PREPARATION AND CHARACTERIZATION OF THE MECHANICAL PROPERTIES OF TiO₂/EPOXY RESIN NANOCOMPOSITES BY DIFFERENTIAL SCANNING CALORIMETRY AND RAMAN SPECTROSCOPY

L. Merad [1*]**, M. Bouchaour** [1]**, M. J. M. Abbadie** [2]**, B. Benyoucef** [1]

[1] *Université de Tlemcen, Faculté des Sciences, Département de Physique Unité de Recherche*
"Matériaux et Energies Renouvelables", 119, Fg Pasteur, Tlemcen, 13000, Algeria;
e-mail: merad@mail.univ-tlemcen.dz
[2] *School of Materials Science & Engineering, Nanyang Technological University,*
Academic Complex North, 6399798, Singapore

The aim of this work is to establish the correlation between differential scanning calorimetry and Raman spectroscopy in the determination of the mechanical properties of TiO₂/epoxy resin nanocomposites. Commercial RTM6 epoxy resin with TiO₂ nanoparticles of 21 nm in diameter is used. Magnetic stirring for 5, 30, and 60 min is employed for the preparation of this epoxy. The rate of the reticulation of epoxy is reinforced by different percentages of TiO₂ nanoparticles and is strongly affected by the cure temperature. The results indicate that the 1255 cm^{-1} peak intensity, corresponding to the C–C stretch, decreases during the cure leading to the variation of the mechanical properties (hardness) of the nanocomposites.

Keywords: epoxy resin, hardness, differential scanning calorimetry, Raman spectroscopy, TiO₂, nanocomposite.

ПОДГОТОВКА И ХАРАКТЕРИЗАЦИЯ МЕХАНИЧЕСКИХ СВОЙСТВ НАНОКОМПОЗИТОВ TiO₂/ЭПОКСИДНАЯ СМОЛА МЕТОДАМИ ДИФФЕРЕНЦИАЛЬНОЙ СКАНИРУЮЩЕЙ КАЛОРИМЕТРИИ И СПЕКТРОСКОПИИ КОМБИНАЦИОННОГО РАССЕЯНИЯ СВЕТА

L. Merad [1*]**, M. Bouchaour** [1]**, M. J. M. Abbadie** [2]**, B. Benyoucef** [1]

УДК 535.375.5;620.3

[1] *Университет Тлемсена, Тлемсена, 13000, Алжир; e-mail: merad@mail.univ-tlemcen.dz*
[2] *Школа материаловедения и инженерии, Технологический университет Наньян, 6399798, Сингапур*

Установлена корреляция между дифференциальной сканирующей калориметрией и спектроскопией комбинационного рассеяния света при определении механических свойств нанокомпозитов TiO₂/эпоксидная смола. Исследована коммерческая эпоксидная смола RTM6 с наночастицами TiO₂ диаметром 21 нм. Для получения этой эпоксидной смолы использовано магнитное перемешивание в течение 5, 30 и 60 мин. Скорость ретикуляции эпоксидной смолы усилена варьированием процентного содержания наночастиц TiO₂, причем она сильно зависит от температуры отверждения. Показано, что интенсивность максимума при 1255 см$^{-1}$, соответствующего растяжению связи С–С, во время отверждения и, следовательно, изменения механических свойств (твердости) нанокомпозитов уменьшается.

Ключевые слова: эпоксидная смола, твердость, дифференциальная сканирующая калориметрия, спектроскопия комбинационного рассеяния света, TiO₂, нанокомпозит.

Introduction. Epoxy resin synthesis is the formation of a molecule containing epoxide groups reacting with a multifunctional amine to form a network structure [1]. They provide a unique balance of chemical and mechanical properties combined with extreme processing versatility. They are used as dominant materials for wind turbine blades and in other applications, including protective coatings, adhesives, and automotive

materials. In general, epoxy resins are of particular interest for structural engineering. In all cases, thermoset resins may be tailored to satisfy particular requirements, so the formulation and processing information are often kept as trade secrets [2].

However, the curing monitored by differential scanning calorimetry (DSC) can be considered as one of the most interesting techniques for macrokinetic analysis of cure reactions of thermosetting systems [3, 4]. On the other hand, Raman spectroscopy offers considerable advantages in comparison with other analytical techniques. In fact, Raman spectroscopy is nondestructive. There is no need to dissolve solids, press pellets, compress the sample, or otherwise alter its physical or chemical structure.

