mol that can indicate a relatively high reactivity system[9]. The values found for the activation energy are consistent with other studies found in the literature (45-56 kJ/mol, in which the polymerization kinetics of polyurethane systems was studied by other techniques such as attenuated total reflection Fourier transform infrared spectroscopy (ATR) - FTIR)[7], Differential Scanning Calorimetry (DSC) [15-16]. The E_a values found showed excellent agreement between experimental and simulated results.

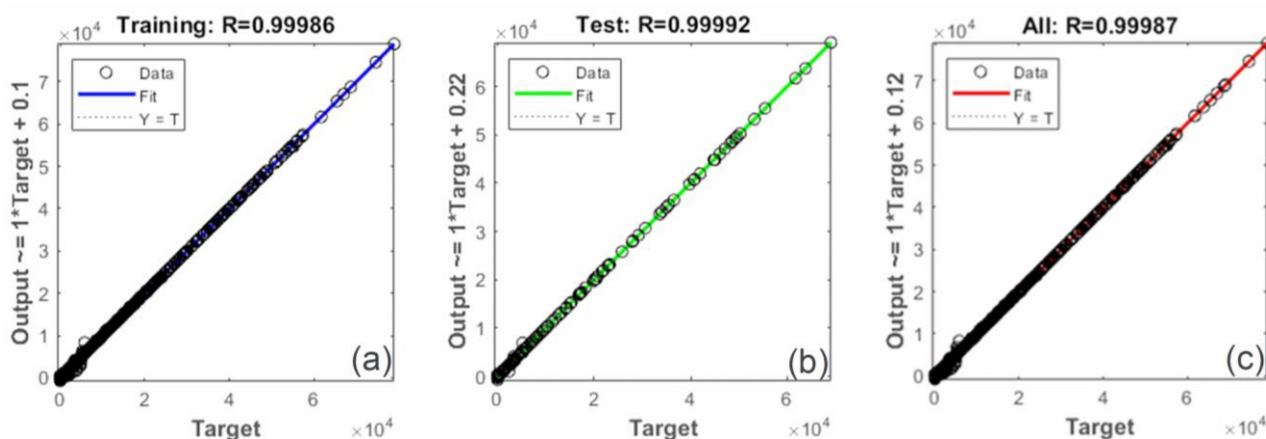


Figure 4: Neural network Regression Charts using Bayesian regularization method for (a) Training, (b) Testing and (c) Validation.

As can be seen from Fig. 4, the highest NN performance is achieved when training the network using the Bayesian regularization method, with values of correlation coefficients bigger than 0.999. The best performance of the model occurs in the last 896th epoch of the learning iteration cycle, with an associated final mean squared error of approximately $8,176 \times 10^{-7}$, which is significantly lower than the target MSE value of 1×10^4 , indicating that the best-fit function of the training targets was perfectly estimated.

Conclusions

In this study was possible to obtain the E_a during the polymerization of castor oil-based polyurethane using oscillatory rheometer. It was possible to evaluate the experimental result using NN simulation with a high level of reliability. The results of E_a found studied system was (49.98 and 50.41) kJ/mol for experimental and simulation respectively. The results presented contribute to optimizing polymerization reactions and future applications of this type of resin in the production of composites based on castor oil polyurethanes.

Acknowledgements

The authors acknowledge Brazilian Agency Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) for scholarships, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) and also thanks the Universidade Federal do Rio Grande do Sul (UFRGS).

References

1. A. Pearson and H. E. Naguib, *Composites Part B: Engineering*, vol. 122, pp. 192–201, 2017.
2. R. Gogoi, M. Alam, and R. Khandal, *International Journal of Basic and Applied Sciences*, vol. 3, 2, 2014.
3. L. Mihail, *Chemistry and Technology of Polyols for Polyurethanes*, 1st ed., vol. 14, no. 3. Shawbury, Shrewsbury, Shropshire: British Library., 2005.
4. S. Oprea, *Journal of the American Oil Chemists' Society*, vol. 87, no. 3, pp. 313–320, 2010,
5. B. Lucio and J. L. De La Fuente, *Thermochimica Acta*, vol. 625, pp. 28–35, 2016
6. A. Atiqah, M. T. Mastura, B. A. A. Ali, M. Jawaid, and S. M. Sapuan. *Polymer Composites*,” pp. 233–248, 2017.
7. S. T. Cho, J. il So, J. Y. Jung, S. Hwang, S. H. Baeck, and S. E. Shim. *Macromolecular Research*, vol. 27, no. 2, pp. 153–163, 2019,
8. O. Dmitriev and A. Barsukov. *Decision and Control*, vol. 337, Springer Science and Business Media Deutschland GmbH, 2021,
9. A. C. Milagnese, M. O. Cioffi, H. Voorwald, and C. Shigue, *Journal of Applied Polymer Science*, vol. 122, pp. 3168–3171, 2011.
10. D. K. Chattopadhyay and K. V. S. N. Raju. *Progress in Polymer Science (Oxford)*, vol. 32, no. 3, pp. 352–418, 2007
11. F. Chambon, Z. S. Petrovic, W. J. MacKnight, and H. H. Winter. *Macromolecules*, vol. 19, no. 8, pp. 2146–2149, 1986.
12. G. Santhosh, S. Reshmi, and C. P. Reghunadhan Nair, *Journal of Thermal Analysis and Calorimetry*, vol. 140, no. 1, pp. 213–223, 2020.
13. B. Lucio and J. L. de La Fuente. *Thermochimica Acta*, vol. 625, pp. 28–35, 2016.
14. M. Costa, M. Cerqueira, and L. Pardini. *Química Nova*, vol. 3, p. 1999.
15. A. Olejnik, K. Gosz, and Ł. Piszczyk. *Thermochimica Acta*, vol. 683, 10, 2019.
16. L. Dall Agnol, H. L. Ornaghi, F. Monticeli, F.T.G. Dias, O. Bianchi. *Polymer Engineering and Science*. Vol 61. 2021.