

Abstract of the PhD thesis

„Obtaining (meth)acrylate adhesive binders by bulk photopolymerization”

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Acrylate resins (ARs) are a raw materials used for the production of various types of articles (from adhesives, decorative and protective coatings to medical, opto-electronic or 3D printed materials). They are made of acrylate monomers, i.e. acrylic acid, methacrylic acid and their esters. A large group of monomers available on the market allows for designing, in a wide range, the properties of ARs and products made of them. Most often, acrylate resins are produced by radical polymerization in a solvent. This process is carried out for several hours at an elevated temperature (usually 60-180°C), using a thermal initiator and organic solvents.

It turns out that the ARs synthesis process can be significantly improved by using the photopolymerization method, which is mainly associated with photocrosslinking / photocuring of thin-film materials. Free radical bulk photopolymerization (FRBP) is a method that gives the opportunity to shorten the synthesis time of acrylate resins and exclude organic solvents, while drastically reducing energy consumption. This process is carried out in a glass reactor, in an inert gas atmosphere, without the use of organic solvents. As a UV light source, cheap and widely available LED diodes can be used. So far, it has not been described how the conditions of the bulk radical photopolymerization process used for the production of resins, i.e. mixing speed, radiation intensity, type and amount of photoinitiator or chemical structure of monomers, affect the course of the process and the properties of polymers and products produced from them. Determining the impact of the mentioned above parameters of the process, seems to be necessary to thoroughly understand and develop this method of obtaining ARs. With this knowledge, it would be possible to produce resins in a sustainable and environmentally friendly manner (much faster, with lower energy consumption and a drastic reduction of the volatile organic compounds used).

This doctoral thesis focuses on determining the effect of selected conditions of bulk photopolymerization on the course of the process, the properties of the obtained (meth)acrylate resins and on the thermal and mechanical properties of thermosetting structural adhesives, with self-adhesive properties, obtained from them. This type of adhesives are used e.g. in aircraft structures. They are applied in the form of a self-adhesive film / tape, and after thermal hardening they form high durable joints, with a shear strength of at least 7 MPa.

Such assumptions of the work determined the choice of a mixture of monomers for the bulk photopolymerization process, e.g. functional acrylates and methacrylates (i.e. with an epoxy/oxetane and hydroxyl group). The dissertation was classically divided into theoretical and experimental parts. The theoretical part presents a literature review on the radical photopolymerization of acrylates but also the photoinitiators and monomers used in this process. Information about structural adhesives, in particular those with self-adhesive properties, is also included. In the research part, preliminary research and proper research were highlighted. In the first part, the key parameters of the resin synthesis process were identified and their values were initially determined, which allowed the preparation of the first acrylate resins, and from them the first adhesives. The next part of the research was devoted to research on the influence of the type of photoinitiator, mixing speed and additional monomers on the course of syntheses and the properties of the obtained products (resins and adhesives). As part of the research, the kinetics of the photopolymerization reaction was determined (photo-DSC). The obtained ARs were characterized by average molecular weights of copolymers (GPC), monomers conversions (NMR), solids content (TGA) and dynamic viscosity. Self-adhesive structural tapes produced from them were tested for self-adhesive properties (adhesion, cohesion and tack), and after thermal hardening their thermo-mechanical properties (DMTA) and shear strength were determined. The process of thermal curing was also tested (DSC, FTIR) and the cross-linking density of the resulting adhesive joints was determined.

The results of the conducted research show that the bulk photopolymerization method allows for effective and without organic solvents obtaining acrylate resins with the desired properties. Using resins obtained from butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA) and glycidyl methacrylate (GMA), self-adhesive structural tapes with shear strength above 17.7 MPa were prepared. In addition, it has been shown, how much influence the investigated parameters have on the course of the process and product properties. By increasing the mixing speed of the reactor charge, the effect of extending the reaction time is obtained (milder, more controlled course of the synthesis) and the possibility of obtaining higher conversion of monomers without the occurrence of the gel effect. Moreover, by choosing the amount of photoinitiator and the mixing speed of the batch, higher monomer conversions can be obtained, while lower average molecular weights and viscosity can be achieved. Significant differences in the course of syntheses were also noted as a result of introducing a small amount of the fourth comonomer to the mixture of basic monomers (BA/HEA/GMA). The biggest change was caused by the introduction of styrene, which extended the synthesis time

almost 20 times (from 7 to 120 minutes). The conversion of monomers was 64% at a viscosity of 3.5 Pa·s (for basic monomers only 37% was obtained at a viscosity of 3 Pa·s, and attempts to obtain a higher conversion resulted in the appearance of a gel in the system). In addition to the monomers introduced, the type and amount of the photoinitiator is of course also of great influence. Various type I photoinitiators were tested, and the best results (highest efficiency) were obtained with acylphosphine oxides.

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