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"Design of experiments" analysis in study of solventless UV crosslinkable acrylic pressure sensitive adhesives

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ABSTRACT

A 2^4 full factorial design was employed in the study of solventless acrylic UV crosslinkable pressure sensitive adhesives. The effect of four different factors (acrylic acid, t-butyl acrylate azobisisobutyronitrile initiator, and chain transfer agent) on different responses (prepolymer viscosities, final overall monomer conversion, tack, peel, and shear strength) was studied. Prepolymers were synthesized using a batch bulk polymerization procedure. The reaction mixture consisted of acrylic monomers (2-ethylhexyl acrylate, acrylic acid, and t-butyl acrylate), azobisisobutyronitrile initiator, chain transfer agent n-dodecylmercaptan, and unsaturated UV photoinitiator 4-acryloyloxybezophenone, which was copolymerized into the polymer backbone. The adhesive properties of the acrylic coatings were evaluated using tack, peel, and shear strength tests. Results showed that statistical analysis of the studied factors on polymer properties meets theoretical expectations. Analysis showed that the acrylic acid and the chain transfer agent (CTA) had the greatest effect on the prepolymer viscosity. None of the factors had a major impact on the final conversion of the synthesized products. The acrylic acid had a significant impact on the adhesive properties of the coating, i.e. tack and peel strength due to molecular hydrogen bonding. The impact of the studied factors could not be ascertained for the shear resistance of the adhesive coating.

1. Introduction

The design of experiments (DOE) technique is a useful tool in studies, where multiple parameters determine the final product performance. The most commonly used approach in today's studies is application of One-Variable-At-Time (or OVAT), where only one variable is changed, while all other are kept at fixed values. This type of study requires a large number of experiments, especially when studying the influence of multiple parameters on final outcome. The solution for more time efficiently and reliably study is application of statistical methods—DOE analysis. In a designed experiment, deliberate changes in the multiple input variables (or factors) are made, and after statistical analysis, the influence of variable factors on monitored output is determined. The objective of a carefully planned designed experiment is to understand which set of variables in a process affects the performance most and then to determine the best levels for these variables to obtain satisfactory output functional performance in products [1].

The emerging technology in the pressure sensitive adhesives (PSA) field of research is production of ultraviolet (UV) crosslinking PSAs, especially due to increasing environmental concerns such as reductions in volatile organic compounds (VOC), wastewater, and reduction of energy. UV crosslinkable PSAs may be synthesized either by solution or bulk polymerization process. The latter technique covers all of the stated environmental requirements, while no organic volatile compounds or water are used during the synthesis. The synthesized prepolymer have low molecular masses, which give low viscosities and enable coating at ambient temperature using conventional roll coating equipment. The appropriate applied properties of the adhesives can be obtained only after curing reaction, which must be fast and highly efficient. According to recent papers, the most work in this filed of research covers the synthesis and characterization of UV crosslinkable PSAs synthesized in organic solvents by solution polymerization. Most of the work in this field of research was accomplished by Czech, who synthesized a copolymer of 2-ethylhexyl acrylate and 4-acryloyloxybenzophenone in ethyl acetate and acetone [2]; he studied the influence of different crosslinker types on adhesive removability [3], and also performed a study of solvent free acrylic PSAs [4,5]. Czech et al. also developed UV crosslinkable solvent based PSAs with very low shrinkage [6]. They found, that the used 4-acryloyloxybezophenone photoinitiator was the most efficient among all of the tested photoinitiators. In a study published by Do et al. [7], an unsaturated photoinitiator (2-(acryloyoxy)ethyl

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4-(4-chlorobenzoyl) benzoate) was used for the syntheses of UV crosslinkable acrylic PSAs. The unsaturated photoinitiator was also incorporated into the polymer backbone via the solution polymerization process in ethyl acetate with different monomer ratios. Do et al. [8] also evaluated the effect of electron donor comonomer (2-hydroxyethyl methacrylate) on photoreaction efficiency and on adhesive properties (probe tack, peel, and shear adhesion failure temperature). Ozawa et al. [9] investigated the PSA properties of non UV cured and UV cured blends of acrylic adhesive polymer and urethane oligomer. Beside the UV copolymerizable photoinitiators, also metal chelate additives [10] can be used for crosslinking of the low molecular prepolymers. Descriptions of various types of photoinitiators are published in a study by Allen [11] and the photoreactivity of the adhesive prepolymers can be adjusted in different ways [12]. New types of copolymerizable photoinitiators were tested in a research published by Czech [13].

