



Study of the Effect of Epoxy Reinforcement with C⁶⁰ on the Rheological and Adhesion Properties

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Abstract

Cold curing was used to evaluate the rheological properties of epoxy resin which was reinforced with fullerene (C⁶⁰) at different concentrations (0, 0.07, 0.11, 0.16, 0.25, 0.33, and 0.66 wt%). The kinetics of changes at complex viscosities was studied, by investigating the relationship between resin viscosity and resin with nanoparticles temperature dependency, the effect of fullerene reinforcements on the viscosity of the constituent epoxy-polymer compositions was evaluated. We studied how the complex viscosity changed with time when adhesive compositions doped with C⁶⁰ at various concentrations polymerized. By changing the concentrations of fullerenes, the time to reach the gel-point was determined for the mixtures and materials used. It was observed that the reinforcement at the beginning of the mixture with reinforcement changes with the time curing of the composition at a concentration of 0.16 wt.%, the maximum effect (30%) is achieved. The Young's modulus is shown to increase when the polymer is doped with fullerenes at 0.15 wt.% and decrease when the polymer is without filler.

Keywords: fullerene, epoxy resin, rheological, viscosity, composite materials.



دراسة تأثير تدعيم الايبوكسي مع C60 على الخواص الانسيابية والالتصاق

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الخلاصة

تم استخدام المعالجة الباردة لتقييم الخصائص الانسيابية لراتنج الايبوكسي المعزز بالفوليرين (C^{60}) بتركيزات مختلفة (0، 0.07، 0.11، 0.16، 0.25، 0.33، 0.66 %). تمت دراسة حركية التغيرات عند اللزوجة المعقدة. من خلال دراسة العلاقة بين لزوجة الراتنج والمدعم بالجسيمات النانوية مع الاعتماد على درجة حرارة، تم تقييم تأثير تدعيم الفوليرين على لزوجة متراكبات الايبوكسي. تم دراسة كيفية تغير اللزوجة المعقدة مع مرور الوقت عندما يتم بلمرة المتراكبات المتلاصقة مع C^{60} بتركيزات مختلفة. عن طريق تغيير تركيزات الفوليرين، تم تحديد وقت الوصول إلى نقطة الهلام للمواد الممزوجة المستخدمة. لوحظ أن التدعيم في بداية الخليط يعزز التغيرات مع وقت معالجة التركيبة. يكون التأثير الأقصى 30% عندما يكون تركيز المركب 0.16%. يتضح أن معامل يونج يزداد عندما يُشوب البوليمر بالفوليرين بتركيز 0.15% بالوزن وينخفض عندما يكون البوليمر بدون تشويب.

الكلمات المفتاحية: الفوليرين، راتنجات الايبوكسي، الانسيابية، اللزوجة، المواد المتراكبة.

Introduction

The composition of epoxy resin is commonly utilized due to its high strength characteristics, good adhesion to a variety of materials, resistance to external factors, and low shrinkage [1]. In the practical application of adhesive matrices and composite materials based on them, the determining parameters are the temperature dependence of viscosity and a conversion degree, which determine the "viability" of the binder and its curing time. In a broad manner, the kinetics of curing reactive oligomers is one of the main issues, the approach that enables, firstly, to evaluate of the process's chemistry; secondly, to apply of numerical parameters for comparing various materials with each other; and, thirdly, to give reasonable forecasts of the productivity and efficiency of real technological processes [2]. In recent years, studies of nano-composite materials (modifier - particles with a size of less than 100 nm) have become relevant. Physical alteration of current polymers, their combination with substances of a different nature, and different structure make it possible to give them a special desired set of properties, depending



