

Determination of The T_g , T_d and the Refractive Index (n) of the Poly (PEA) Network as a Function of the Degree of Crosslinking.

N. Benmessaoud^{1,2}, T. Bouchaour¹, U. Maschke²

¹Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Abou Bakr Belkaid, 13000 Tlemcen, Algeria

^{1,2} nouarab87@gmail.com

¹ bouchaour@yahoo.fr

²Laboratoire de Chimie Macromoléculaire (UMR CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

² ulrich.maschke@univ-lille1.fr

Abstract— In this work, we present a characterization of the physical properties of a crosslinked network of poly (2 phenoxy ethyl acrylate) (poly (PEA)) prepared by UV photopolymerization. Glass transition temperature (T_g), thermal degradation temperature (T_d) and refractive index (n) of poly (PEA) networks are determined experimentally. The study of behavior of variation of these parameters as a function of the degree of crosslinking was made. Empirical models of Askadskii et al are also used to calculate these physical parameters. The estimated parameters have been compared with the available experimental values.

Keywords— crosslinked network, UV photopolymerization, Glass transition temperature, thermal degradation temperature, refractive index.

I. INTRODUCTION

Poly (2-Phenoxyethyl acrylate) networks are chemically synthesized by UV radiation. This method has proven effective with acrylates, particularly because of its advantages. UV radiation polymerization is a method that shows its reliability compared to other methods of synthesis and considered the cleanest method since it does not require additives that can alter the properties of the polymer so it usually occurs at ambient temperatures [1].

The study of the physical properties of materials, whether natural or artificial, and their relationship with the environment, is very important in the field of application and industrial. As a result, many methods are developed as well as many academic studies are conducted to study the relationships between physical properties and the extraction of the laws that connect them.

On the other hand, several theoretical models have been developed to predict these properties. There are models based on the chemical structure of the repeating unit. The approaches that derive the best predictions from these properties are those of: van Krevelen [2], Bicerano [3], [4] and Askadskii - Matveev [5] – [10]. These three models are different in the treatment method but have given good results compared to the experimental ones for the case of linear polymers and copolymers. However, polymer networks are

much more processed by Askadskii et al. They have succeeded in presenting empirical models for calculating the physical properties of polymer networks by taking into account the presence of the crosslinking point as well as its functionality.

In this work we will study the variation of vitreous transition temperatures and those of thermal degradation as well as the variation of the refractive index as a function of the degree of crosslinking experimentally using different techniques; An attempt has also been made to compare the experimental results with those obtained by calculations based on the Askadskii's model.

II- MATERIALS AND METHODS

1- Materials

The acrylic monomers used for this study is 2-Phenoxy Ethyl Acrylate (PEA) (from Aldrich). The cross-linking agent is: 1,6-Hexane Diol Diacrylate (HDDA) (supplied by Cray Valley, France). The photo-polymerization agent used is: 2-hydroxy-2-methyl-1-phenyl-propane-1 (Darocur 1173, from Ciba Geigy). The chemical structures of the different components are given in Figure 1.

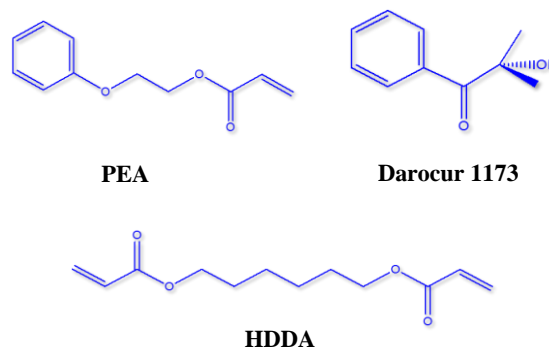


Fig 1: Chemical structure of the components of the initial mixtures.

The kinetics of polymerization were carried out using a Fourier Transform Infrared Spectrometer (FT-IR "Perkin Elmer").

2- Polymer networks synthesis:

Blends of PEA/HDDA/Darocur1173, were prepared in different weight fractions by varying the quantity of HDDA and keeping the amount of the photo initiator constant (PEA/HDDA/Darocur1173=99/0.5/0.5wt.%,...), These initial mixtures were stirred mechanically for some hours before they were cast in small flat sample holders, exhibiting a single homogeneous phase. The samples were exposed to UV radiation under nitrogen atmosphere, using Philips TL08 UV lamps exhibiting a wavelength $\lambda=365$ nm and an intensity $I=1.5$ mW/cm². The exposure time was fixed at 20 minutes to achieve complete conversion of all monomers in the precursor system. The samples obtained are optically transparent cross-linked polymer networks.

