UDK 665.944.2:544.022.822
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 56(3)323(2022)

A REVIEW OF MEASURING THE GELATION TIME IN UNSATURATED POLYESTER RESINS

PREGLED MERJENJA ČASA GELIRANJA NENASIČENIH POLIESTERSKIH SMOL

Mohamed Farsane[1*], Soufia Lhasnaoui[1], Abdellah Anouar[2], said Dagdag[3], Miloud Bouzziri[1]

[1]Laboratory of Physico – Chemistry of Processes and Materials (PCPM). Faculty of Science and Technology of Settat, University Hassan 1st, BP 577, Settat 26000, Morocco
[2]Hassan First University of Settat, Faculty of Science and Technology, Laboratory of Applied Chemistry and Environment, Morocco
[3]Hassan First University of Settat, Faculty of Science and Technology, Laboratory of Environmental and Developmental Sciences, Morocco

Prejem rokopisa – received: 2021-12-15; sprejem za objavo – accepted for publication: 2022-04-17

doi:10.1722/mit.2021.337

Unsaturated polyester resins (UPRs) are commonly used as matrix resins for fiber-reinforced composites. During processing, the resins undergo a molecular cross-linking process called curing, during which they change irreversibly from viscous liquids to rigid and highly cross-linked polymer solids. The gelation time is critical for the success of a resin system, but it is difficult to measure accurately. It depends on several parameters. In this study, the parameters investigated are the effect of choice and their relative proportions. Parameters such as catalyst, accelerators, inhibitor, and fillers were examined. Various combinations of catalyst, accelerator, inhibitor, temperature and filler were analyzed to investigate the effect on the gel time of the unsaturated polyester resins. Then, this review assembles the scientific data on the gelation of unsaturated polyester resins to help readers better understand this process. Students, researchers, technologists, engineers, and chemists involved in the technology of synthesizing these monomers and polymers will benefit from this material.

Keywords: unsaturated polyester resin, gel time, catalyst, accelerator, inhibitor, filler

Nenasičene poliesterske smole (UPRs; angl.: Unsaturated polyester resins) se v glavnem uporabljajo kot materiali za matrice polimernih kompozitov ojačanih z vlakni. Med postopkom izdelave kompozita pride med njegovo toplotno obdelavo do zamreženja molekul, kar ireverzibilno (nepovratno) spremeni viskozno kapljevino v togo in močno zamreženo polimerno trdno snov. Čas gelacije oziroma zamreženja je pomemben faktor pri izdelavi izbranega polimernega sistema, vendar ga je zelo težko meriti oziroma določiti. Odvisen je namreč od več parametrov. V tem članku avtorji opisujejo študijo in raziskavo parametrov, ki vplivajo na čas geliranja. Analizirali so vplivne parametre kot so katalizatorji, pospeševalci, zaviralci in polnila. Natančno so analizirali vplive različnih kombinacij katalizatorja, pospeševalca, zaviralca, temperature in polnila na čas geliranja nenasičenih poliesterskih smol. Nato so avtorji zbrali še dodatne znanstvene podatke o geliranju nenasičenih poliesterskih smol, kar bralcu pomaga bolje razumeti ta proces. Študentje, raziskovalci in tehnologi, ki se ukvarjajo s tehnologijo sinteze monomerov in polimerov bodo z branjem oz. s študijem tega prispevka pridobili nova znanja.

Ključne besede: nenasičena poliesterska smola, čas geliranja (zamreženja), katalizator, pospeševalec, zaviralec, polnilo

1 INTRODUCTION

Unsaturated polyester resins (UPRs) are commonly used as matrix resins for fiber-reinforced composites. Curing or cross-linking, is achieved at room temperature by adding a catalyst plus an accelerator, and at elevated temperatures, just by adding a catalyst and heating. At ambient temperature, this reaction is usually initiated by peroxides (the catalyst) and activated by metallic compounds or tertiary amines.[1–4] The curing of the polyester backbone by the unsaturated acid constituent in combination with a vinyl component creates a three-dimensional structure.[5] The crosslinking process involves copolymerization of the added monomer with the double bonds of the unsaturated polyester. The copolymerization reaction can be written as presented in **Figure 1**.