on the type and concentration of the filler. Their main modifications from macro- and micro-composites are in the huge particular surface area of the filler-matrix interface, in the large volume fraction of the interfacial boundary, and the small average distances between the filler particles. Among such modifiers, carbon nanoparticles are broadly used, such as single-walled CNTs, nanofibers, fullerenes, and Graphenes [3]. Studies of the physicochemical, calorimetric, and electrical properties of a several of polymeric materials doped with nanomodifiers are widely represented in the literature [4]. In specific, it has been displayed that small reinforcing of carbon nanoparticles alter the materials' dielectric properties of such materials [5]. Here, the ambiguity of the influence of the filler concentration on the physicochemical features of materials reinforced by fullerene is also noted. In general, the structure of a polymer composite material can be represented as consisting of one continuous polymer phase (matrix) and one or more dispersed phases (filler) distributed in a certain way in the matrix [6-7]. It has been determined that such materials are characterized by percolation behavior, when, with a smooth change in one of the system parameters (for example, concentration), the properties of the system change un homogeneous: their most dramatic change is noted, as a rule, in a narrow region of filler concentration, this enables the term "percolation transition" to be used (percolation threshold). Above the percolation threshold, the system's behavior is undefined. In a number of researchers [8-9], it was shown that with an additional rise in the filler concentration, the change in the properties of the composite material is less intense. However, a number of experiments have shown that with a further increase in the concentration of fullerenes (or nanotubes), the properties of the polymer do not improve, but become the same (as before the introduction of the modifier) or even deteriorate [10, 11]. When studying the processes of polymerization of epoxy oligomers, two essentially different approaches are possible: microkinetic and macrokinetic. Microkinetic methods give illustrative results, but are far from always unambiguous for assessing changes in the mechanical properties of a material [12-13]. From the point of view of practice, the macrokinetic approach is more effective, based on observing the change in time of one or another integral parameter, which reflects the entire set of chemical and physical transformations that occur during the polymerization of the oligomer [14]. From this point of view, rheological analysis has great potential, which is a



method for monitoring the course of the polymerization process; it allows one to identify several essential features of this process. [15–16]. The rheokinetic approach was successfully used in [17–18] to study the curing of the “hot curing” epoxy oligomer ED-20. In this research, rheological studies of the process of polymerization of the "cold-curing" binder based on resin L and hardener ERN 161 were carried out depending on the concentration of C⁶⁰ fullerenes. It investigated how changes occur at high viscosities. By analyzing the relationship between resin viscosity and resin with nanoparticle temperature dependence, the effect of fullerene reinforcements on the viscosity of the matrix epoxy-polymer compositions was evaluated.

Experimental Work

A modified version of epoxy resin L with EPH 161 hardener (Momentive, USA) distributed by R&G composites (Germany), (mixing ratio in parts by weight 4:1) was used in this research with C⁶⁰ (98+) fullerenes produced by LLC NPK "Modern Synthesis Technologies". The measurements were made by a rotational rheometer oscillation Physica MCR 501 at different concentrations (0, 0.07, 0.11, 0.16, 0.25, 0.33 and 0.66 wt%). During the preparation of the samples, the weighed epoxy with the C⁶⁰ was mixed using an electromechanical stirrer. Next, the composite materials were dispersed in an ultrasonic bath (Digital Ultrasonic Cleaner CD 4820) at a temperature of 60 °C until an unchanging distribution of the converter in the liquid resin was achieved. The last operation also contributes to removing the air bubbles from the composite materials. The total preparation time for the concentration was 12–16 hours. Furthermore, a hardener was added to the resulting mixture. The composition was again mixed with an electromechanical mixer and, additionally, in an ultrasonic bath at room temperature.

Research Sample Characterization

A Physica MCR 501 rotational rheometer was used to measure rheological properties. The cone-plate system was used in the main measurements. Cone diameter $d=25$ mm, angle $\alpha=1^\circ$. The geometry used ensures the uniformity of the shear rate gradient across the measuring gap. To maintain and change the temperature regime, a special temperature device H-PTD 200 based on the Peltier effect was used. Through the research, about 0.07 ml of the solutions were placed

on the surface of the rheometer plate. The solution layer was 0.047 mm thick along its outer radius, which ensured the rapid establishment of the operating temperature in the sample even when there is heat release from the polymerization activity. It is possible to assess both the viscous and the viscoelastic properties of the samples since the tests were carried out under shear deformation of the blend utilizing a harmonic law with a 1 Hz frequency. All measurements were made in a discrete mode of temperature variations to reduce heat release in the sample caused by shear flow. Each experimental point's measuring period lasted 15 s. In the standby mode, measurements actually occur every 30 to 5 seconds. All measurements were performed at 25°C.

