Coatings obtained through cationic UV curing of epoxide systems in the presence of epoxy functionalized polybutadiene

M. SANGERMANO, G. MALUCELLI, R. BONGIOVANNI, G. GOZZELINO, F. PEDITTO, A. PRIOLA

Dipartimento di Scienza dei Materiali, e Ingegneria Chimica, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Torino, Italy E-mail: priola@fenice.polito.it

The cationic photopolymerization of a biscycloaliphatic and a di-glycidyl epoxide monomer was investigated in the presence of an epoxy hydroxy functionalized polybutadiene (PBE). Triphenylsulfonium hexafluoroantimonate was used as photoinitiator. The kinetics of UV curing, in the presence of the additive, was determined via FT-IR analysis, showing an increase of the rate of photopolymerization and of the final epoxy groups conversion. Comparison experiments were performed with hydroxy functionalized polybutadiene. Evidences are obtained that PBE is incorporated via a copolymerization reaction involving the epoxy groups and via a chain transfer reaction involving the OH groups. The investigation of the properties reveals a flexibilization effect due to the presence of the additive, evidenced by a sharp decrease of T_g of the cured films. © 2002 Kluwer Academic Publishers

1. Introduction

The UV curing process is a polymerization technique in which radiations induce a fast transformation of a liquid monomer into a solid polymer. Radical or cationic species are generated by interaction of UV light with a suitable photoinitiator [1]. Onium salts initiate the cationic curing process by generating very strong Brönsted acids upon photodecomposition [2].

Cationic photoinduced process presents some advantages over the radical one [3]; in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. In addition, the monomers employed are generally characterized by low irritation and toxicity properties. Different types of monomers and oligomers have been proposed and reported in literature [4, 5]; among them mainly epoxides are currently used in industry because of their availability and good properties after curing. One of the main limitations to the use of UV curable epoxy resins lies in their relatively low reactivity, especially when compared to the widely used acrylate based resins [6].

Biscycloaliphatic diepoxides are known to be more reactive than glycidyl ethers, because of the strain of the adjacent cyclohexane ring [7]; for this reason they are the most used in today's industrial cationic photocuring applications [8].

In such network forming systems, polymerization proceeds rapidly in the first step, then polymerization markedly slows down but can still occur as monomer diffuses to the fixed propagating sites within the swollen gel. However, as the T_g of the network approaches the curing temperature vitrification sets in. At this point diffusion of the monomers is prevented and polymerization actually stops before all the polymerizable groups are consumed. As a result a large amount of epoxy groups can remain unreacted. While such resins have excellent solvent resistance, their rigid structures contribute to their rather poor elongation and flexibility characteristics. In many coatings applications there is a need for tough, flexible materials having considerable elongation at break. For this reason, it is desirable to find ways of obtaining good mechanical characteristics.

In the literature systems based on the photopolymerization of epoxy monomers in the presence of vinyl ethers or propenyl ethers are reported; they show an increase of the UV curing kinetics [9, 10]. Another way to obtain a fast and complete polymerization consists of introducing reactive plasticizing agents. They delay the point of vitrification by increasing the mobility of the chains, so that the polymerization rate remains high and a higher epoxy group conversion is achieved [11].

The presence of a plasticizing agent linked to the epoxy network increases the flexibility of the cured product and the impact resistance giving rise to a good balance of the mechanical properties typical of the epoxy resins, and of the resilience behaviour.

In a previous paper is reported the use, as plasticizing agent, of epoxide soybean oil [12]; evidences are given that a true copolymerization occurs between the different types of epoxy groups. In this work we