Cross-linking is distinguished by the occurrence of gelation at some point in the polymerization. At this point, termed the gel point, we observe the visible formation of a gel or insoluble polymer fraction. The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponds to the formation of an infinite network in which the polymer molecules are crosslinked to each other to form macroscopic molecules. The gel is, in fact, considered as a single molecule. The non-gel portion of the polymer remains soluble in solvents and is re-

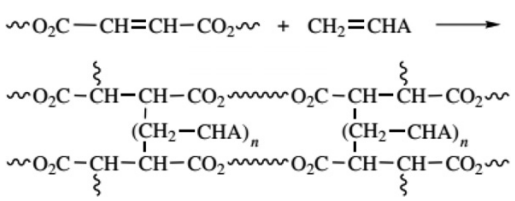

Figure 1: Copolymerization reaction

*Corresponding author's e-mail:
mfarsane@hotmail.fr (Mohamed Farsane)

ferred to as sol. As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more polymer chains in the sol are cross-linked to the gel. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.[6]

The phase transformations that occur during the curing of thermosetting resins are gelation and vitrification. Gelation is defined as the point at which the curing system transforms suddenly from a viscous liquid into an elastic gel, the viscosity of the system becomes infinite, and the shear increases from zero to finite values. In a free-radical polymerization, the gel point takes place early in the curing reaction at a very low degree of conversion, as a consequence of the formation of micro gel particles. Then, vitrification strongly limits the mobility of the reactive groups, causing the polymerization to end. This happens as the glass-transition temperature, which continuously increases during the curing, approaches the cure temperature.[7]

The point of gelation can be identified most easily by occasional stirring, although other, more sophisticated, methods are available. The gelation time corresponds closely to the initial rise in temperature[8]; therefore, the induction period of the reaction corresponds closely to the gel point. In addition, the gel times for free-radical cross-linkage are known to occur at low conversion.[9] In order to properly control the gel time, we must precisely adjust the stoichiometric imbalance of the additives or of the monofunctional monomer. It is therefore important to understand the quantitative effect of the stoichiometric imbalance of the reactants on the cure reaction. This is also necessary to know the quantitative effect of any parameters that may be present in the reaction. The inorganic compounds such as filler can drastically lower the gel time unless we can quantitatively take their presence into account. Considering that a tri-dimensional structure develops soon after the initiation of free radical curing, it is important to understand how the induction process is influenced by the initiator systems, the control of gelation, and the curing rate for polyester resins.

In this review paper we have tried to summarize the findings from research on the influence of various parameters, such as the initiator, accelerator, inhibitor, and filler, on the gelation time of polyester resins. We also review some methods and parameters for determining the gelation time of resins.

In addition to the main technological characteristics of the processes already mentioned, economic and safety considerations are made for the monomers and their polymers. Although in the case of unsaturated polyester and styrene, some monomers are mentioned, nothing is said about the curing of the UP resin. For the sake of consistency of the points discussed, it would be better if this article provided information on this important group of copolymers. Students, researchers, technologists, engineers, and chemists involved in the technology of synthesizing these monomers and polymers will benefit from this material.

2 METHODS AND CRITERIA FOR DETERMINING GELATION TIME

Gel is divided into two classes by the structure of the cross-linking point. One is called a chemical gel and the other is known as a physical gel.[10] Chemically, gelation implies the formation of a continuous network of covalent bonds in the system. The viscosity of the system increases gradually, which makes it very difficult to define the gel point precisely. It is also difficult to differentiate gelation from vitrification. This also leads to the formation of a solid, but does not involve the formation of a continuous network of covalent bonds. This makes the gelation time determination methodology a matter of great concern. Gelation time is an important factor in the manufacture of all composites, and gelation temperature is important for thick or large-cross-section composites.[11]

The most widely used methods for measuring the gelation time of resins are described in.[12] The author notes that measuring gelation time accurately is very difficult. Of the numerous standardized experiments, the manual methods are highlighted.[13] Manual methods are challenging and require prior knowledge of resins and processing mechanisms. The main problem is that results are not reproducible. However, despite the low accuracy of the results, these methods are widely used because they cost little and require no specialized equipment. Currently, manual methods are usually automated because of their simplicity and reproducibility. Both methods are subject to standardization, and there are more and more patents for novel design solutions for the instruments. A thermal scanning rheometer (TSR) can be used to measure the gelation time effectively in two ways.