Results and Discussion

The time characteristics of the change in the complex viscosity during the polymerization of adhesive compositions doped with C^{60} in different concentrations (0, 0.07, 0.11, 0.16, 0.25, 0.33 and 0.66 wt%) as shown in Figure 1. To minimize the effect of shear flow on the viscosity of the composites, the measurements were performed in the oscillation mode with a frequency of 1 Hz. In all experiments, the value of tangential stresses equal to 10 Pa was used, which ensures that the flow curves reach the second Newtonian viscosity.

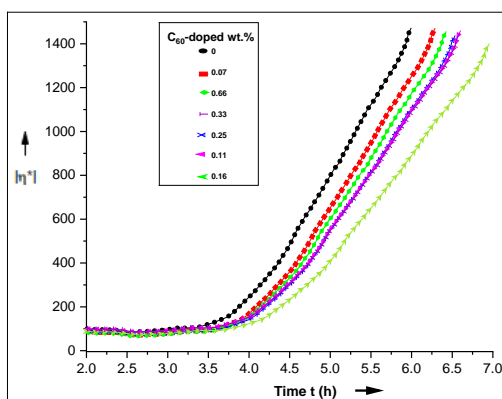


Figure 1: The complex viscosity of composite materials as a function of polymerization time

In preliminary experiments, the effect of fullerene additives on the viscosity of the constituent epoxy-polymer compositions was evaluated. Temperature dependences of resin viscosity and resin with nanoparticles are shown in Figure 2. It can be seen that the maximum concentration of fullerenes in our experiments is 1 wt.%, which practically does not affect the viscosity of such a solution.

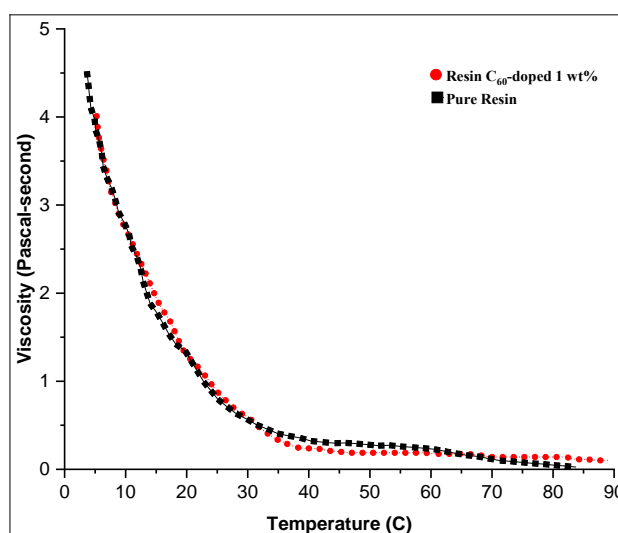


Figure 2: Viscosity of pure epoxy resins and resin doped with C^{60} as a function of temperature.

It can observe the concentration of fullerenes increase, and there was a tendency to decrease the polymerization. So, the time to reach the same viscosity level (1000 Pa) at a concentration of 0.16 wt% is 30% less than the same value of pure binder. At a concentration of fullerenes above 0.16 wt.%, the reverse process occurs: the time to reach the same value of the viscosity of the solutions begins to increase and, in the studied concentration range, reaches the limiting constant value. The general trend in polymerization time is shown in Figure 3.