In this study, the cure behavior of a commercially available epoxy resin system with a varying concentration of TiO_2 nanoparticles is characterized. The epoxy system is based on the standard diglycidyl ether of bisphenol A (DGEBA) and a modified aliphatic amine as a curing agent. The crosslinking of the epoxy system is characterized by means of DSC and Raman spectroscopy; we compare the percentage of reticulation of epoxy resin with different concentrations of inclusions. We also investigate the influence of the TiO_2 concentration on the mechanical properties (hardness) of epoxy.

Experimental. The used material matrix is diglycidyl ether of bisphenol-A (DGEBA). Epoxy resin (trade name LY 556) and 4,4-diaminodiphenylsulfone (DDS) are given in Fig. 1. Epoxy resin is superior in terms of its mechanical properties and has better resistance to degradation by water and other solvents.
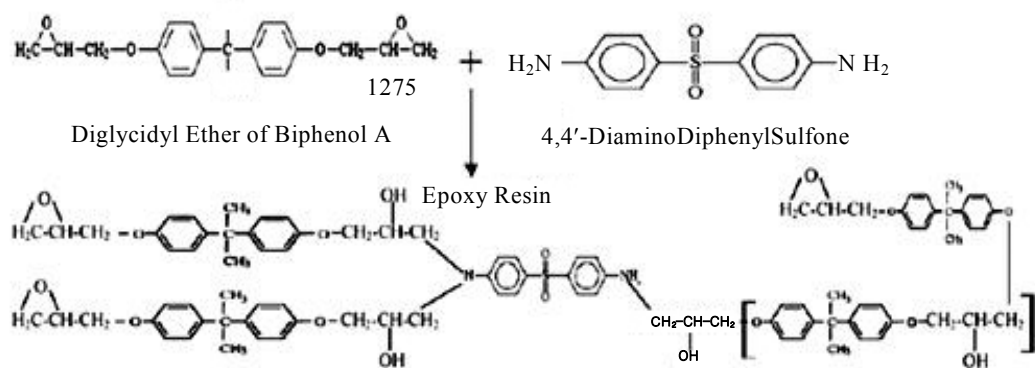

Fig. 1. Chemical structure and cure reaction of DGEBA and DDS [5].

The characteristics of TiO_2 nanoparticles [6] are as follows: nominal average diameter 21 nm, specific area 50 m^2/g, purity 99.5%, improvement of the ageing properties at 200°C. TiO_2 nanoparticles were selected as the reinforcement agent in order to investigate their effect on the percentage of reticulation. They are usually synthesized by calcinating the anatase of TiO_2 nanoparticles or amorphous TiO_2 at high temperatures (> 450°C).

Sample preparation. Epoxy resins are prepared with a varying concentration of TiO_2 nanoparticles (1, 2, 5, and 10 %). To prepare the sample, the desired amount of resin and the hardener is added to a vial and mixed using a magnetic stirring bar to ensure a homogeneous mixture. The sample is then immediately flash frozen using liquid nitrogen to avoid premature curing reactions. One weight percent of nanometer TiO_2 particles is added to the epoxy resin, mixed with a glass rod, and then dispersed by placing the mixture in a beaker in an ultrasonic bath for about 5 min. At the end of the sonication the hardener is added.

Magnetic stirring. Magnetic stirring is performed by a 50-HI322N-1 into which a timer control system is incorporated. The specifications are: maximum stirring capacity 5 L, speed range from 100 to 1.000 rpm, reverse interval from 30 s to 3 min; safety – an internal electronic speed control device limits the maximum speed up to 1000 RPMs, even if the load is suddenly removed.

DSC. Thermal analysis is performed on a DSC (Mettler Toledo TC11) differential scanning calorimeter. All samples are placed in standard aluminum pans and subjected to temperatures ranging from 50 to 300°C at a scan rate of 10°C/min. Isothermal tests are performed at 100 and 120°C with variable time depending on the stabilization of the cure reaction in order to achieve the heat evolved in an isothermal scanning at the desired temperature. Non-isothermal scans are then performed on the same samples obtaining the dynamic heat necessary to complete the cure of the reactive system.

The enthalpy of the residual cure is obtained from the loss part of the heat capacity by integration of the area of the exotherm. A spline baseline is used since the actual baseline is not horizontal. The percentage of reticulation is given by the following equation

$$\text{Reticulation\%} = (\Delta H_{\text{total}} - \Delta H_{\text{residual}})/\Delta H_{\text{total}} \times 100\%. \qquad (1)$$

Raman. Raman scattering spectra are recorded with a Jobin-Yvon micro-Raman LabRam system in a backscattering geometry. A 785 nm He–Ne laser with optical filters is used as the light source. By using a 100× objective lens, the illuminated spot on the sample surface is focused approximately up to 2 mm in diameter. The resolution of the Raman spectra is better than 1 cm^{-1}.