Many gelation-time measurement approaches are based on dynamic mechanical analysis (DMA), where an especially significant variable is the viscoelastic nature of the material. Dielectric analysis (DEA) methods measure the polarization of the resin in an alternating electrical field. The limitation of the sample thickness is the main drawback of DEA methods and their polar nature.[14]

Differential scanning calorimetry (DSC) is also often used for the gelation-time determination. In this method, two resin samples are analyzed: the fresh resin right after mixing with the hardener, and the cooled resin just after gelation. By comparing their heat of reaction, a graph of the degree of conversion versus time can be obtained. The latest methods for measuring the gelation time are ultrasonic methods.[15,16] The gelation time is measured as a function of the damping of high-frequency mechanical vibrations.

3 THE CURING REACTION

Control of cross-linking is critical for processing thermoset plastics, both the reaction prior to the gel point and that subsequent to the gel point. The period after the gel point is usually referred to as the curing period. Too slow or too rapid cross-linking can be detrimental to the properties of a desired product. Thus, in the production of a thermoset foamed product, the foam structure may collapse if gelation occurs too slowly. On the other hand, for reinforced and laminated products the bond strength of the components may be low if cross-linking occurs too quickly. The gel point is usually determined experimentally as that point in the reaction at which the reacting mixture loses fluidity, as indicated by the failure of bubbles to rise in it.[6]

Curing is a time-dependent, exothermic, irreversible chemical reaction in which a low-molecular-weight liquid is converted into a high-molecular-weight cross-linked solid, which serves as a matrix for the fibers.[11]

The free radicals in the cure reaction are provided by the peroxide as it decomposes. The rate at which these free radicals are produced determines the gelation and curing times of the resin.

The MEKP initiator decomposition using a metal promoter can be described by Equations (1) and (2).

$$\mathrm{ROOH + Co_2 + RO + OH^- + Co^{3+}} \quad (K_{d1}) \qquad (1)$$

$$\mathrm{ROOH + Co_3 + ROO + H^+ + Co^{2+}} \quad (K_{d2}) \qquad (2)$$

where ROOH and Co denote the MEKP and cobalt species, and K_{d1} and K_{d2} denote the rate constants for the formation of alkoxy (RO) and peroxy (ROO) radicals, respectively. The decomposition of ROOH is the rate-limiting step in free-radical polymerization. Beaunez et al.[17] note that the peroxyradicals are considerably less reactive with ethylenic monomers than the alkoxy radicals, and therefore Equation (1) determines the initiation rate. However, Equation (2) is also important, as this step regenerates the Co^{2+}, yielding a pseudo-stable state for the concentration of Co^{2+}.

The induction step is affected by the inhibitor, which consumes the radicals produced by the initiators. Due to the consistently high reaction-rate constant between the radical and the inhibitor, the propagation of radicals is eliminated by the inhibition reaction, if the inhibition reactions are faster than the propagation reactions. Thus, the inhibitor concentration is greater than the radical concentration; consequently, no significant polymerization occurs. As the inhibitor is depleted, the monomer begins to react with the radical.

It has been demonstrated that the initial initiator concentration, catalyst concentration, and induction period are related by Equation (3). When there is no inhibitor left, the polymerization reaction can commence. Therefore, the rate of inhibitor loss is the rate-limiting step in free-radical polymerization, and it determines the induction time of the curing reaction.

The inhibition time, t_z, is the time when the concentration of radicals is zero (Equation (3)).

$$t_z = \frac{Z_0}{k_d[\mathrm{ROOH}][\mathrm{Co}^{2+}]} \qquad (3)$$

The curing kinetics of UPRs are usually very complex because numerous reactive processes take place at the same time.[18] In addition, a number of events are crucial in the curing of thermosets, such as the kinetics of reactions, phase separation, changes in rheology, microstructure formation, etc.[19] This is known as gelling. Hsu et al.[20] broke down the process of curing into five steps: induction, microgel formation, etc.