There are only a few published articles about statistical design of experiments in pressure sensitive adhesives field of research. Pichavant et al. [14] published a study concerning the influence of composition and processing parameters on the properties of UV cured films. They used screening and quantification tools of experimental design methodology. The approach described allowed formulating a reactive blend yielding a coating exhibiting sufficient elasticity without exhibiting tackiness by blending the two types of prepolymers. An optimal composition was defined by implementing a Scheffe's mixture design. Kim et al. [15] studied the influence of prepolymer (urethane acrylate or polyesteracrylate) type, triacrylate (trimethyolpropane triactylate or ethoxylated trimethylolpropane triacrylate) type, and the concentration of silicone acrylate on the surface properties of UV cured films by using a full factorial experimental design. Additionally, the predictive a mathematical model was obtained through analysis of variance. Kardar et al. [16] used a mixture method as a tool for experimental design for studying the effect of the chemical structure of monomers on some of the physical–mechanical properties of the resins and their cured films, such as viscosity, T_g, hardness, and scratch resistance. The selected method was found to be a useful tool to minimize the number of experiments.

2. Materials and methods

2.1. Materials

Monomers 2-ethylhexyl acrylate (2-EHA), acrylic acid (AA), and t-butyl acrylate (t-BA) were purified by conventional methods. They were washed three times with dilute sodium hydroxide solution, then washed three times with distilled water and dried over calcium chloride and then subjected to vacuum distillation under nitrogen. Initiator azobisisobutyronitrile (AIBN), chain transfer agent n-dodecylmercaptan (CTA), and unsaturated photoinitiator 4-acryloyloxybezophenone (4-ABF: Chemitec Company) were used in the commercially available form without further purification.

2.2. Polymerization procedure—prepolymer synthesis

The solventless UV crosslinkable adhesives were synthesized in a 250 ml glass reactor equipped with a reflux condenser, an anchor impeller, N_2 purge, and thermometer. Different formulations were tested and the polymerizations were carried out at equal process parameters. The total amount of reaction mixture was 200 g. The anchor impeller was operating at stirring rate of 100 min^{-1} and was identical for all experiments. After 30 min of mixing and nitrogen purging, the reaction mixture was heated to 83 °C at heating rate of 2.9 °C/min. Due to highly exothermic effect of bulk polymerization, the temperature of the reaction mixture reached approximately 180 °C. After the exothermic phase of the polymerization, was the reaction mixture stirred at 80 °C for another 60 min.

Due to the previous knowledge about the bulk polymerization of UV crosslinkable PSAs, no screening experiments were necessary [17]. Screening is normally used to reduce the number of process or design parameters by identifying the key ones that affect product quality or key performance [1]. In this study full factorial design was chosen with four different factors at two levels: amount of acrylic acid (A), amount of t-butyl acrylate (B) amount of polymerization initiator (C), and amount of chain transfer agent (D). The four factors play an important role by determination of key prepolymer and product properties. By changing the AA amount, adhesive properties may be changed due to hydrogen bond formation. Next, the amount of t-BA comonomer influences the prepolymer viscosity due to steric effect of a rigid t-butyl functional group on polymer backbone. Lastly, the CTA and AIBN concentration in the reaction mixture influence the prepolymer molecular weight, which determines the synthesized prepolymer viscosity as well as the adhesive properties.

A full factorial designed experiment consists of all possible combinations of levels for all factors. The total number of experiments for studying k factors at 2 levels is 2^k. In this case, the number of experiments was 16. In order to estimate the error variance, or variation in results within the experimental trials, each experiment was replicated twice. The total number of experiments equals 32. To minimize the effect of uncontrollable external factors or undesirable disturbances, the experiments were randomized. The experimental layout was generated with Minitab software and is presented in Table 1.

In this study the influence of specified parameters on five different responses was studied. Responses were prepolymer viscosity, final overall monomer conversions, and three basic adhesive properties: peel strength, tack, and shear strength.

2.3. Prepolymer characterization

Viscosities of synthesized prepolymers were measured using a Brookfield viscosimeter with spindle number 4 at 20 °C. The overall gravimetrical monomer conversion monitoring was performed for all syntheses. The synthesized prepolymer samples were dried in vacuum dryer at room temperature for 12 h, and then at 70 °C for 12 h.

2.4. Adhesive coating characterization

Synthesized prepolymer mixtures were coated on siliconized glassine paper using a Mayer bar coating system (wire thickness—0.3 mm). The coating weight of adhesive was approximately 28 ± 3 g/m^2. Then, the coatings were subjected to UV light (medium pressure Hg vapor lamp, 400 W/in.) and then transferred to 80 g/m^2 paper.

For the adhesive performance characterization of the produced PSAs, three different test methods were used: the peel adhesion at 180° (FTM 1—Finat test method 1), the loop tack (FTM 9), and the shear resistance (FTM 8). FTM 1 test is designed to quantify the permanence of adhesion or peelability of PSA adhesives. Peel adhesion is defined as the force required to remove pressure sensitive coated material, which has been applied to a standard test plate under an angle of 180° and speed of 300 mm/min [18]. The FTM 8 test method is used to determine the ability of an adhesive to withstand static forces applied in the same plane as the coated adhesive. Resistance to shear surface is defined as the time required for a standard area of pressure sensitive coated