The mixture of DGEBA/DDS is introduced into the oven accessory of the Raman spectrometer and heated up to the desired temperature. Then, spectra are acquired *in situ* every 30 s to monitor the decrease of the 1250 cm^{-1} peak corresponding to the epoxide vibration, epoxide functions being consumed by the cure reaction. The 1255 cm^{-1} peak intensity is normalized on its value corresponding to the phenyl ring, which is unaffected by the curing process and thus remains constant.

From these data, the percentage of reticulation is calculated as:

$$\text{Reticulation\%} = (I_{1255}^{0} - I_{1255}^{t})/I_{1255}^{0} \times 100\%. \qquad (2)$$

Results and discussion. *DSC cure characterization.* The curing reaction is monitored through *in situ* DSC using a dynamic temperature scan. The curing reactions are monitored for epoxy resins with a varying TiO$_2$ concentration. The heat flow is measured as a function of temperature, at a heating rate of 10°C/min (sample heated from 50 to 360°C). The typical decrease of the 1255 cm^{-1} peak intensity corresponding to the epoxide group consumption is observed during all the curing reaction. At 100°C almost 70% of the epoxide groups are converted, while for 120°C we see that 80% of the epoxide groups are converted. The total heat of the reaction (as determined by integration of the peak area of the DSC thermogram): $\Delta H_{\text{total}} = 439.29$, 435.32, 437.00, 434.05, 432.89, and 439.57 J/g at heating rates of 1, 2, 5, 10, 20, and 30°C/min, respectively.

The DSC plots are also fitted using the equation described by Karkanas and Partridge [1]

$$\partial\alpha/\partial t = (k_1 + k_2\alpha^m)(1 - \alpha)^n, \qquad (3)$$

$$\partial\alpha/\partial t = k_1(1 - \alpha)^{n1} + k_2\alpha^m(1 - \alpha)^{n2}, \qquad (4)$$

where k_1 and k_2 are the rate constants, and m and n are the reaction orders. This means that the reaction at these stages has an auto catalytic character. The estimated parameters of the kinetic models are obtained from Eq. (3): $A_1 = 22420$ s^{-1}, $E_1 = 71.10$ kJ/mol, $A_2 = 10256$ s^{-1}, $E_2 = 55.65$ kJ/mol, and Eq. (4): $A_1 = 25820$ s^{-1}, $E_1 = 73.60$ kJ/mol, $A_2 = 25460$ s^{-1}, $E_2 = 61.84$ kJ/mol. The model can also be used to predict the degree of the cure under isothermal conditions, which is found to be consistent with the experimental results. In general, the degree of the cure is strongly affected by the cure temperature; a higher cure temperature accelerates the cure process.

TABLE 1. Parameters Obtained from Fitting the Isothermal Curing Results Using DSC

Cure temperature, °C	k_1, 10^{-5} s^{-1}	k_2, 10^{-3} s^{-1}	m	n	n_1	n_2
Equation (3)						
100°C	2.21	0.53	0.95	0.59	–	–
120°C	3.52	0.92	1.09	0.66	–	–
Equation (4)						
100°C	2.15	0.51	0.95	–	0.52	0.66
120°C	3.43	0.89	1.07	–	0.58	0.73

Raman spectroscopy characterization. Raman spectroscopy measures rotational and vibrational transitions in molecules, and it is specifically used to detect chemical bonds and their changes during a chemical reaction. The rotational and vibrational information specific for the chemical bonds allows the simple identification of the sample. The relative intensity of Raman peaks is directly proportional to the relative concentration of the components in a sample.