4 THE EFFECTS OF VARIOUS PARAMETERS ON GELATION TIME

Many reviews discuss the effects of different parameters, such as the catalyst, accelerator, inhibitor, temperature, film or laminate, and fillers, on the gel time of resins. Yang and Suspene[21] studied the effect of MEKP and cobalt salt on the gelation time of unsaturated polyester resin, but did not incorporate inhibitors into their work.

Table 1 provides values of the gel time found in published sources. These results show the effects of the amount and the type of these factors on the gel time value. A review of the literature shows that there is some evidence that increasing the amount of MEKP and the promoter cobalt naphthenate reduces the gelation time. Special attention has been given to the gel time in the literature.[22] Most organic peroxides are used at a concentration of 1–4 *w*/% based on the resin weight.

4.1 The effect of the catalyst

Various initiators are employed for the experimental evaluation of the gel time of UPR. Ketone peroxide is the main catalyst used with polyester resins. The peroxides included in this class are methyl ethyl ketone (MEKP) peroxide and cyclohexanone peroxide acetyl-acetone peroxide, methyl isobutyl ketone peroxide and various ketone peroxide mixtures. These curing agents can be used alone, or two or more can be used in combination. The benzoyl peroxide initiated cure of unsaturated polyester resin at 20 °C shows an increasing order of dependence of the gel time as the catalyst decreases. The dependence is 9 min at 2 *w*/% and increases to 13 min at 1 *w*/%. These effects might be caused by a dependence of the initiation rate on the monomer concentration.

It has been found that the reaction rate (determined by DSC) was raised and the gel time reduced with increasing concentrations of MEKP. However, while the gel time was also reduced by increases in the cobalt level, the reaction rate was lowered. This was attributed to the dual nature of the cobalt in the polymerization pro-

cess and the differing sensitivity of the gel times and DSC data to these roles.[27] By adding 2 *w*/% MEKP and 0.5 *w*/% cobalt octoate, the authors substantially reduced the curing time. Hence, the addition of the MEKP catalyst during polymerization of the polyester resin is very important for inducing its curing.[28] As a result, the curing of the resin at room temperature depends on the presence of three components: a catalyst, such as methyl ethyl ketone peroxide (MEKP), which initiates the polymerization; an accelerator, such as cobalt salt, which increases the reactivity of the catalyst and the content of filler, which increases the gel time of the UPR.[24]

In a previous investigation, at 30–50 °C, the reaction was initiated by an amine-accelerated system with 3 *w*/% benzoyl peroxide (BPO), 0.3 *w*/% N-dimethyl aniline (DMA) and 0.3 *w*/% p-tert-butyl catechol (NLC-10, an inhibitor). They found that via DSC, the higher the temperature, the faster the reaction rate. The induction time, and the time to maximum rate, are shorter with increasing temperature. **Table 1** shows the corresponding overall gel time, and as expected the ultimate overall time decreases with temperature.[29]

4.2 The effect of the accelerator

Many oxidation–reduction reactions produce radicals that can be used to initiate polymerization (Equations (1) and (2)). This type of initiation is referred to as redox initiation, redox catalysis, or redox activation. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0–50 °C and even lower. This allows a greater freedom of choice of the polymerization temperature than is possible with the type and level of promoter that can be used. In support of this effect, the rate of initiation increases with the increasing level of the promoter. Accelerators are substances that, when used in association with a peroxide catalyst, accelerate the rate at which the organic peroxide decomposes into free radicals. Therefore, they accelerate the curing of the polyester resin in a controlled manner. They are used mainly to allow the use of peroxides that are not suitable for curing polyester resins at room temperature. In general, the mixed cobalt/tertiary amine accelerators are used to give very short gelation times. **Table 1** deals with the experimental data received in the different studies.

