Effect of the Carbon Filler on the Curing Kinetics of Epoxycyanate Cooligomer

Alexander Fainleib[1]*, Elena Slinchenko[1], Olexander Brovko[1], Ludmila Sergeeva[1], Valentina Dubkova[2], Harry Frisch[3]

[1]Institute of Macromolecular Chemistry, National Academy of Science of Ukraine, Kharkivs'ke shose, 48, 253160, Kyiv-160, Ukraine

[2]Institute of General and Nonorganic Chemistry, Academy of Science of Belarus, Surganova street, 9, 220072, Minsk, Belarus

[3]State University of New York, Albany, New York 12222, USA

SUMMARY: The influence of carbon fibre on the curing kinetics of the prepolymer based on bisphenol A cyanurate and epoxy resin has been studied using infra-red spectroscopy. It was found that curing process of prepolymer is very complicated. It is shown that in curing the prepolymer a number of the sequential transformations of ones cycle structure into others occurs. An introduction of the carbon fiber (CF) of two types, original CF and modified CF (MCF) containing phosphate groups, affect strongly the prepolymer curing. Both CF and MCF accelerate the conversion rate of epoxy groups. In the case of cyanate groups, the former does not practically affect their conversion whereas the latter decelerates strongly this process. In the paper the influence mechanism of CF is considered.

Introduction

The formation of filled linear or cross-linked polymers has been defined to differ from that of unfilled polymers even though there is not a chemical interaction on the polymer-filler interface[1)]. The filler influence is caused by an adsorption interaction of monomer and/or oligomer with the filler surface leading to the change of both the reaction kinetics and the final properties of the polymer formed. The investigation of cross-linked polymer formation in the presence of the filler which is capable of chemical bonding on the interface is a difficult task, however, its decision is necessary to define the curing mechanism of such kind systems and to regulate the final parameters of the materials.

In this paper the chemistry and curing kinetics of the copolymer based on dicyanate ether of bisphenol A (DCBA) and diglycidyl ether of bisphenol A (DGBA) as well as the influence of the carbon fibre (initial carbon fibre (CF)) and that modified by orthophosphoric acid and

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containing phosphate groups on their surface (PCF)) on the formation process were studied.

Experimental

Copolymer. Copolymer of DCBA (99%) and DGBA (>98%) was chosen in a weight ration of 60/40 wt/wt. The copolymer was made using a two-step procedure. In the first step, the prepolymer of DCBA and DGBA was synthesised. The DGBA was heated up to 100°C and thoroughly mixed with DCBA powder. During mixing the temperature was increased to 140 - 150°C. At this temperature the mixture was held for 45 min. In the second step, the prepolymer was cured at 150°C for 5 h and postcured at 180°C for 3 h.

Carbon fibre. Carbon fibre of both types was used to be a product of carbonisation of hydrated cellulose fibre at the temperature 500-600°C[2-4]. The introduction of phosphate groups into hydrated cellulose fibre was carried out by the method described in Ref.[3]. The phosphorus concentration was found to be 12% wt. in PCF. The diameter of both types of fibre was (10-12) • 10^{-6} m. Both CF and PCF were ground by hand in an agate mortar prior to use. After grinding the fibre length was measured to be equal (100 - 200)•10^{-6} m.

Filled composition. In preparing the filled composition the dispersed carbon fiber was mixed with prepolymer for 10-15 min and then curing was carried out in accordance with above procedure for unfilled composition.

Measurements. In this study an infra-red (i.r.) spectrophotometer "Specord M80" was used for kinetics investigation. The i.r. band at 2968 cm^{-1} was used as an internal standard. The samples for i.r. investigation were prepared by the following way. One drop of prepolymer (5-10 mg) was pasted between two NaCl plates, which were then mounted on a sample holder located in the i.r. chamber. The curing was carried out according to above procedure.

Results and discussion

There are a few reviews of publications concerning the reaction of epoxies with cyanates. All the researchers observed the cyclotrimerization of cyanate followed by transformation of cyanurate formed to oxazolidinone. However there is no clear understanding if the epoxide can react directly with cyanate with oxazoline cycle formation[5-6].

The curing at 150°C leads to the drastic decrease in an optical density of cyanate group band at 2272/2236 cm^{-1} and to some decrease of the stretching vibration band of epoxy cycle at 915 cm^{-1}. At the same time the absorption peaks of bands at 1566 and 1370 cm^{-1} strongly increase and the intensity of the band at 1680 cm^{-1} grows also. The band at 1565 cm^{-1} is related to triazine ring vibration and that at 1370/1365 cm^{-1} caused by absorption of -O- fragment in

cyanurate[7]. The 1680 cm^{-1} band is probably related to C=N-vibration of the oxazoline[8]. After 30 min only following the beginning of heating at 180°C vibration band of cyanate groups disappears completely. In 1 h approximately after heating at the temperature 180°C the band at 1750 cm^{-1}, which is caused by oxazolidinone cycle vibration becomes marked[9]. After curing at 180°C results in both the increase of the optical density of this band and the decrease of the intensity of that at 1680 cm^{-1}. Besides the redistribution of the intensities of the bands at 1680 and 1750 cm^{-1} a high frequency shoulder appears on the side of the band at 1680 cm^{-1}. After 2 h approximately the shoulder separates into individual band with maximum at 1696 cm^{-1}. The optical density of the band at 915 cm^{-1} drops synchronously with above process.