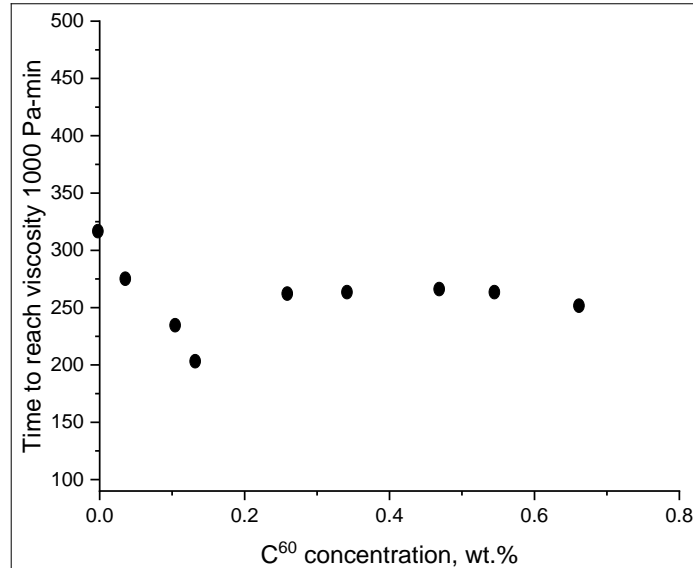


Figure 3: Time to reach viscosity 1000 Pa.s as a function the concentration of C⁶⁰.

It is shown that doping of the binder with fullerenes to a concentration of 0.15 wt % leads to an increase in Young's modulus with its subsequent decrease to the level of the binder without filler [9]. In general, viscosity changes occur throughout the complex process of epoxy resin curing. So, it is not possible to approximate the time dependences of viscosity by one functional dependence: polymerization reaction takes place in at least two stages. The initial sections of viscosity change are well approximated by the kinetic-type equation

$$\eta = \eta_o \exp (k t), \dots\dots\dots (1)$$

Where

η_o – the initial viscosity, k – a constant describing the kinetics of viscosity rise and t – time.

The results of calculations of the dependences of the coefficients η_o and k on the concentration of fullerenes are shown in figures 4 and 5.

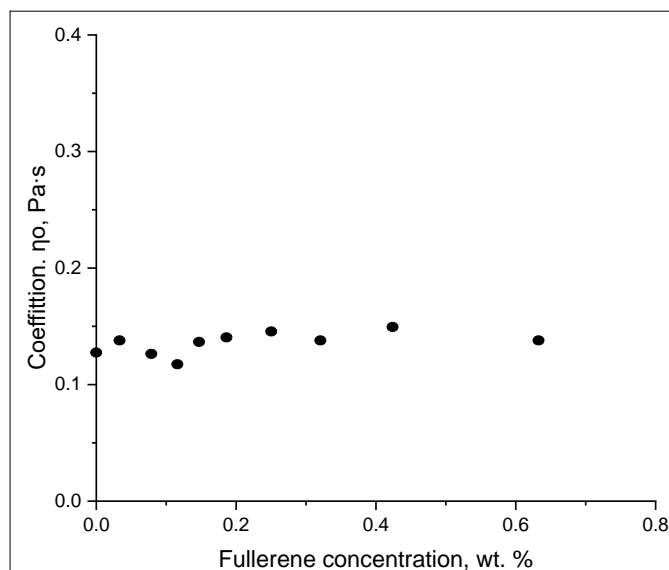


Figure 4: The coefficient η as a function the concentration of fullerenes

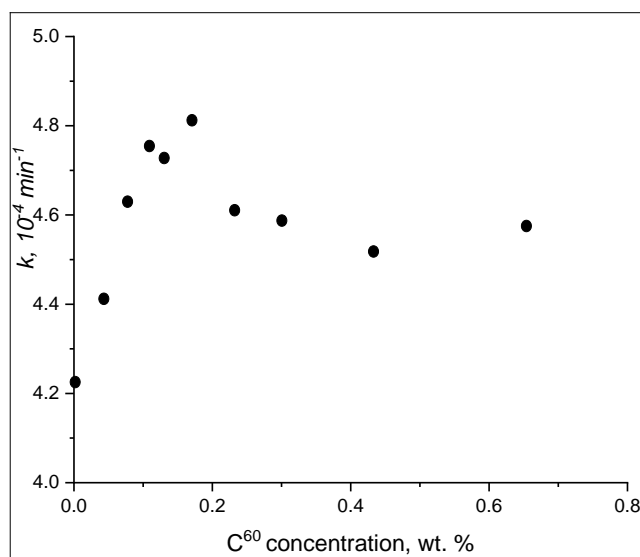


Figure 5: The coefficient k as a function of C^{60} concentration.