Figure 2 shows the Raman spectra obtained at different temperatures and at various cure times, the last four curves being shifted down for better illustration of the reaction progress. The peak at 1255 cm^{-1} corresponds to the epoxide group, and the intensity is observed to be decreasing over time during the cure reaction. The decrease in intensity can be explained by the opening of the epoxide group during the cure reaction. The Raman peaks at 1112 and 1225 cm^{-1}, corresponding to the C–C stretch, remain unchanged throughout the cure reaction. Another peak at 1300 cm^{-1}, assigned to the stretching of the phenyl ring, also remains constant throughout. All these peaks are consistent with what has been reported in [7, 8]. As a result, these three constant peaks can be used as a reference to observe the degree of the cure of the epoxy resin, which is indicated by the change in the intensity of the epoxide group.
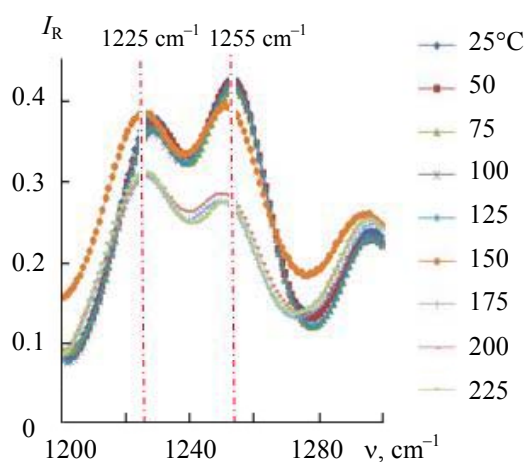

Fig. 2. Raman spectra for the different temperatures.

Figure 3 shows the influence of the percentage of TiO$_2$ versus the percentage of reticulation by DSC and Raman spectroscopy. From Fig. 3a, the percentage of reticulation decreases with increasing the percentage of TiO$_2$ nanoparticles because the high weight percent of TiO$_2$ prevents the complete polymerization reaction. The presence of a high percentage of TiO$_2$ nanofillers has the effect of reducing the "free volume", and therefore the mobility of the chains and thus their reactivity [9]. The nanocharges hinder the reactivity of the epoxy/hardener pair. The presence of very large aggregates act as sites of boot failure, like a bubble, and aggregates start to form [10, 11]. From Fig. 3b, the Raman intensity is proportional to the concentration of the substance (or the bonds) in the sample, what can be interpreted as the consuming of the free epoxide
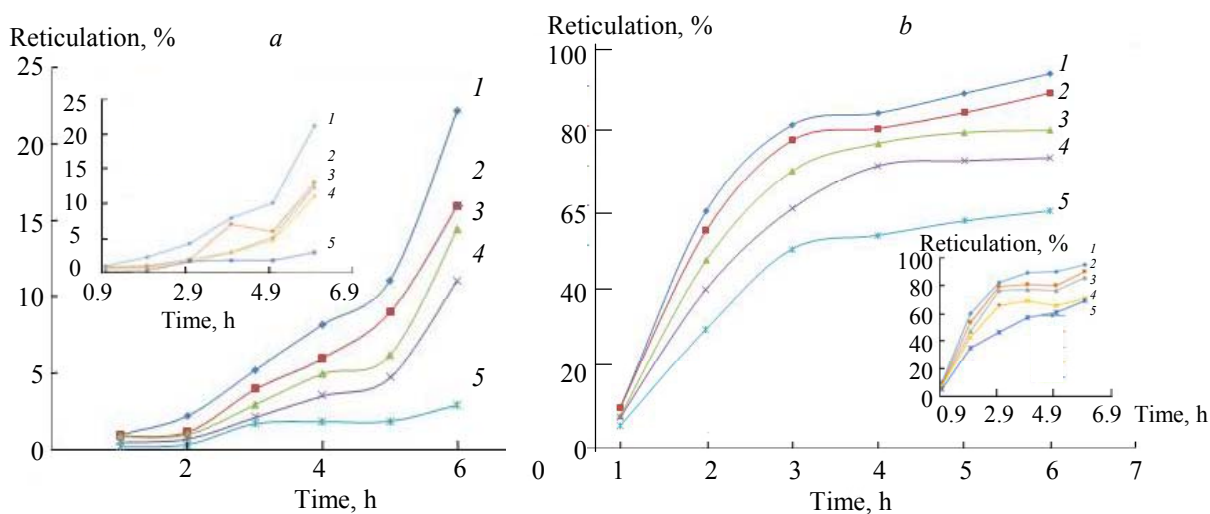

Fig. 3. Influence of TiO$_2$ nanoparticles (neat epoxy (1), 1, 2, 5, and 10% TiO$_2$ (2–5), respectively), on the reticulation at 100°C (a) and 120°C (b) obtained by DSC and Raman spectroscopy (inset)

groups during the vitrification of epoxy resin curing process. It is important to notice that the information obtained from each cure method should lead to the same or similar results in order to investigate the possibility of *in situ* cure monitoring. Hence, the degree of the cure from the DSC and Raman spectroscopy is compared at two isothermal cure temperatures: 100 and 120°C.

DSC measures the heat of reaction generated in a sample, and Raman spectroscopy observes the rotational and vibrational transitions in molecules and detects chemical bonds and their changes during the reaction. The two methods deliver a good agreement in the degree of the cure, thus confirming the possible use for *in situ* cure monitoring.

