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Carbohydrate Polymers 57 (2004) 225–228

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Short communication

Synthesis of acrylated ethylcellulose for UV-curing ink

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Received 4 March 2003; accepted 6 April 2004

Abstract

A modified synthesis of acrylated ethylcellulose was developed. Ethylcellulose reacts with acryloylchloride in anhydrous conditions producing ethylcellulose derivative with UV-reactive acrylate groups. FTIR spectroscopy was used to study the products. The UV-curable (polymerizable) formulations studied here were mixtures of ethylcellulose acrylate, solvents and photo-initiators. Rheological measurements were used to verify the cross-linking reaction and the viscosity behaviour of the system resulting from UV irradiation. The acrylated ethylcellulose was utilized as an UV-curable ink binder component in conductive ceramic inks to control the ink's viscosity and the ink transfer printing process.

Keywords: Printing; Thick-film; UV-cure; Ethylcellulose acrylate; Photo-initiator

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1. Introduction

UV-curing inks are used in the printing of graphics. There are also other important areas of UV-cured resins, such as the filling of tooth cavities or their applications as resist materials in electronics and optoelectronics. In general, these materials are based on similar chemical systems, consisting of initiators and monomers and reactive diluents. As the use of UV-systems increases, so the environmental aspects of chemical safety become more important because the use of UV curing reduces volatile organic compound emissions and also permits faster printing processes and saves energy.

The developed ink component was to be used for the gravure offset printing. This method is frequently used in roller or pad type printing in the graphic industry. The gravure offset printing technique can also be used for printing of electronic circuitry in a variety of applications (Hahne et al., 2001; Leppävuori, Väätäinen, Lahti, Kukkola, & Uusimäki, 1994). In printing of electronic conductors, 'ceramic' ink with a high metal solid content is printed on a substrate (ceramic) and then fired at temperatures >800 °C to remove the organic material and sinter the metal. Alternatively, polymer ink based on epoxy type binders is printed on plastic substrates and then cured at temperatures of 140–200 °C (Prime, 1992; Pudas, Hagberg, & Leppävuori, 2004).

In traditional UV-curing printing inks, a solvent or a diluent is a photo-reactive monomer and is cross-linked with the oligomers and prepolymers by using irradiation. Many photo-reactive monomers also tend to have relatively high toxicity and volatility features (Leach, Pierce, Hickman, Mackenzie, & Smith, 1999). However, a problem in the gravure offset printing technique using UV ink technology has been the reactive diluent residues, which remain on the non-image areas of the gravure. This has caused some limitations in the use of UV-curing in some printing applications (Frecska, 1984). This paper presents a simple synthesis and a study of an UV-curable cellulose derivative used as a binder in ink applications. This ink component could be used to increase the ink's viscosity and enhance its transfer in the printing process instead of hardening it completely.

Many chemical modifications of cellulose have been performed using various organic acids, anhydrides and acid chlorides in the presence of a catalyst (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). Acroloyl groups can be introduced into ethylcellulose by using acroloylchloride and the resulting acrylated cellulose has

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doi:10.1016/j.carbpol.2004.04.014

a high potential to be used as the UV-active component in UV-curing inks. A photo-initiator is added to the formulation to generate the free radicals necessary to start the polymerization process.

The synthesized ethylcellulose acrylate was analyzed with FTIR spectroscopy to determine the acroloyl group content of the prepolymer. Various formulations containing different amounts of prepolymer, solvent and photo-initiator were prepared and exposed to UV light. The viscosities of test mixtures before and after UV-exposure were determined by using rheometrical methods. The principle of this test method is based on the fact that the viscosity of the system increases when the degree of polymerization (cross-linking reaction) increases (Leach et al., 1999).

2. Experimental

The commercially available ethylcellulose (Aqualon, N4, $DS_{Et} = 2.41-2.51$) was used as a starting material in the synthesis of ethylcellulose acrylate. The ethylcellulose reacts with acroloylchloride ($CH_2{=}CH-COCl$) in the presence of pyridine in tetrahydrofuran according to the reaction scheme shown in Fig. 1.

The ethylcellulose was dried at 115 °C for about an hour. Tetrahydrofuran and pyridine were dried with molecular sieves. According to calculations, the theoretical amount of free hydroxyl groups of ethylcellulose is approximately 2.3 mmol/g. Equivalent amounts of pyridine and acroloylchloride were used.

2.1. General procedure

Ethylcellulose (10.0 g, 0.023 mol free hydroxyl groups) was dissolved in tetrahydrofuran (200 ml) Pyridine (2.0 ml, 0.023 mol) was added continuously with stirring. The reaction vessel was equipped with a condenser and cooled in an ice bath. A mixture of acroloylchloride (2.0 ml, 0.023 mol) and tetrahydrofuran (40 ml) was added to the solution drop-by-drop over 20 min to the open reaction container. The total reaction time was 4 h. The pyridinium hydrochloride was formed as a white precipitate soon after the acroloylchloride solution was added. The product was precipitated by adding water (500 ml) to the reaction mixture and separated by centrifugation. Finally, the product was dried at room temperature. The synthesized products were white or slightly pink. The product was stored for only short times in a fridge. Rheological measurements and printing experiments were done under yellow light.

2.2. The acroloyl group content determination

The content of acroloyl groups attached to ethylcellulose was determined with FTIR spectrometer (Bruker IFS 66). The acroloyl group absorbs at a wavelength of about $1640\ cm^{-1}$. A calibration curve was produced from commercial dodecylacrylate. The area of absorption peak at $1640\ cm^{-1}$ was integrated and presented as a function of the acroloyl group content.

