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PHYSICAL PROCESSES ACCOMPANIED OLIGOMER CURING

Олигомер материалдардың қатаю химиялық процесіндегі ілесіп өтетін әр түрлі физикалық құбылыстар қарастырылған. Үш өлшемді химиялық байланыстар торы түзілу себебінен сұйықтың қатаюы байқалады. Гель-нүктенің орналасуы динамикалық және вискозиметриялық әдістермен анықталған.

Обсуждены различные физические явления, которые могут сопровождать химические процессы отверждения олигомерных материалов, имеющих общее и принципиальное значение. Обсуждены экспериментальные доказательства образования микрогелевой фазы как прямое свидетельство гетерогенности реакции структурирования.

Introduction

The oligomer curing process is an important technological operation used in different field of polymer application including electro-technique, civil engineering, automobile industry and so on. So, the understanding of general features of the process and the influence of technological factors on the quality of final articles is of primer interest. Meanwhile, it is worth stressing that the oligomer curing is not a chemical process only, because the complex of physical transformation takes place along chemical reactions as well. In this paper we will not touch on the chemistry of curing, which strongly depends on the great variety of the nature of the component, but will focus on the physical effects accompanied oligomer curing.

Actually two effects are of the dominating importance. Firstly, that is the transition from a low viscous liquid to the solid state, and the second one is the phase separation taking place along with the curing.

Transition from a fluid into a solid state — gel-point

Initial state of a composition used for the formation of the final items is a relatively low viscous liquid. This is a mixture of low-molecular-weight components, which then will react to form a three-dimensional network. So, just after the reaction starts, viscosity being initially equal to η_0 begins to grow and finally it approaches infinity (Fig. 1). The time, t^*, at which viscosity grows to infinity and thus the material losses fluidity is called the gel-point. This is the formal limit of processability of a material, though practically it is usually assumed that the processes related to flow ceased at the viscosity level of the order of 10^3 Pa*s.

The correct determination of the gel-point is of real practical importance because if to jump through this point we will receive the incomplete filling of the mold. On the other side if to carry out the process much before the gel point it will lead to undesirable loss of time for curing a material inside a mold.

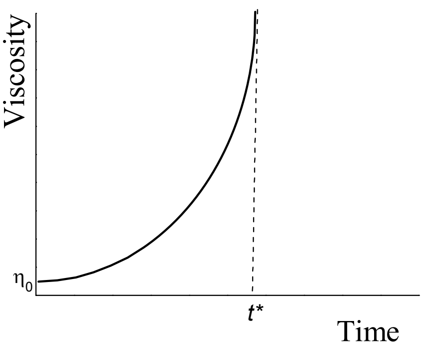

Fig. 1. Viscosity growth at the initial stage of curing and the determination of the gel-point

Meanwhile it is not convenient to use curves like shown in Fig. 1 because if the uncertain curvature of the $\eta(t)$ dependence. Thus, the following method of the t^* estimation has been proposed. Time dependence of viscosity measured rather far from the gel point is presented in the $1/\eta(t)$ vs. t coordinates. The example of such presentation is shown in Fig. 2 for an epoxy resin composition. It is clearly seen that the $\eta^{-1}(t)$ cs. Time dependencies are linear that allows one to make a convenient and reliable extrapolation to the point $\eta^{-1} = 0$ (crossing with the x-axis). The cross-points are, by definition, t^*, because at these points $\eta \to \infty$.

Moreover the presentation of such kind gives us a possibility to find the temperature dependence of t^* and thus to find the optimal conditions of curing for this or that case.

The other method of the gel-point determination is based on measurements of the evolution of the elastic (dynamic) properties of the composition in time.

Typical example of such dependencies is shown in Fig. 3 for a silicon-organic compound used in electric industry.