A characterization by the infrared spectroscopy technique (FT-IR) before and after polymerization showed the total disappearance of the characteristic strip of the acrylates (C=C) at 1635 cm⁻¹, indicating that the conversion is very important (see Figure 2).

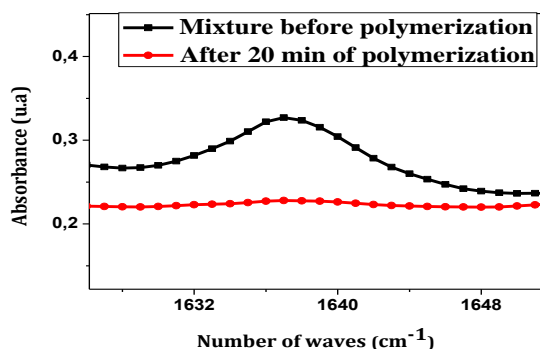


Fig 2: Illustration of the disappearance of the characteristic band C=C (1637cm⁻¹).

III- EXPERIMENTAL PART

A. Determination of glass temperature:

Analysis of transition temperatures and enthalpies of polymers networks were performed on a Pyris Diamond DSC apparatus (Perkin-Elmer model 8000).

Figure 3 shows the characteristic thermograms for Poly(PEA) / HDDA polymer networks.

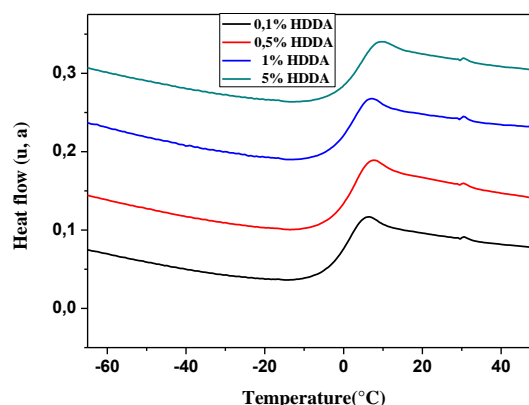


Fig 3: Influence of the degree of crosslinking (% HDDA) on the thermograms of isotropic networks of poly 2-Phenoxy-Ethyl-Acrylate (Poly (PEA)).

To visualize the influence of the increase of the glass transition temperature T_g , we have traced (Figure 4) the evolution of the glass transition temperature as a function of the degree of crosslinking of the Poly (PEA) networks. On this graph, it is clear that the T_g increases following the increase in the degree of crosslinking. We also note that this increase to a parabolic form.

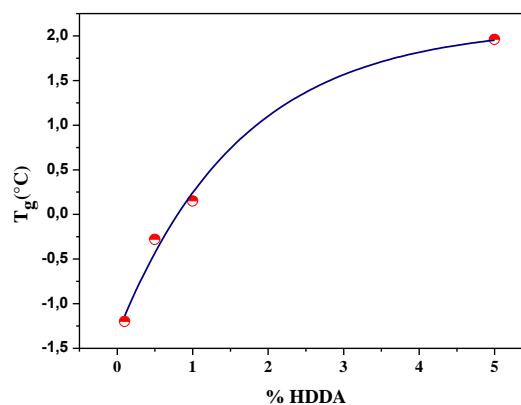


Fig 4: Influence of the degree of crosslinking (% HDDA) on the glass transition temperature of Poly (PEA) networks.

The increase of the glass transition temperature of a polymer matrix following the increase in crosslinking is a phenomenon that has already been observed in the literature [11] – [12]. This effect is not surprising and can be explained in terms of the internal mobility of the system. Indeed, the presence of crosslinking points (ie chemical bridging) between the polymer chains reduces the overall mobility of the system. Therefore, a reduction in the mobility of the molecules leads to an increase in the T_g because it requires more thermal energy to cause the movements of the polymer chains.

B. Determination of the temperature of thermal degradation:

Thermogravimetric analyzes were performed using a TGA apparatus Pyris 1 from Perkin Elmer.

The weight loss curves were recorded over the 20-700 °C temperature range at a rate of 10 ° C / min in a nitrogen atmosphere and are shown in Figure 5.

The network Poly (PEA) cross-linked at 0.1% HDDDA has a thermal stability in the range 20- 100 ° C (Figure 5), and then the network manifests a more significant loss of mass from the temperature 320 ° C to 95% decomposition to 430 °. The presence of a second domain for total decomposition may be due to an oxidation reaction due to the presence of oxygen.

