KINETIC PECULIARITIES OF POLYCYCLOTRIMERIZATION OF CYANATE ESTER RESINS. INFLUENCE OF CURING SCHEDULE AND THE PRESENCE OF ORGANIC AND INORGANIC MODIFIERS

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ABSTRACT

Polycyclotrimerization of cyanate esters of bisphenols (CEB) is a high temperature process, which is usually catalyzed by acetylacetonates of such metalls as Cu, Fe, Zn, Co, Pb and others [1]. As a result polycyanurate network (PCN) consisting of sim-triazine cycles in the network junctions connecting by short residues of bisphenols is formed. The proces is usually carried out by step-by-step method: heating of the reactive system from about 120-150 ^{o}C to around 250-300 ^{o}C with holding at some temperature shelves for several hours [2]. This way is obligatory because on eash step the PCN of certain crosslink density is formed and in order to proceed with further increasing conversion of the cyanate groups of growing PCN the temperature has to be increased higher than the glass transition temperature of the network formed on the step. This will lead to relaxation of the network skeleton and the cyanate groups belonging to the network will have a chance to meet each other and to react. By this way the conversion of cyanate groups and crosslink density of the networks are increased from previous step to the next step. In this work we have developed first the continuous method of CEB polycyclotrimerization. It is carried out without any catalysts by heating of initial cyanate monomer from 120 ^{o}C to 320 ^{o}C with a heting rate of 0,5-1,0 ^{o}C/min. This method is faster and simpler compared to the conventional ones. Secondly, at synthesis of PCNs in the presence of reactive (oligo(ε-caprolactone [3]) or inert (dimethyl phthalate, dibutylphthalate) porogens, as precursors for porous polycyanurates, it has been found that the porogens accelerate the CEB curing process. Thirdly, at synthesis of PCN-based nanocomposites with different inorganic nanofillers the catalytic effect of the fillers on polycyclotrimerization of CEB has been found independently on the filler nature. Study of the process by DSC technique has shown that in the presence of the porogens or nanofillers the exothermic peak moved to the region of lower temperatures, the activation energy reduced. This effect was observed for organically modified montmorillonite [4], carbon nanotubes [5], functionalized polyhedral oligomeric silsesquioxanes. One can suppose that the catalytic effect is provided by functional groups of porogens or those on a surface of nanofillers.

References

(1) *Chemistry and Technology of Cyanate Ester Resins.* Ian Hamerton, editor. Chapman & Hall, Glasgow, 1994.
(2) *Themostable Polycyanurates. Synthesis, Modification, Structure and Properties.* Alexander Fainleib, editor. Nova Science Publishers Inc., NY, USA, 2010.
(3) Fainleib A.; Grigoryeva O.; Garda M. R.; Saiter J. M.; Lauprêtre F.; Lorthioir C.; Grande D. *Journal of Applied Polymer Science* **2007**, *106*, 3929-3938.
(4) Bershtein V.A.; Fainleib A.M.; Pissis P.; Bei I.M.; Dalmas F.; Egorova L.M.; Gomza Yu. P.; Kripotou S.; Maroulos P.; Yakushev P.N. *Journal of Macromolecular Science Part. B. Polymer Physics* **2008**, *47(3)*, 555-557.
(5) Fainleib A.; Bardash L.; Boiteux G. *eXPRESS Polymer Letters* **2009**, *3(8)*, 477-482.