Note that the factor η_0 practically does not depend on the concentration of fullerenes as shown in Figure 2. On the contrary, the dependence of the exponent k is a non-monotonic function with a maximum at $\varphi \approx 0.16$ wt %.

When using a rotary rheometer for studies of the kinetics of curing processes a number of difficulties arise, the main of which is related to the fact that the viscosity of the analyzed material varies over an extremely wide range. To do this, during the experiment, it is necessary to replace the working units of the device, which is usually almost impossible. In other words, the change in the polymerization materials' rheological properties from the start of the reaction to its nearly complete completion cannot be recorded using a conventional rheometer.

On the other hand, often practical interest does not represent the entire range of viscosity changes, but only the time of transition from the viscous flow regime to the viscoelastic state and the time of complete polymerization (curing) t^* .

Equation (1) is convenient for carrying out practical calculations at the initial stage of polymerization. However, its use does not allow one to determine the gelation time, which formally corresponds to the condition $\eta \rightarrow \infty$, since the exponential function does not imply the existence of such a limit. Thus, an asymptotic function is required to characterize the process once the time since the start of polymerization reaches a specific critical value. We had proposed using a hyperbola to estimate the mixture's cure time [15]. In this situation, the flow loss time t^* can be calculated by extrapolating the normalized viscosity's time dependency η_0/η to the value $\eta_0/\eta \rightarrow 0$.

The result of processing a series of data in the coordinates $(\eta_0/\eta)(t)$ is shown in Figure 6. All dependences are well approximated by a straight-line segment with the coefficient of determination $R^2 = 0.99$, and the intersection with the abscissa axis makes it possible to determine the moment when infinite viscosity is reached, i.e., gel dots. When extrapolating the value of η_0/η to zero some uncertainty may occur, however, according to [19], the error in determining the gel point t^* by this method does not exceed 5%. The dependence of the time to reach the gel-point on the concentration of fullerenes is shown in Figure 7.

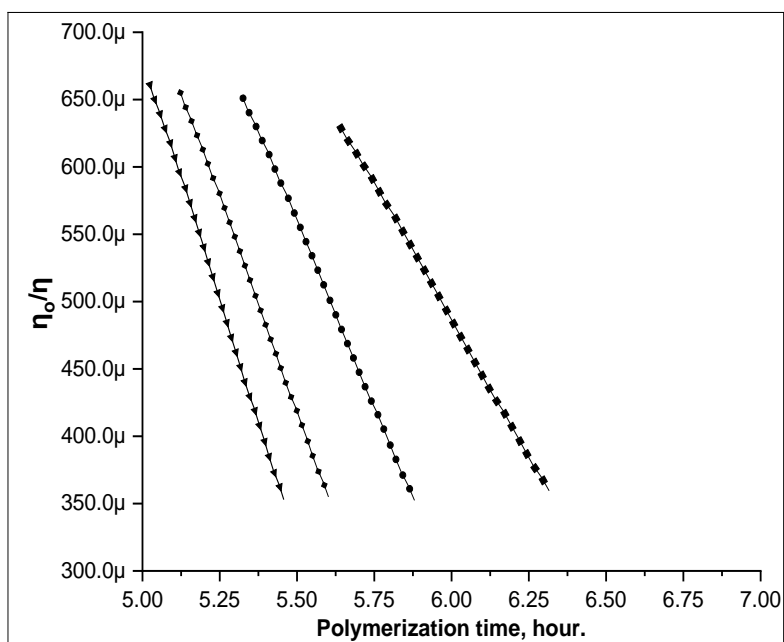


Figure 6: Normalized viscosity on final stages of curing as a function of curing time