Noting in this study that the rate of crosslinking has no more influence on the system behavior and its temperature of degradation of fate that one marks the same value of T_d whatever the degree of crosslinking.

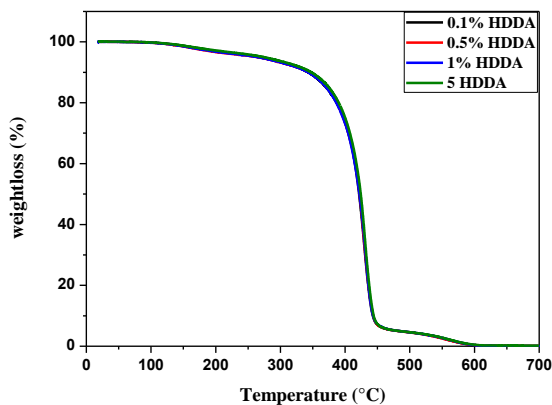


Fig 5: Thermogravimetric curves of system (Poly (PEA) / HDDDA)

C. Determination of the refractive index:

The refractive index (n) is an important optical property of polymers and is widely used in materials science. As it is characteristic for each material, it can be used for identification purposes or for the prediction of other properties. For example, the refractive index undergoes a second order transition at the glass transition temperature and can therefore be used to determine its value.

The refractive index is defined as the speed of light in vacuum relative to the velocity in the polymer. It is directly related to polarizability and depends on the wavelength of light.

Most polymers are amorphous and are, therefore, isotropic. Their refractive indices are the same for all the senses that the path of light can take through the solid. Several methods for determining the refractive indices of amorphous polymers have been carefully described in the literature.

To measure the refractive index of our polymer networks, we adopted a simple method that gives more precise results invented by M. Gharbia at al. [13].

The principle of the optical experimental technique consists of measuring the deflection by reflection of a laser beam ($\lambda = 633 \text{ nm}$) at normal incidence (Figure 6).

To measure the refractive index, we illuminate a vacuum prism that gives a first rectangular point. The same prism containing the polymer network thin film gives a second rectangular deflection point. The laws of Descartes make it possible to measure the index of refraction.

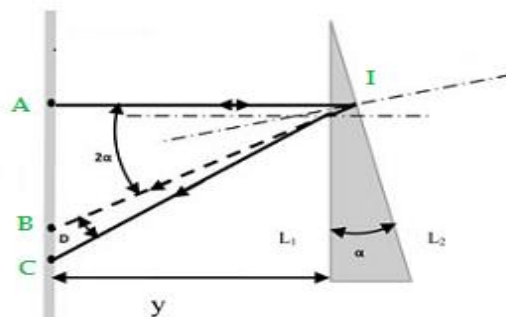


Fig 6: picture of typical spots of light by reflection through the vacuum prism and the isotropic prismatic sample centered on the reflected laser beam [13]

According to the law of Snell-Descarte we have:

$$n = \frac{\sin(2\alpha + D)}{\sin(2\alpha)}$$

the variation of the refractive index as a function of the degree of crosslinking is illustrated in figure 7. it is observed that the refractive index increases in the denser networks. As a beam of light enters a medium, it causes a disruption of the electron density, slowing down the electromagnetic wave. Dense materials slow down the wave, increasing the refractive index (n). the appearance of the variation of (n) is similar to that of the variation of the glass transition temperature (T_g); a growing parable.

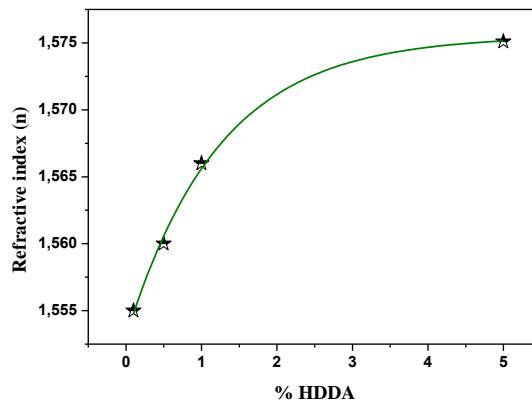


Fig 7: variation of the refractive index as a function of the degree of crosslinking (% HDDDA)

IV- CALCULATION PART

A. Calculation of the glass transition temperature of Poly (PEA) polymer networks:

It has been determined experimentally that the glass transition temperature, as well as many other properties of the network systems, depends on the number of repeating units between the cross-linked points 'm', in other words the degree of crosslinking.