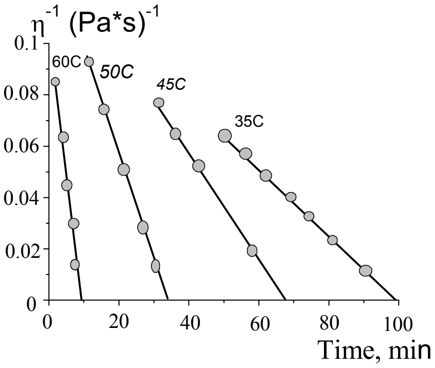

Fig. 2. Estimation of the gel-points for an epoxy compound at different temperatures

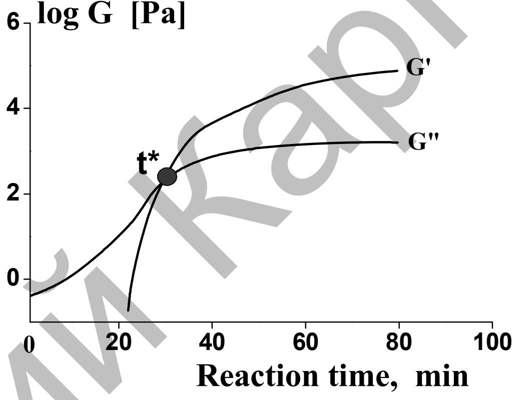

Fig. 3. Determination of the gel-point by means of dynamic measurements, curing of a silicon-organic compound

The gel-point (shown in the Figure) is assumed as the cross-over point of the $G'(t)$ and $G''(t)$ dependencies, i.e. the state of a material, in which loss tangent equals 1.

It is important that both methods of the gel-point determination provide the correlative results.

In discussing the dynamic method of the gel-point determination, it is worth noting that this point does not correspond to any definite value of the elastic modules. It is shown in Fig. 4, where the rates of curing of two compositions of epoxy resin are compared. The compositions include different curing agent — one contained bifunctional curing agent and the second one has polyfunctional curing agent.

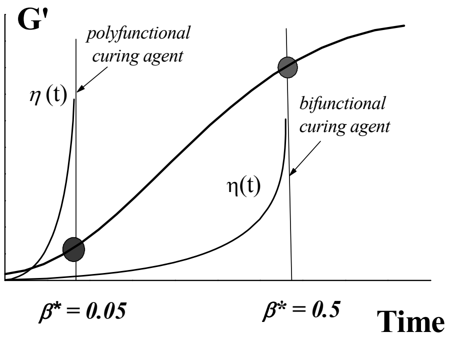

Fig. 4. Comparison of two curing epoxy-based compounds with bi- or polyfunctional curing agents

Looking at this Figure one can see that the gel-point is reached at quite different times and at different degrees of transformation, β. Surely, using a polyfunctional agent leads to shorter gel-time, and the formation of a three-dimensional network happens at much smaller values of the critical degree of transformation β*.

So, the conclusion from this part of the work is that there two different (viscometric and dynamic) methods of the gel-point determination, which lead to the close results. This point is of the main importance in technology of the oligomer curing processes.

Phase separation and inhomogeneity of the cured products

The phase separation in the process of curing has two sides. First, the forming three-dimensional polymer is unsolved in the reactive medium, and, second, as the result of different interaction of a forming polymer at different intermediate stages of the process with a reactants the final product appears inhomogeneous, (sometimes strongly inhomogeneous) that influences its quality because properties of these products depend not only on the average the density of the chemical network but on the local differences in the polymer structure.

Cured oligomers are rather difficult objects for chemical analysis, because they are not soluble compounds. So, just rheokinetic methods are the most suitable to following the process of curing of such systems [1].

There are several rheological evidences for heterogeneous nature of curing. Maybe the most clear is the separation of the micro- and macrogelation processes [2]. Fig. 5 illustrates the difference between the gelation on the micro-level and curing of a reactive system in whole. This picture is quite typical for curing of many different oligomeric resins, phenolic and melamine resins in particular (see also [3]). Let us discuss what the unlimited growth of optical density means. It reflects the appearance of insoluble microgel particles at some characteristic time t_f. In all cased studied by us $t_f < t^*$, i.e. microgelation occurs earlier than the gel-point is reached. The formation of microgel particles is the reflection of the phase separation of the cured particles and the other medium.

This experimental result clearly demonstrates that the curing process proceeds in two stages, firstly, insoluble fraction appears, and secondly, the gelation of the whole material takes place. Surely it leads to inhomogeneity of a final product.

