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Spray-applied 100% volatile organic compounds free two component polyurethane coatings based on rapeseed oil polyols

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ABSTRACT

Spray applied, two component, 100% volatile organic compounds-free polyurethane coatings were prepared from bio-based rapeseed oil polyols. Six polyol systems were developed using rapeseed oil polyols and different chain extenders (diethylene glycol, triethylene glycol, dipropylene glycol, *N*-methyl diethanolamine), defoamers, molecular sieves. Systems were formulated with and without dibuthyltin dilaurate catalyst. Then polyurethane coatings were developed by reacting polyol systems with isocyanate components with different functionalities (a polymeric methylene diphenyldiisocyanate (MDI) Voratec SD 100, MDI prepolymer Suprasec 2416, a polymeric MDI Suprasec 2651). The impact of polyol and chain extender structure and parameters on development of polyol systems was discussed. Technological parameters (gel time, tack-free time) were studied and results showed that formulations have short gel time and thus can be applied on surfaces in up-right position. Coatings showed good physical and mechanical properties that meet the requirements that are defined for V type two component polyurethane coatings in the ASTM D16 standard. Using The Fourier transform infra-red spectral analysis and Shore D hardness measurement the post-curing of polyurethane coatings was studied. Hydrolytic stability tests showed that developed coatings are suitable for application with water involved since they display water absorption <2% during 48 h. Thus the synthesized polyurethane coatings have the potential to be used as a coating for inside walls of potable water tanks.

1. Introduction

In recent years, the coating industry has been driven to develop new types of coatings due to the depletion of non-renewable resources, environmental concerns and stricter legislation of volatile organic compounds (VOCs) that are highly toxic and carcinogenic for humans and also cause harm to the environment [1,2]. Limiting emissions of VOCs from coatings is the most important issue in the coatings industry. Also, the importance of using renewable resources in industrial processes has become very clear from the standpoint of sustainability [3].

In addition, polyurethane (PU) has become one of the most widely used polymers. It is estimated that PU demand will grow from 14.2 million tons in 2011 to 22.2 million tons by 2020 [4]. It is expected that global revenue for the PU coating market will reach more than $18 billion by 2018 [5]. To date, PU has been a petrochemical-based polymer, but due to the depletion of petrochemical resources, a wide variety of bio-based feedstock has been studied as potential raw materials for the PU industry. The demand for eco-friendlier coatings (low or no VOCs) and bio-based feedstock that offer equal or greater technical performance has motivated academia and industrial organizations to research and develop new coatings systems [6]. It also should be noted that the use of catalysts is not desired from the environmental and health hazard standpoint. Tertiary amines are widely used catalysts in PU production, but they present handling problems due to their unpleasant odor and toxicity. Also, amine catalysts are often very volatile and therefore contribute to VOC emissions and should be avoided [7–10]. On the basis of the above mentioned environmental concerns, legislation and the growing PU coating market, a study was carried out in which VOC-free (or 100% solids), spray-applied two-component (2K) PU coatings were obtained from rapeseed oil (RO) polyols. One of the major PU application areas is coatings for different surfaces. Coatings are used to enhance the properties of

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a surface. By finishing surfaces with the coating, different performance characteristics are achieved—for example, hardness, impact resistance, suitable gloss, chemical resistance and increased lifespan and higher durability against environmental deterioration. PU coatings are protecting many different structures today, such as storage tanks, oil and gas pipeline, water and wastewater, bridges, ships, floor, wall and textile protection and other facilities [11,12].

Vegetable oils as raw materials for PU coating production have been studied intensively. Castor oil has been used in the synthesis of 2-package waterborne PU wood coatings [13], as well as in the synthesis of hyperbranched PUs as advanced surface coating materials [1]. Olive oil is used for the synthesis of eco-friendly room temperature-cured poly(ether amide urethane) coatings, producing coatings with good scratch hardness, flexibility and corrosion resistance [14]. A bactericidal surface coating material for antibacterial and biomedical applications is produced from *Mesuaferrea L.* seed oil based polyester/clay silver nanocomposites [15]. PU coatings from neem oil based polyetheramide were synthesized in a solventborne system from cyclohexanone and tetrahydrofuran solution (50% solids) in the presence of dibuthyltindilaurate (DBTDL) as a catalyst [16]. Mannari et al. obtained high solid 2K PU coatings from soy polyols using DBTDL, the wt% of VOCs in PU coatings formulations was in the range from 25.00 to 32.82% [17]. Vegetable oils have been used to prepare PU coatings for different applications. Eucalyptus tar derivatives (biopitch and heavy oil), along with castor oil, have been used to synthesize PU coatings for possible application on metallic surfaces [18]. Gaikwad et al. reports preparation of eco-friendly PU coatings from cottonseed and karanja oil based polyester polyols with promising use in the formulation of coating binders [19]. Biobased dimer fatty acid was used in preparation of two pack PU with good mechanical properties and weather resistance and showed suitable coating properties to be applied as wood finished coatings [20]. Vegetable oil based palmitic acid was used as a starting material for biobased PU films and coatings with high transparency [21]. Bio-based 2K PU coatings were synthesized from 5 different vegetable oils (canola, sunflower, camelina and two types of flax oil) by Kong. Authors find that PU coatings based on vegetable oils with a high linolenic acid content show better physical properties [22]. Castor oil has been used as a raw material for green PU insulator coatings prepared by Moeini et al. [23].

