



Mechanical properties of polymer layers fabricated via hybrid free radical-cationic polymerization of acrylate, epoxide, and oxetane binders



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ABSTRACT

This work is aimed at the hybrid free radical-cationic polymerization of acrylate, epoxide, and oxetane monomers. Studied hybrid systems were prepared as mixtures of binders polymerizing via free radical mechanism (pentaerythritol triacrylate, thioacrylate dendritic oligomer) and binders polymerizing through cationic mechanism (3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate epoxy monomer, bis[1-ethyl(3-oxetanyl)]methyl ether oxetane monomer) in various ratios. As radical and cationic photoinitiators, 2-hydroxy-2-methyl-1-phenyl-propan-1-one and (4-methylphenyl) [4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate, respectively, were used. The process of polymerization was monitored using Fourier-transformed infrared spectroscopy giving degree of conversion data for each reaction. Cured polymer layers were evaluated in terms of their mechanical properties. Based on experimental data, best mechanical properties (adhesion and flexibility) and the highest degree of conversion were achieved in hybrid samples containing thioacrylate dendritic oligomer radical binder in combination with (3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate and bis[1-ethyl(3-oxetanyl)]methyl ether (ratio 1:1) cationic monomers.

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1. Introduction

To date, systems cured by UV-vis radiation are used in many industrial applications. For example, UV curable compositions are exploited for coatings of various materials such as fibres, wood, metals, plastics or paper [1]. Other applications cover production of adhesives, solder mask [2], inks [3], microelectronic photoresists, and stereolithography [4]. Systems cured by visible light are used in the printing industry, imaging, medical applications, holographic recording, and nanoscale micromechanics. Dental filling materials, photoresists, printing plates, highly pigmented inks/coatings are only some of the applications where these systems are utilized [5,6]. The big advantage of UV curable compositions lies in the instant curing and high efficiency. This technology is environmentally friendly with adjustable performances (from brittle to very flexible films) [1]. In comparison with conventional coatings (e.g.

solvent-based coatings), UV cured layers offer energy saving and low content of volatile organic compounds [7].

Systems cured by UV radiation generally employ free radical or cationic mechanism; both mechanisms have their distinct advantages and disadvantages. Acrylates, polyurethane acrylates, polyester acrylates, and acrylic acrylates are commonly used binders cured by free radical mechanism [1]. Their main advantages are fast curing (fraction of a second) and great offer of existing monomers, oligomers, photoinitiators, and additives to set the final properties [8]. On the other hand, main drawbacks of free radical polymerization are the inhibition of curing by atmospheric oxygen, irritant effect of some acrylate monomers [2], and contraction of the coating's volume during curing (shrinkage between 10 and 15% can occur) [1]. On the other hand, through cationic mechanism, epoxides, oxetanes, vinyl, propenyl and butenyl ethers [2,9,10] can be cured. Main advantages of cationic polymerizations are as follows: (1) there is no inhibition of the polymerization by atmospheric oxygen [6], (2) polymerization leads to small shrinkage only (for epoxides approximately 5%), and (3) formation of a large amount of hydrogen bonds, which leads to increased adhesion between the coating and the substrate [1]. Cured coatings have also high

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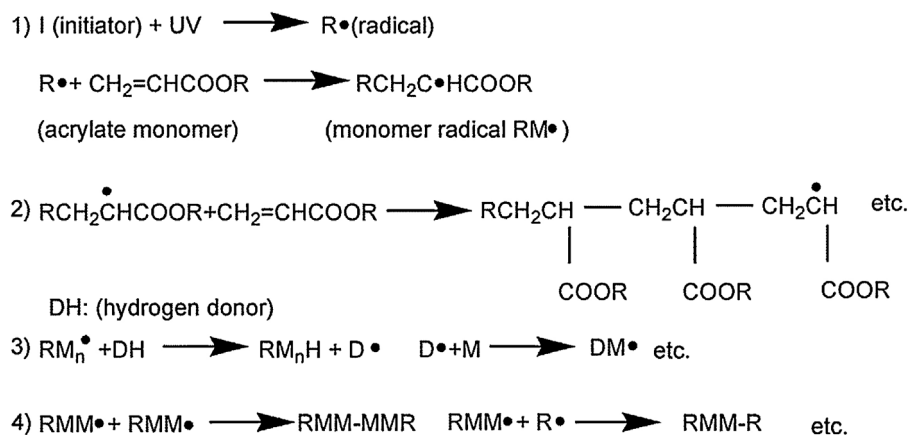


Fig. 1. Mechanism of free radical polymerization: (1) initiation, (2) propagation, (3) chain transfer, (4) termination [11].

heat resistance and good chemical resistance [10]. In contrast with free radical polymerization, cationic polymerization is much slower (final properties of the cured film can be obtained after approximately 24 h) [9] and this type of polymerization can be inhibited by humidity and bases [2,9].