The Fig. 1 shows the kinetic curves of epoxy and cyanate groups conversion during the prepolymer curing.

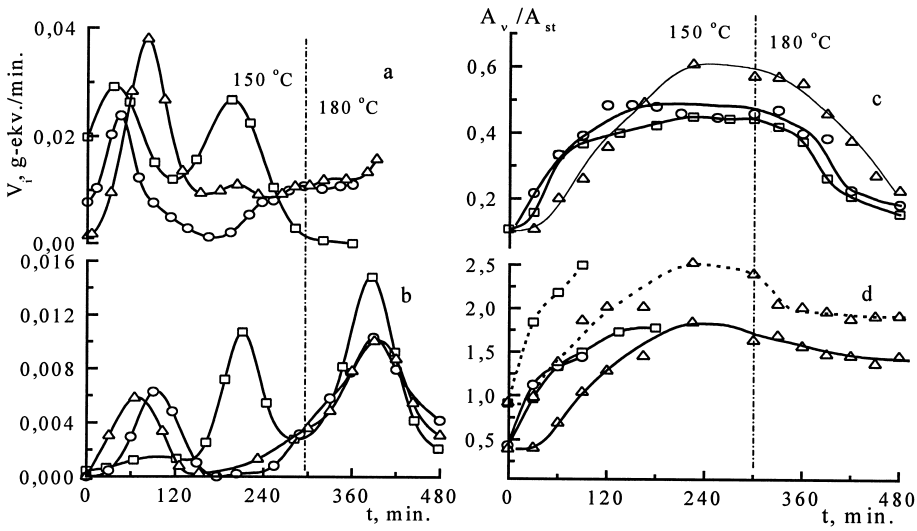
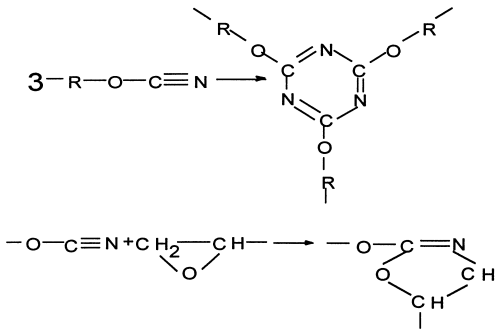


Fig.1. Kinetics curves of cyanate (a), epoxy (b) groups conversion, oxazoline (c), and cyanurate (d) (band at 1370 cm^{-1} (- -), band at 1566 cm^{-1} (-)) cycles conversion in the unfilled reactive blend (□) and filled reactive blend by 2% CF (○), 2% PCF (Δ).

The dependencies of the optical densities of the bands at 1680, 1566, 1370 cm^{-1} upon the heat treatment time are shown in Fig.1, where V_I is rate of reaction and the value of optical density (A_v) standardized to the internal standard (A_{st}).

One can see (Fig.1) that the reaction of cyanate groups starts since first minutes of initial

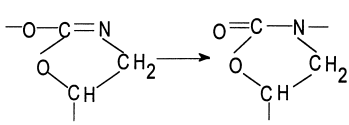
system heating and the rate achieves a maximum value just after 60 min. The reaction of epoxy groups has an induction period and the rate begins to increase after 120 min of heating. This fact together with very high speed of the increase in the optical density of the bands at 1370, 1566 cm^{-1} evidence that at the initial stage the cyanurate cycle formation has a highest rate in comparison with other reactions and these data are in a good agreement with those early reported in the Ref.[6]. Simultaneously the formation of oxazoline cycle proceeds but this process has a lower speed. The schemes of the corresponding reactions follow below.



From the kinetic curves presented in Fig.1 one can see that the synchronous drastic acceleration of both cyanate and epoxy groups conversion accompanied by some jump in the optical density of the band at 1680 cm^{-1} occurs in the time interval from 180 to 225 min at 150°C. The jump is observed at 55% cyanate groups conversion. The 55-60% cyanate groups conversion region corresponds to a gel formation for the system studied[10,11] and the observed acceleration of the curing process of prepolymer appears to be caused by the shift of reactive equilibrium, after the gelation point, in the direction of the oxazoline cycle formation that in the same time does not exclude the acceleration of the cyclotrimerization process.

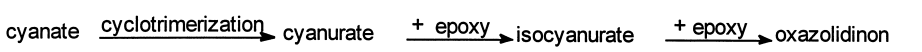
After heat treatment at 180°C for 60 min cyanate groups are completely consumed. At this stage the formation of cyanurate and oxazoline cycles is ended. At the same temperature the transformation of oxazoline cycles into oxazolidinone ones begins also. In this case an intensity of the band at 1680 cm^{-1} is decreased and that at 1750 cm^{-1} is increased.

The possibility of oxazoline cycle being transformed into oxazolidinone one has been shown in Ref[12]:



At the temperature 180-250°C, simultaneously with above reaction, the sequential transformations of cyanurate cycle into isocyanurate and then into oxazolidinone ones take place at their interaction with an excess of epoxy groups[9].