Askadskii at al's approach to calculating the glass transition temperature is based on considering the unit as a set of anharmonic oscillators, connected by different types of intermolecular bonds. The magnitudes of the increments, put into the calculation, have a definite physical meaning and are energetically characterized both as weakly dispersive interactions and as strongly intermolecular interactions (dipole-dipole interaction, H bonds, etc.).

The general formula used to calculate the glass transition temperature of polymer networks is as follows:

$$T_g = \frac{\left(\sum_i \Delta V_i \right)_{f.r.}}{\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_{l.ch.} + \left(\sum_i K_i \Delta V_i \right)_{crl.p}}$$

Where:

$\sum \Delta V_i$ is the van der Waals volume of the repeated fragment in the network.

$(\sum a_i \Delta V_i + b_j)_{l.ch.}$ is a selection of constants for linear strings participating in the repetitive fragment of the network such as:

- a_i is a selection of constants, which characterizes the energy of a weak dispersion interaction as the average contribution of each atom in this interaction.
- b_j is a selection of constants that characterizes the energy of a strong specific intermolecular interaction (dipole-dipole, hydrogen bonds, etc.).

$(\sum K_i \Delta V_i)_{crl.p}$ is a selection of constants for the network link point.

We will apply this equation to our poly (PEA) network. This network displays the structure (Figure 8). He owns.

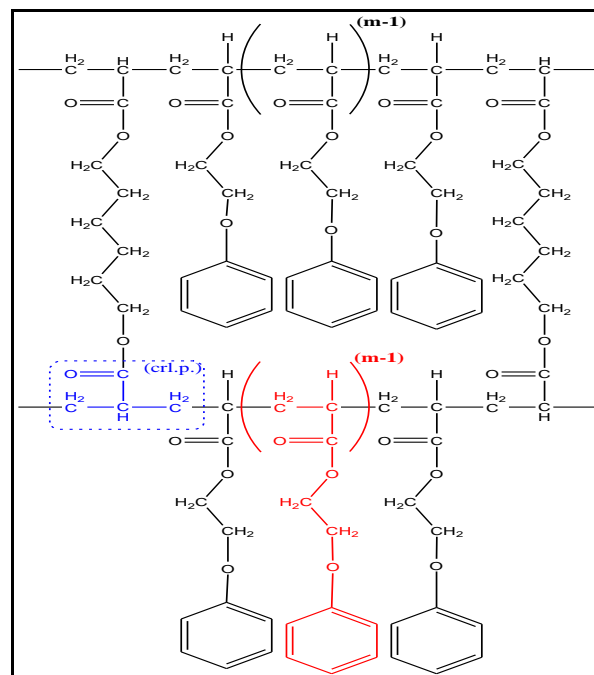


Fig 8: representation of the poly (PEA) polymer network structure.

The general formula of the glass transition temperature T_g obtained is as follows:

$$T_g = \frac{181 * m + 107.6}{677.42 * m + 317.08} \cdot 10^3 (K)$$

B. Calculates thermal degradation temperature T_d for Poly (PEA) networks:

The approach for calculating the temperature of the thermal degradation T_d is the same as for the estimation of the glass transition temperature T_g . But in this case, the energy of the chemical bonds, but not that of the intermolecular interaction, is taken into account in the calculations, although the latter also has a significant influence on the dissociation energy of the chemical bonds.

The form that describes the degradation process is as follows:

$$T_d = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i}$$

Or

- T_d : is the 'Onset' temperature of thermal degradation.
- K_i : are contributions of the individual atoms to the initial degradation.

using the same structure of Figure 8 to perform the calculations. we thus obtain the equation which describes the variation of T_d as a function of the number of monomers between two crosslinking points as follows:

$$T_d = \frac{181 * m + 107.6}{249.21 * m + 164.12} \cdot 10^3 (K)$$

C. Calculates the refractive index 'n':

The refractive index is the most important optical property of polymers. The index of refraction n is determined from the following relation which is derived from the famous Lorentz-Lorentz formula:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{k_{av} \sum_i R_i}{N_A \sum_i \Delta V_i}$$

Where:

- N_A : is the number of Avogadro;
- K_{av} : is the average molecular packing coefficient (for voluminous monolithic bodies, $K_{av} = 0.681$ and for films, $K_{av} = 0.695$);
- $\sum R_i$: is the molecular refraction which includes the refractions relative to each atom and the type of bond (double, triple, etc.).

the application of this formula on the structure shown in figure 8 gives us the following expression:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{0.695(50.494 * m + 28.262)}{0.6023(181 * m + 107.6)}$$

D. Result and discussion:

the table below shows a comparison between the experimental results and those calculated by the empirical models of Askadskii.

knowing that the values of m corresponding to those of % HDDA are calculated from the following equation [14]:

$$m = \frac{\overline{M_c}}{M_r}$$

- $\overline{M_c}$ is the number average molecular weight between crosslinks.
- M_r is the molecular weight of the PEA repeating unit.

we also note that the values of a_i , b_j , ΔV_i and K_i of individual atoms in the repeating unit of the polymer are obtained from the reference [5].