As suggested by Equation (3), gelation time is inversely dependent on the initiator level over the majority of the initiator range investigated. The experiments show that a decrease in the cobalt concentration prolongs the induction period. At low cobalt concentrations, the gelation time is reciprocally related to the promoter concentration.

The gel time values are (9.15, 6.3, and 4.45) min, respectively, for (0.12, 0.5 and 1) *w*/% of cobalt accelerator. In addition, corresponding values of the gel time are included in **Table 1** for comparison.

Table 1: The effect of catalyst, accelerator, inhibitor, filler and temperature on gel time of UPR

Proportions (parts by weight)				t_{gel} (mn); T (°C)		reference
Catalyst	Accelerator	Inhibitor	Filler			
MEKP (2) MEKP (2) CHP (2) CHP (2) BPO (2) CHP (2) MEKP (2) MEKP (2) MEKP (2) MEKP (2)	Co (1) Mg (1) Co (1) Mg (1) DEA (1.5) DMA (1.5) DMT (1.5) Co (1) Co (1) + DMA (0.1) Co (1) + DEA (1)			18 495 22 316 100; 20 20 20 36 23 16	8; 50	[23]
MEKP (2) MEKP (1) MEKP (2) MEKP (2) MEKP (1) MEKP (1)	Co (0.5)		PP (28.5) PP (50) PP (28.5) PP (28.5)	6.3 13 9.45 13; 20 16 25.30		[24]
BPO (0.5)		TBPB (1.5)	Na-M (0.00) Na-M (1.00) Na-M (5.00)	13.01 12.75;20 10.75		[25]
MEKP (2)	CoNp (1)		Q (15) T (15) OS (5) OS (20)	15.8 6.4 12.7; 20 5.2 4	5.3 3.4 5.8; 40 1 0.8	[26]

Table 1 notation: BPO – benzoyl peroxide; TBPB – tert-butyl peroxybenzoate; OS – olive stones; T – talc; Q – quartz; PP – porcelain powder; M – montmorillonite; DMA – dimethylaniline; DEA – dimethylaniline; CHP – cyclohexanone peroxide; DMT – dimethyl-ñ-toluidine; Co – cobalt salt; Mg – manganese salt; CoNp – cobalt naphthenate

Usually, the cobalt content of a normal polyester resin is around 0.5–2 *w*/%, added as a 1 *w*/% cobalt solution. They provide a short gel time at room temperature when used to accelerate ketone peroxides.

In addition, only three tertiary amines are normally used for accelerating, the most common of which is dimethylaniline. They are used to accelerate peroxide catalysts such as benzoyl peroxide to achieve room-temperature curing. Metal compounds, such as cobalt naphthenate, are excellent for accelerating hydroperoxides and mixed peroxides, but have little or no effect on true peroxides. Tertiary amines, on the contrary, operate well with peroxides and are frequently used in conjunction with cobalt naphthenate as co-accelerators for mixed peroxides, such as MEK peroxide.

Dimethylaniline gives normal gelation times and quick curing when used to accelerate diacyl-peroxide-catalyzed systems. It can also be used as a co-accelerator with cobalt-accelerated ketone-peroxide-catalyzed systems to shorten the gel time. In addition, NN-diethylaniline gives long gelation times, but fast curing at room temperature when used as an accelerator in benzoyl peroxide catalyzed resin systems and finally dimethylptoluidine gives short gelation and curing times in conjunction with benzoyl peroxide catalyzed resin systems.

The combination of metal salts and tertiary amines can accelerate ketone-peroxide-catalyzed systems.[23]

4.3 The effect of inhibitors

The addition of certain substances suppresses the polymerization of monomers. These substances act by reacting with the initiating and propagating radicals and converting them to either nonradical species or radicals of reactivity too low to undergo propagation. Such polymerization suppressors are classified according to their effectiveness. Inhibitors stop every radical, and polymerization is completely halted until they are consumed. Retarders are less efficient and stop only a portion of the radicals. In this case, polymerization occurs, but at a slower rate and lower polymer molecular weight. Inhibitors such as hydroquinone, 1,4-naphthoquinone, p-benzoquinone, chloranil, catechol and picric acid stop the polymerization completely, whereas retarders (2,4-pentanedione) slow the polymerization rate.