The microgelation is the formation of the two-phase colloid system. Consequently, the rheological properties of this system are quite different in comparison with its precursor. Indeed this colloid system behaves as a non-Newtonian liquid (though it remains fluid), while a solution in the initial stage of curing was a simple Newtonian liquid. Non-Newtonian behavior is typical for a two-phase solution, while at t^* a system completely losses its fluidity due to the formation of three-dimensional space network.

As was said, just the fact of the difference is the proof of the heterogeneous character of curing, and the situation of the equality $t_f = t^*$, which should be observed in homogeneous curing, has been never observed in our experiments.

The above presented picture actually forced us to suppose that the gel-fraction in curing materials must appear before the gel-point of a system in while. Indeed, such experimental facts are well known, and we also observed this effect.

One of the examples of this effect is presented in Fig. 6 for phenolic resin. It is clearly seen that the gel fraction appears much before the gel point and even before the microgelation in a reactive medium.

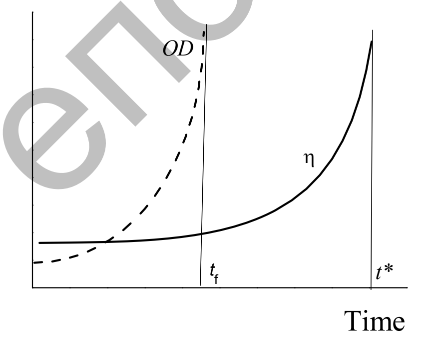

Fig. 5. Time dependencies of optical density (OD) and viscosity observed in curing phenolic and melamine resins

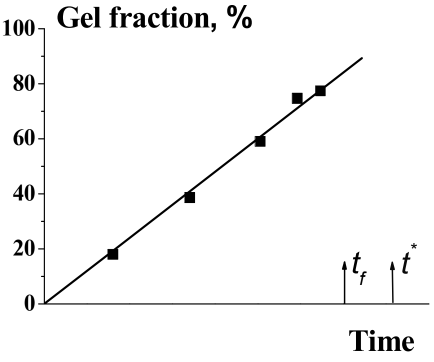

Fig. 6. Time dependence of the gel fraction share in curing of a phenolic resin

Several other experimental facts also say about the strong heterogeneity of the curing process. One of them is the dependence of the degree of transformation at the point of gelation on temperature. An experimental example illustrating this dependence is presented in Fig. 7.

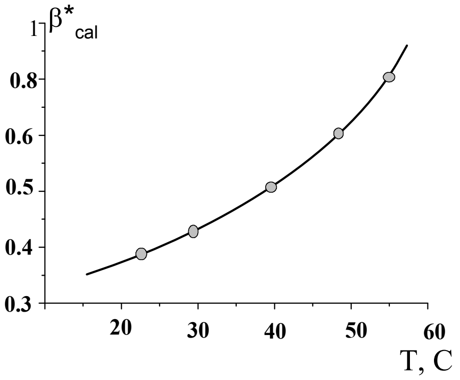

Fig. 7. Temperature dependence of the critical degree of transformation (at the point of gelation) found by the calorimetric method for a silicon-organic resin

It is well know that the conception of a unique critical degree of transformation plays a key role in the Flory geometrical model of gelation, supposing the uniform mode of this process. One can see that the critical degree of transformation actually depends on temperature. It is evident that the degree of deviation from the universal Flory's rule increase in the decrease of temperature. It means that the decrease in temperature leads to stronger heterogeneity of the formed three-dimensional network providing the gelation of a reactive medium.

Conclusions

The chemical reactions taking place in the process of oligomer curing are accompanied by different physical effects. One of them is the liquid-to-solid transition occurring at the gel-point. The time of this threshold situation can be estimated either by viscometric method (in presentation the reciprocal viscosity as a function of time) or by the dynamic method, when the evolution of elastic and loss modulii is followed in time. In this case the gel-point corresponds to the cross-over of these two curves. The process of curing proceeds in a strongly expressed inhomogeneous mode that is expressed in formation of the gel-fraction much before the gelation of a reactive medium in whole and appearance of microgel particles of colloid size. Different arguments supporting this understanding the process of oligomer curing have been introduced and discussed.

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