TABLE I: ESTIMATED AND AVAILABLE VALUES OF PHYSICAL PARAMETERS OF POLY (PEA) NETWORK

Parameter	% HDDA	Estimated value	Experimental value
Glass-Transition Temperature (T_g)	0.1	-6	-1.2
	0.5	-5.6	-0.28
	1	-5.5	0.15
	5	-4.3	1.96
Temperature of Initial Degradation (T_d)	0.1	450°C	430°C
	0.5	450°C	430°C
	1	450°C	430°C
	5	450°C	430°C
Refractive Index (n)	0.1	1.557	1.555
	0.5	1.556	1.56
	1	1.556	1.566
	5	1.556	1.575

V- CONCLUSIONS

determination of different physical parameters of poly (2-phenoxyethyl acrylate) networks was obtained using different techniques. the study of the variation of these parameters as a function of the degree of crosslinking shows that the latter has an influence on the glass transition temperature and on the refractive index. the variation behavior of these two parameters is similar and shows increasing parabolic speeds. This observation leads us to think that there is a relationship between the two properties. but more work is needed to confirm this remark. the degree of crosslinking has no influence on the temperature of thermal degradation. the calculated calculations based on the empirical models of Askadskii are in good agreement with what has been obtained experimentally for the case of glass transition temperatures and thermal degradation, while the calculation of the refractive index shows that the latter is not affected by the degree of crosslinking which is not the case in the experimental. Overall, the comparison between the theoretical results and the applied results is acceptable, even the difference between the results is in the standards.

ACKNOWLEDGMENT

REFERENCES

- [1] C. Decker, Kinetic Study and New Applications of UV Radiation Curing, *J Macromol Rapid Commun*, Vol. 23, pp.1067–1093, (2002).
- [2] D.W. van Krevelen, and K. Nijenhuis, *Properties of Polymers*, Amsterdam: Elsevier, 2009.
- [3] D.W. van Krevelen, *Properties of Polymers*, Amsterdam: Elsevier, 1997.
- [4] Bicerano, J., *Prediction of Polymer Properties*, New York: Marcel Dekker, 1993.
- [5] A. A. Askadskii, *Computational Materials Science of Polymers*, Cambridge: Cambridge Int., 2003.
- [6] A. A. Askadskii, *Physical Properties of Polymers: Prediction and Control*, Amsterdam: Gordon and Breach, 1996.
- [7] A. A. Askadskii, *Analysis of the Structure and Properties of High_Crosslinked Polymer Networks*, London, Paris, New York, Melbourne: Harwood, 1992.
- [8] A. A. Askadskii, influence of crosslinking density on the α properties of polymer networks, *Polymer Science U.S.S.R.* Vol. 32, pp. 2061-2069, 1990
- [9] A. A. Askadskii, Methods for Calculating the Physical Properties of Polymers. *Review Journal of Chemistry*, Vol. 5, pp. 83–142, (2015)
- [10] A. A. Askadskii, T. A. Matseevich, and V. A. Markov, Determination of Glass-Transition Temperatures of Polymers: A Modified Computational Scheme, *Polymer Science, Series A*, Vol. 58, pp. 506–516, (2016).
- [11] R. Vera-Graziano, F. Hernandez-Sanchez, *J. Appl. Polym. Sci.*, Vol. 55, pp. 1317-1327, (1995)
- [12] M. Richard Vendamme, PhD thesis of the University of Science and Technology of Lille (2004).
- [13] I.Loubiri, S. Fadhel and M. Gharbia, "Refractive index and dispersion measurements in prismatic thin film of phasmodic columnar liquid crystals" *Molecular Crystals and Liquid Crystals*, Vol. 648, pp. 22-28, (2017).
- [14] C. T. Reinhart and N. A. Peppas, solute diffusion in swollen membranes. Part ii. Influence of crosslinking on diffusive properties, *Journal of Membrane Science*, Vol. 18, pp. 227-239, (1984).