Some inhibitors increase the gelation time and curing time as well as the pot life, while others increase only the pot life, so that demolding can still take place after gelation. If the pot life is extended by decreasing the accelerator concentration rather than by using an inhibitor, the gelation and demolding times are both extended

Yang and Suspene[21] found that the inhibitors slowdown the curing reaction of the resin, leading to more homogenous curing and defect-free products. They also create an induction period before the resin is cured, and increase the shelf life of the resins. The latter is in good accordance with the data collected in the literature.[30]

4.4 The effect of fillers

For different applications filler particles are often used to reduce the price, but also to improve some mechanical and thermal properties of the product. Because of their high specific weight, the filler tends to sediment in the resin. In spite of the fact that reinforced thermoset polyester composites contain a large quantity of inorganic particulates as fillers, relatively little information is available in the literature, which discusses how the particulates affect the curing behavior of UP resins.[25] These additives are usually added in a few weight percent, to reduce the viscosity, to avoid sedimentation of the fillers, which may be present in high amounts. In addition, gelation can be controlled by varying the level of catalysts, accelerants, and inhibitors introduced into the resins during lamination. Then, a good selection of such additives and the amounts in which they are added, can be used to eliminate delays in gelation time. It is appropriate to mention that a manufacturer's primary objective is to optimize profit. One of the methods to reach this goal is to overcome the operational issues associated with material waste. However, the main source of material waste during lamination is gelling before the end of the work. Thus, it is necessary to have an exact prediction of the gelation time of the laminating resin in order to prevent this material waste. In addition, production costs will increase when material waste increases and this will decrease the profit. And one of the ways to eliminate material waste in fiber lamination is to have a good understanding and control of the resin's curing kinetics. Therefore, FRP production requires a detailed knowledge of the curing times of the resin and its additives to eliminate waste caused by over-curing, over-slow curing or no curing at all.

Rheological measurements carried out previously[26] show that the different fillers lead to an increase in the gel time. Fillers prevent microgels from closing, delaying the transition stage and then the macro gelation. Kubota[31] reports that the presence of a large amount of filler in the curing system increases both the thermal conductivity and the viscosity of the resin; however, it reduces the concentration of reactive double bonds per unit volume. With greater filler content, curing began at a lower temperature; however, the total heat of curing was also lower. Lucas et al.[32] reported a decrease in the induction period of a UPR cured in the presence of a calcium carbonate filler. This effect was attributed to the preferential adsorption of inhibitors, including dissolved oxygen, in the filler-rich phase.

The effect of nanoclay content on the cure reaction of a UP resin was studied using DSC and FTIR.

According to these results, the nanoclay content does not affect the network formation during the reaction and the final conversion at a constant temperature.

The authors found that nanoclay acts as a co-promoter in the copolymerization between UP and Stand decreases the gel time. This could be obtained because of

the presence of long chains of alkyl ammonium ions.[25] In a recent study,[24] the authors showed that the progressive addition of porcelain powder from 20 *w*/% to 50 *w*/% causes an elongation of the gel time from 9.45 min to 13 min using 2 *w*/% of MEKP and Co promoter of about 1 *w*/% and the detailed results are given in **Table 1**. In our recent study, we found that this filler used is essentially silica, mullite and other minor constituents based on the results of X-ray analysis. These authors have shown via the infrared technique that porcelain powder had no effect onf the resin, and they concluded that the increase in gelation time can be attributed to slower cross-linking of the UPR and to the absorption of the heat generated in the exothermic reaction.

5 CONCLUSIONS

The gel times of unsaturated polyesters are largely dependent on the type and concentration of the organic or inorganic substances used for curing (initiators, accelerators), other substances (inhibitor, fillers, reinforcement additives) and finally on the temperature. The gel time in the presence of the organic filler decreases compared with that of the neat unsaturated polyester.

Gel time is important because it affects the way a resin can be processed during the production of polymeric laminates. The exact gelation time is difficult to set due to the complex nature of resin cross-linking processes. To date, multiple methods have been devised to determine the gel time. They give consistent results, but their accuracy is variable.