The forming isocyanurate ring has an absorption band of (C=O)-groups in the region 1690 -



1765 cm^{-1} depending of the substituent type[13].

It will be noted that the oxazolidinone cycle formation proceeds in two courses: the first, through the isomerization on oxazoline cycles formed owing to the reaction between cyanate and epoxy groups; the second, owing to a number of the sequential transformations

It has been determined that the introducing of fibers affects essentially the rate of the process' occurring during the cure. Both the CF and PCF decrease the rate of cyanate groups conversion in filled systems as compare to unfilled one. What's more the PCF decelerates stronger this process. As it can be seen (Fig.1) the rate of cyanate groups conversion decreases harshly and achieves the maximum value later (after 30-40 min of heating) than in composition filled with unmodified CF (after 90 min of heating). Contrary the reaction of epoxy groups at early stages quickens with the introducing of the both the types of fibers. The reaction of epoxy groups in unfilled system has an induction period when the rate is minimal and does not change. This induction period vastly decreases in system filled with CF and is absolutely absent in system filled with PCF. Rate of epoxy groups conversion at the first stage of heating at 150°C achieves the maximum value after 200 min for unfilled system, 90 min for system filled with CF and 60 min for system filled with PCF.

One of the reasons of the PCF influence on curing the prepolymer may be the interaction of PCF with α-oxide cycles as follows[14]. The reaction product is the alkyl-substituted phosphate groups. Besides the hydrogen-containing active groups of the PCF surface are able to react with cyanate groups[15]. These two processes is certain to influence on the conversion rate of the functional groups of the system studied.

At the same time they do not explain the drastic retardation of the cyanate groups conversion rate for the filled system. A comparison of the kinetic curves, given in Fig.1, shows that the retardation is considerably caused by inhibition of the cyclotrimerization process of cyanate groups at the reaction initial steps. And in this case an adsorption of cyanate onto the fiber surface appears to play an important role in result of reactive groups are partly excluded from the initial stage of reaction and on they react with active phosphorous-containing groups located on the fiber surface, but the rate of this reaction is lower than that of cyclotrimerization.

Conclusion

The kinetic investigation of cross-linked copolymer based on bisphenol A dicyanate and bisphenol A diglycidyl ether showed that at the initial stage of curing at 150°C with the highest rate the cyanurate cycles are formed. Simultaneously, but with lower rate, the formation of oxazoline cycles occurs, which as the temperature is increased up to 180°C transform into oxazolidinone ones. In addition when the excess of epoxy groups takes place the formation of oxazolidinone cycles is possible from isocyanurate cycles formed, in its turn, from cyanurate ones.

No CF effect on the conversion process of cyanate groups is observed whereas the PCF, at the first stage of curing, decelerates shortly the cyanurate groups conversion. The latter is explained by the reaction of the reactive groups of carbon fibre with epoxy and cyanate groups of a prepolymer.

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References

1. Y. Lipatov. *Polymer Reinforcement*. Chem. Fec. Publishing 1994.
2. I. Yermolenko, I. Lyubliner and N. Gul'ko. *Element-containing Carbon Fibre Materials*. Nauka & Technic, Minsk 1982, p.272.
3. I. Yermolenko, E. Buglov, I. Lyubliner, S. Dovgalev, I. Danilov and M. Longin. *Khimiko-Pharmatsevticheski J.* **12**, 33 (1968).
4. I.Yermolenko, I. Vygovski and I. Lyubliner. *Vesti AN BSSR. Ser. Khim. Nauk.* **4**, 78 (1974).
5. *Chemistry and Technology of Cyanate Ester Resins;* I. Hamerton, Ed.; Chapman & Hall, Glasgow, 1994.
6. I.Hamerton, J.N.Hay. *Polymer International* **47**, 465 (1998).
7. D. Shimp, F. Hudock and S. Ising. *Preprint, 33rd International SAMPE Simposium*, March 7-10 (1988).
8. A.Fainleib, T. Shantali and L. Sergeeva. *Plasticheskie massy.* **1,** 16 (1995).
9. V. Korshak, V. Pankratov, L. Komarova, Ts. Frenkel, A. Fainleib and S. Vinogradova. *Izvestiya AN SSSR, Ser. Khim.* **10**, 2369 (1983).
10. V. Pankratov, A. Ladovskaya, V. Korshak and S. Vinogradova. *Vysokomol. Soed.* **A21**, 1014 (1979).
11. L. Ming-Cherug and H. Jin-Long. *Polymer.* **35** , 2822 (1994).
12. Sh. Sukyurov and V. Pankratov. unpublished results.
13. P. Tiger, L. Sarynina and S. Entelis. *Uspekhi Khimii.* **41**, 1672 (1972).
14. I. Yermolenko, V. Dubkova and I. Lyubliner. *Vysokomol. Soed.* **A20** , 2180 (1978).
15. D. Martin and R. Bacaloglu. *Organische Synthesen mit Cyansaureestern*. Akademie., Vergal Berlin 1980, p.300.