The most important components of PU are a compound with a polyhydroxylated (—OH)-containing coreactant and chain extenders (CEs) and an isocyanate-containing (—N=C=O) compound [10,11]. In general, the characteristics and properties of the PU coating depend predominantly on the properties of the polyhydroxylated coreactant—polyol. The impact of polyol and the CE structure, structure parameters and functionality has a significant effect on the properties of the resulting PUs [10]. CEs are di-functional, low molecular weight compounds that are used to improve the properties of the final products. However, CE usage presents several problems: CE-containing hydroxyl groups are often slow to react with the isocyanates and require the catalysts to achieve a sufficiently fast reaction, and CEs sometimes have limited solubility in polyol [24]. The solubility parameter (δ) calculation by Fedors group contribution method can be used as a first estimate of the behavior of the untested materials to predict the compatibility and solubility of the materials.

The aim of this study is to characterize 100% VOC-free, spray-applied 2K PU coatings based on RO triethanolamine esters and diethanolamide polyols. Rapeseed oil was chosen as a raw material because it is a widely-cultivated oil crop in Latvia and Europe. In the present study, six PU coating formulations were developed using different CE, isocyanates and with or without a catalyst. A great deal of attention was paid to explain the factors that must be considered for the polyol system development for PU formulations applied using industrial spraying equipment. The effect of different CE (diethylene glycol, triethylene glycol, dipropylene glycol and *N*-methyl diethanolamine) on technological parameters for spray-applied PU coatings was analyzed; the physical and mechanical properties and hydrolytic stability of spray-applied PU coatings was also studied. Changes in the PU structure and hardness during the post-curing process at room temperature were studied using FTIR-ATR and changes in the PU coating Shore D hardness. Possible application areas for these PU formulations are provided.

2. Materials and methods

2.1. Materials

A list of the chemicals used for the synthesis of RO polyols and PUs is shown in Table 1. All the chemicals were used without any prior treatment.

2.2. Rapeseed oil polyol synthesis

RO polyols were synthesized using transesterification with TEA or amidization with DEA. Transesterification with TEA was

Table 1
Chemicals used for the synthesis of RO polyols and PUs.

Materials	Source	Description
Rapeseed oil (RO)	Iecavnieks&Co Ltd, Latvia	Iodine value = 117 mg I_2/100 g, acid value = 2.1 mg KOH/g, saponification value = 192 mg KOH/g
Triethanolamine (TEA)	BASF, Germany	99.5%
Diethanolamine (DEA)	Huntsman, The Netherlands	99.2%
Diethylene glycol (DEG)	Sigma Aldrich, Germany	99.0%
Triethylene glycol (TEG)	Sigma Aldrich, Germany	99.0%
Dipropylene glycol (DPG)	Sigma Aldrich, Germany	≥99.0%
N-Methyl diethanolamine (MDEA)	Sigma Aldrich, Germany	≥98.5%
Dibutyl tin dilaurate (DBTDL)	Sigma Aldrich, Germany	Organotin catalyst
A polymeric methylene diphenyldiisocyanate (MDI) Voratec SD 100	Dow Chemical, Belgium	NCO = 31.2%, f_n = 2.7
MDI prepolymer Suprasec 2416	Huntsman, Belgium	NCO = 24.0%, f_n = 2.1
A polymeric MDI Suprasec 2651	Huntsman, Belgium	NCO = 32.2%, f_n = 2.3
Defoamer BYK-320	BYK-Chemie GmbH, Germany	
Molecular sieves Albolith MS C 350	Alberdingk Boley, Germany	50% in castor oil
Anti-adhesion agent ACMOSAN 82-7001	Cmos Chemie, Germany	