Acknowledgments

The author would like to thank Professors M. M. Bouzziri, M. M. Hmyene and M. A. Anouar, who gave many helpful comments and suggestions during this work.

6 REFERENCES

[1] K. Horie, I. Mita, H. Kambe, Calorimetric investigation of polymerization reactions. IV. Curing reaction of polyester fumarate with styrene, J. Polym. Sci. Part. A-1 Polym. Chem., 8 (**1970**), 2839–2852, doi:10.1002/pol.1970.150081010

[2] R. R. P. Kuppusamy, S. Neogi, Influence of curing agents on gelation and exotherm behaviour of an unsaturated polyester resin, Bull. Mater. Sci., 36 (**2013**), 1217–1224, doi:10.1007/s12034-013-0591-8

[3] ASTM D 2471-99, Standard test method for gel time and peak exothermic temperature of reacting

[4] Y. S. Yang, L. J. Lee, Polymerization of polyurethane-polyester interpenetrating polymer network (IPN), Macromolecules, 20 (**1987**), 1490–1495, doi:10.1021/ma00173a008

[5] S. Y Tawfik, J. N. Asaad, M. W. Sabaa, Effect of polyester backbone structure on the cured products properties, Polym. Test., 22 (**2003**), 747–759, doi:10.1016/S0142-9418(03)00008-4

[6] G. Keifer, F. Effenberger, Odian principles of polymerization, Angewandte Chemie International, 6 (**1967**)

[7] J. M. Kenny, A. Maffezzoli, L. A. Nicolais, A model for the thermal and chemorheological behavior of thermoset processing: (II) Unsaturated polyester based composites, Compos. Sci. Technol., 38 (**1990**), 339–358, doi:10.1016/0266-3538(90)90020-6

[8] W. D. Cook, M. Lau, M. Mehrabi, K. Dean, M. Zipper, Control of gel time and exotherm behaviour during cure of unsaturated polyester resins, Polym. Int., 50 (**2001**), 129–134, doi:10.1002/1097-0126(200101)50:1<129::AID-PI598>3.0.CO;2-C

[9] C. Walling, Gel formation in addition polymerization, J. Am. Chem. Soc., 67 (**1945**), 441–447, doi:10.1021/ja01219a026

[10] M. Tokita, Transport phenomena in gel, Gels, 2 (**2016**), doi:10.3390/gels2020017

[11] S. D. Gordin, A. M. Eslami, H. L. Price, Gel time and temperature for two thermosetting resins, ASEE Annu. Conf. Proc., (**2004**), 6077–6086. doi:10.18260/1-2—12830

[12] A. A. Shimkin, Methods for the determination of the gel time of polymer resins and prepregs, Russ. J. Gen. Chem., 86 (**2016**), 1488–1493, doi:10.1002/(sici)1097-0126(199708)43:4<380:aid-pi816>3.3.co;2-v

[13] DOTD, TR 703-85, Gel Time Determination of Epoxy resin system, http://www.dotd.la.gov/Inside_LaDOTD/Divisions/Engineering/Materials_Lab/TPM_Vol_II_Part_VII/703.pdf

[14] L. Núñez-Regueira, C. A. Gracia-Fernández, S. Gómez-Barreiro, Use of rheology, dielectric analysis and differential scanning calorimetry for gel time determination of a thermoset, Polymer (Guildf), 46 (**2005**), 5979–5985, doi:10.1016/j.polymer.2005.05.060

[15] M. A. Acitelli, R. B. Prime, E. Sacher, Kinetics of epoxy cure: (1) The system bisphenol-A diglycidyl ether/m-phenylene diamine, Polymer (Guildf), 12 (**1971**), 335–343, doi:10.1016/0032-3861(71)90056-5

[16] F. Lionetto, A. Maffezzoli, Monitoring the cure state of thermosetting resins by ultrasound. Materials, 6 (**2013**), 3783–3804, doi:10.3390/ma6093783

[17] P. Beaunez, G. Helary, G. Sauvet, Role of N N-dimethyl-para-toluidine and saccharin in the radical polymerization, J. Polym. Sci. Part A, Polym. Chem., 32 (**1994**), 1471–1480