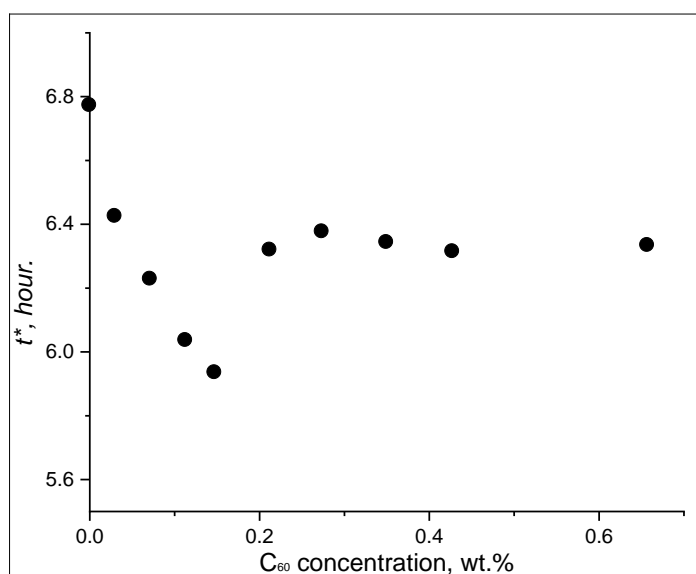


Figure 7: Time to reach the gel-point as a function of C⁶⁰ concentration



Conclusion

It is shown that the viscosity change curves cannot be approximated by a single functional dependence: the polymerization reaction proceeds at least in two stages. One of them can be described by an exponential dependence, the final one by hyperbole. The dependences of the parameters of the approximating curves on the concentration of fullerenes are constructed. The times of reaching the gel point of the mixtures are determined. It is shown that when the binder is doped with fullerenes, the time it takes to reach the gel point to $\varphi \approx 0.16$ wt.% noticeably decreases. With a further increase in the filler concentration, the solidification time of the composition increases and reaches a constant value, which, nevertheless, is less than for the initial composition with $\varphi = 0$ wt.%.

References

1. A. E. Kolosov, Ultrasonic Treatment In The Production Of Classical Composites And Carbon Nanocomposites, Electronic Archive of Kyiv Polytechnic Institute, Chapter 25, 121–221(2018)
2. C. Acebo1, X. Ramis, A. Serra, Physical Sciences Reviews, (2017)
3. H. Gergeroglu, S. Yildirim, M. Ebeoglugil, SN Applied Sciences, 2, 603 (2020)
4. N. A. Nikonorova, G. A. Polotskaya, A. A. Kononov, R. Castro, Journal of Non-Crystalline Solids, 483, 99-105(2018)
5. A. Kausar, Polymer-Plastics Technology and Engineering, 56, 594-605(2017)
6. Q. Zhang, J. Wang, B. Guoa, Z. Guo, Composites Part B: Engineering, 176(2019)
7. J. Chem, The Journal of Chemical Physics, (2021)
8. V. V. Zuev, Yu. G. Ivanov, Polymer Science Series A, 53, 424–429(2019)
9. M. M. Buzmakova, V. G. Gilev, A. Merzlyakov, S. Rusakov, Mechanics of Composite Materials, 54(4), 545–552(2018)
10. S. Tonogai, Y. Sakaguchi, S. Seto, Journal of Applied Polymer Science, 22, 3225–3234(1998)
11. M. Fedoseev, M. Gurina, V. Sdobnov, A. Kondyurin, Journal of Raman Spectroscopy, 27(5), 413-418(1996)
12. J. Barton, G. Buist, I. Hamerton, B. Howlin, J. Jones, S. Liu, Polymer Bulletin, 33, 215–219(1994)
13. S. Pandita, L. Wang, R. Mahendran, V. Machavaram, M. Irfan, D. Harris, G. Fernando, Thermochemica Acta, 543, 9–17(2012)
14. Bornosuz N. V., Gorbunova I. Yu.,” The Curing Rheokinetics of Epoxyphosphazene Binders”, Materials, vol. 13, (2020).



Academic Science Journal

15. N. D. Polychronopoulos, *Polymeric Composites: A Reference Series*, 1-47(2019)
16. V. S. Osipchik, I. Yu. Gorbunova, N. Kostromina, Y. Olikhova, D. Bui, *Journal of Chemistry and Chemical Technology*, 57(3), 19–22 (2014)
17. R. I. Sopotov, S. Zyukin, I. Gorbunova, M. Kerber, Y. Doroshenko, T. Kravchenko, V. Il'in, S. Tuzova, *International Polymer Science and Technology*, 43(10), 7–10(2015)
18. F. A. Amirov, A. A. Mammadova, *iksad publishing house*, (2022)