The disadvantages of free radical and cationic mechanisms can be significantly suppressed by the use of hybrid polymerization, which can be performed sequentially or simultaneously via free radical and cationic mechanism [11]. Materials prepared in this way show many desirable chemical and mechanical properties that are difficult to achieve through separate free radical/cationic polymerization. Hybrid systems combine or modify the properties of both polymers (produced simultaneously by free radical or cationic polymerization) such as glass transition temperature, melting temperature, strength, toughness etc. [3,9]. These hybrid polymerizations may lead to the preparation of unusual hybrid polymer structures such as the multiblock, graft, random copolymers [1,12], and interpenetrating polymeric networks, which are considered to be very promising materials in the field of coatings [1]. They may be used in various applications, such as hard plastics, ion exchange resins, and materials damping sound and vibrations [3]. Other advantages of hybrid compositions include increased cure speed, faster development of final properties of the cured films, lower sensitivity to inhibition of curing by atmospheric oxygen, moisture and other inhibitors, and creation of films of improved properties [9].

The objective of this work is to determine the optimal composition of hybrid polymerizing samples in scope of the final degree of conversion (hereinafter DC) and mechanical properties of cured films. Samples evaluated in this work differ in the type of used monomers (acrylates, epoxides, oxetanes) and in the used ratios of these monomers. DC was determined based on results obtained

with Fourier-transformed infrared (FTIR) spectroscopy. Mechanical properties of the prepared films were evaluated with cylindrical mandrel bend test, falling weight test, cupping test, and pendulum hardness.

2. Theory

Photopolymerization by radical mechanism takes place in four steps: initiation, propagation, chain transfer, and termination (Fig. 1). In the first step (initiation), absorption of radiation by photoinitiator takes place which causes the decay of photoinitiator and formation of radicals. Radicals react with present molecules of monomers and oligomers (e.g. with acrylates) and a reactive alkyl monomer is formed. The radical monomer is highly reactive and reacts in chain reaction with other monomers or oligomers present in the formulation (propagation). Chain transfer is a reaction during which transfer of the reactive centre takes place from one molecule to another one. By proton transfer from the donor of hydrogen, the growth of the polymer radical is terminated and a new reactive centre is created on the molecule of donor (it can react with present molecules of monomers and oligomers which leads to formation of a new polymer chain). Termination is the last phase of the chain reaction during which an interaction or recombination of two radicals and termination of reactive centres on both molecules is taking place. Polymerization is terminated at using up all monomers or at increase of viscosity to the limit of molecule movement and interaction inhibition, even if the system still contains unreacted monomers [13].

Cationic polymerization proceeds also in four phases as stated above. In contrast to the radical polymerization, the reactive centre does not have a form of radical but cation. During initiation, as in previous case, the absorption of radiation by a photoinitiator (e.g.

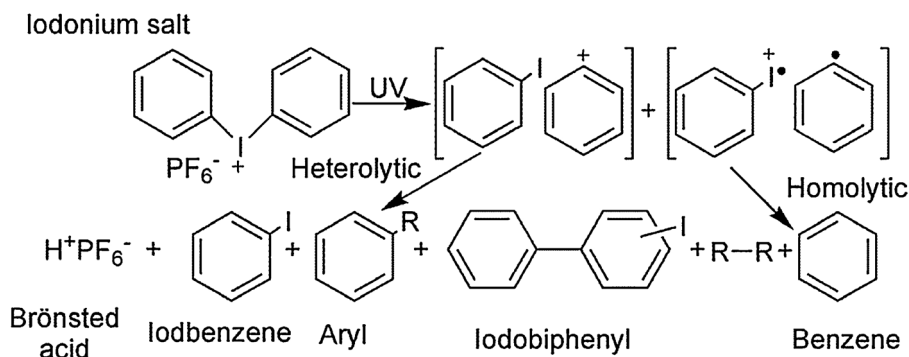


Fig. 2. Photo decomposition of iodonium salt [11].

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