[18] K. De La Caba, P. Guerrero, A. Eceiza, I. Mondragon, Kinetic and rheological studies of two unsaturated polyester resins cured at different temperatures, Eur Polym. J., 33 (1997), 19–23, doi:10.1016/S0014-3057(96)00110-3

[19] C. P. Hsu, L. J. Lee, Free-radical crosslinking copolymerization of styrene/unsaturated polyester resins: 3. Kinetics-gelation mechanism, Polymer (Guildf), 34 (**1993**), 4516–4523, doi:10.1016/0032-3861(93)90158-7

[20] C. P. Hsu, L. J.. Lee, Free-radical crosslinking copolymerization of styrene/unsaturated polyester resins: 1. Phase separation and microgel formation, Polymer (Guildf), 34 (**1993**), 4496–4505, doi:10.1016/0032-3861(93)90156-5.

[21] Y. -S. Yang, L. Suspene, Curing of unsaturated polyester resins: Viscosity studies and simulations in pre-gel state, Polym. Eng. Sci., 31 (**1991**), 321–332, doi:10.1002/pen.760310505

[22] R. G. Weiss, Controlling variables in molecular gel science: how can we improve the state of the art?, Gels, 4 (**2018**), doi:10.3390/gels4020025

[23] R. G. Weatherhead, Catalysts, accelerators and inhibitors for unsaturated polyester resins, FRP Technol., (**1980**), 204–239, doi:10.1007/978-94-009-8721-0_10

[24] M. Farsane, L. Soufia, A. Anouar, S. Chah1,S. Dagdag, M. Bouzziri, Experimental evaluation of the curing of unsaturated polyester resin at various amounts of methyl ethyl ketone peroxide, cobalt octoate and porcelain powder, Rev. Chim., 71 (**2020**), 58–66, doi:10.37358/RC.20.10.8350

[25] L. Xu, L. J. Lee, Kinetic analysis and mechanical properties of nanoclay reinforced unsaturated polyester (UP) resins cured at low temperatures, Polym. Eng. Sci., 45 (**2005**), 496–509, doi:10.1002/pen.20309

[26] J. Simitzis, A. Stamboulis, D. Tsoros, N. Martakis, Kinetics of curing of unsaturated polyesters in the presence of organic and inorganic

fillers, Polym. Int., 43 (1997), 380–384, doi:10.1002/(sici)1097-0126(199708)43:4<380::aid-pi816>3.3.co;2-v

[27] W. D. Cook, G. P. Simon, P. J. Burchill, M. Lau, T. J. Fitch, Curing kinetics and thermal properties of vinyl ester resins, J. Appl. Polym. Sci., 64 (**1997**), 769–781, doi:10.1002/(SICI)1097-4628(19970425)64:4<769::AID-APP16>3.0.CO;2-P

[28] M. Farsane, A. Anouar, S. Chah, S. Dagdag, M. Bouzziri, Study of experimental investigations in the presence of ceramic waste powder, Mater. Plast., 57 (**2021**), 1–12, doi:10.37358/MP.20.4.5401

[29] Y. J.Huang, J. S. Leu, Curing of unsaturated polyester resins, Effects of temperature and initiator: 1. Low temperature reactions, Polymer (Guildf), 34 (**1993**), 295–304, doi:10.1016/0032-3861(93)90080-T

[30] J. Karl Fink, Reactive Polymers: Fundamentals and Applications, 2018 Elsevier Inc., doi:10.1016/c2017-0-01641-5

[31] H. Kubota, Curing of highly reactive polyester resin under pressure: Kinetic studies by differential scanning calorimetry, J. Appl. Polym. Sci., 19, (**1975**), 2279–2297, doi:10.1002/app.1975.070190819

[32] J. C. Lucas, J. Borrajo, R. J. J. Williams, Cure of unsaturated polyester resins: 2. Influence of low-profile additives and fillers on the polymerization reaction, mechanical properties and surface rugosities, Polymer (Guildf), 34 (**1993**), 1886–1890, doi:10.1016/0032-3861(93)90430-I