Figure 4 shows the influence of the TiO_2 percentage on the hardness at 120°C. The hardness is weak, varying between 13 and 29 HV, compared with the hardness of the steel grades between 150 and 700 HV [12, 13]. It can be seen from the graph that 10% of the nanosized TiO_2 has the best hardness because the hardness increase versus the hardness of the neat epoxy [14]. Samples with low nanofiller are more sensitive to this phenomenon, which is related to viscosity. But unless the material is loaded, it is more viscous, and more hardness evolves. The best wt.% of TiO_2 to get the best desired properties of epoxy resin is 10 wt.%.
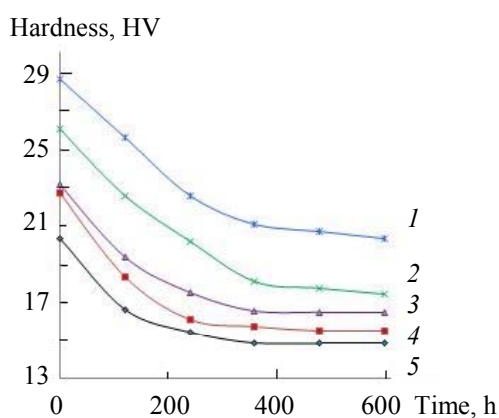

Fig. 4. Dependence of hardness on the time at 120°C;
neat epoxy (1), 1, 2, 5, and 10% TiO_2 (2–5), respectively

Conclusion. The *in situ* cure monitoring of an epoxy resin reinforced with TiO_2 nanoparticles is investigated by means of differential scanning calorimetry and Raman spectroscopy. The cure behavior is characterized using differential scanning calorimetry. The recent developments in the synthesis of TiO_2 nanoparticles have enabled the processing of new nanoparticle/epoxy composites. The magnetic stirring method is used to disperse the nanoparticles in the epoxy. The percentage of reticulation is strongly affected by the cure temperature: a higher cure temperature accelerates the cure process in general. The degree of the cure from Raman spectroscopy is determined quantitatively using a peak at 1255 cm^{-1}, corresponding to the epoxide vibration, and a constant reference peak at 1225 cm^{-1}. The peak at 1255 cm^{-1} is observed to be decreasing due to the opening of the epoxide group during the cure, and therefore is used to calculate the degree of the cure.

REFERENCES

1. Y. Guozhen, R. J. Brian, M. L. Robertson, *Green Materials*, **1**, 125–134 (2013).
2. H. Hansmann, *ASM Handbook/extraction*, **21**, 692–698 (2003).
3. J. F. Aust, K. S. Booksh, C. M. Stellma, N. R. S. Parnas, M. L. Myrick, *Appl. Spectrosc.*, **51**, No. 2, 247–252 (1997).
4. S. C. Lin, E. M. Pearce, *High-Performance Thermosets – Chemistry, Properties and Applications*, Carl Hanser Publisher, Munich (1994).

5. L. Merad, M. Cochez, S. Margueron, F. Jauchem, M. Ferriol, B. Benyoucef, P. Bourson, *Polym. Test.*, **28**, 42–47 (2009).

6. L. Merad, B. Benyoucef, M. J. M. Abadie, J. P. Charles, *Exp. Tech.*, **38**, 37–42 (2014).

7. R. Hardis, *Cure Kinetics Characterization and Monitoring of an Epoxy Resin for Thick Composite Structures*, Master of Science thesis, Iowa State University (2012).

8. V. Hana, K. Vojtěch, *Recent Res. Autom. Control*, **3**, 357–361 (2014).

9. D. Puglia, L. Valentini, J. M. Kenny, *J. Appl. Polym. Sci.*, **88**, 452–458 (2003).

10. K. C. Hong, T. M. Vess, R. E. Lyon, M. L. Myrick, *Proc. 38th Int. Soc. Advancement of Material and Process Engineering (SAMPE)*, May 10–13, 1993, California, USA, 1–12 (1993).

11. B. Ellis, *Chemistry and Technology of Epoxy Resins*, Blakie Academic Professional (1993).

12. B. Degamber, G. F. Fernando, *MRS Bull.*, **5**, 370–380 (2002).

13. C. B. Ng, L. S. Scbadler, R. W. Siegel, *NanoStruct. Mater.*, **12**, 507–510 (1999).

14. A. Naceri, A. Vautrin, *Afrique Sci.*, **2**, 131–141 (2006).