For FTIR analysis the polymer film was formed on KBr tablets by dissolving the sample in dichloromethane, pouring the solution onto a KBr tablet and evaporating the solvent. The spectrum of ethylcellulose acrylate was not totally reliable and accurate because the polymer film formed was quite brittle and cloudy. Uniform and clear polymer films and also more accurate spectra were obtained by mixing the product with ethylcellulose. The known amounts of ethylcellulose and ethylcellulose acrylate were weighed and dissolved in dichloromethane. In order to eliminate the overlapping ethylcellulose signal near $1640\ cm^{-1}$ from the required acroloyl carbonyl signal, the spectrum of pure ethylcellulose was subtracted from the corresponding ethylcellulose–ethylcellulose acrylate mixture signal. The content of the acroloyl groups in the products varied between 1.1 and 2.4 mmol/g.

3. Results and discussion

FTIR was used instead of NMR for the determination of acrylate group content in the products because earlier studies have shown it better for detection of smaller quantities. The synthesis route of ethylcellulose acrylate was easily accomplished. However, according to the FTIR spectroscopic measurements, this route produced prepolymers with varying degree of substitution of acroloyl groups. The content of acroloyl groups in the products varied between 1.1 and 2.4 mmol/g while the calculated theoretical amount of acroloyl groups is 2.57 mmol/g. This quite low repeatability of the reaction is probably due to the water condensed in the materials or equipments used. Hence care should be taken to achieve as anhydrous reaction conditions as possible. This is best achieved by carrying out the reaction in a closed reaction vessel under an inert gas

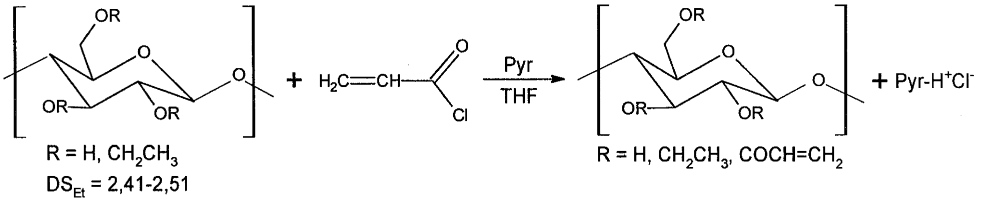

Fig. 1. Ethylcellulose reaction with acroloylchloride.

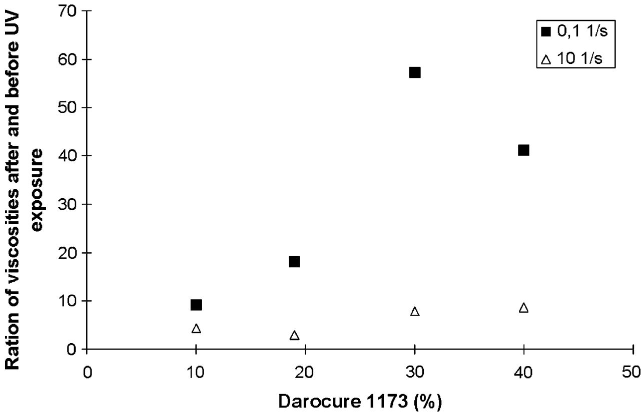

Fig. 2. The viscosity ratio after and before UV exposure as a function of the concentration of Darocure 1173 initiator by shear rates 0, 1 and 10 s^{-1}.

atmosphere and using freshly distilled solvents. In the qualitative work this was considered to be unnecessary.

The basic solution used for UV curing experiments contained 25 wt% of ethylcellulose acrylate and 75 wt% solvent. The ethylcellulose acrylate is dissolved in terpineol (bp. 213–218 °C) which is traditionally used in printing inks. Other suitable solvents that could be used for dissolving and printing were 2-butoxyethanol (bp. 170–172 °C) and butylcarbitol (bp. 230 °C). The photo-initiator was added to these solutions. Various photo-initiators were tested and the most promising results were gained with two photo-initiators: Darocure 1173 obtained from Aldrich and benzoin methylether (prepared from benzoin). The concentrations of these two photo-initiators in a comparative study were 8–10 wt% of the total solution. The viscosity of the test mixtures was measured before and after UV treatment. In the case of Darocure 1173 and 2-butoxyethanol or butylcarbitol as a solvent, the increase of viscosity after UV exposure was evident. This proves that polymerization of ethylcellulose acrylate has occurred. This finding was sufficient for this study and the quantitative determination of the cross-linking reaction was not the goal here. Generally, the polymerization reaction is inhibited by atmospheric oxygen. Higher photo-initiator concentrations are used to solve this problem.

The concentration of photo-initiator affects the rate of curing. This influence was evaluated by studying the increase of the viscosity after UV exposure with different concentrations of photo-initiator in the test solution. Test series were done with mixtures of ethylcellulose acrylate and terpineol (25 wt%/75 wt%) and Darocure 1173 as a photo-initiator. The Darocure 1173 concentrations used were 10, 19, 30, and 40 wt% of the mass of ethylcellulose acrylate and correspond to 2.5, 5.0, 7.5 and 10 wt% of the total mass of the solution to be exposed. The actual percentages of photo-initiator are usually smaller (0.5–5 wt%) in commercial inks, after addition of conductive or pigment particles. High concentrations were used in this study to ensure a sufficient amount of reactive radicals. The viscosity of solution was measured before and after UV exposure. The ratio of viscosity after and before UV exposure with increasing concentration of Darocure 1173 at shear rates of 0.1 and 10 s^{-1} is shown in Fig. 2.

Preliminary printing experiments were done with a roller type gravure offset printer. Printing tests were made with ink of composition 24 wt% ethylcellulose/butylcarpitol-mixture, 3 wt% photo-initiators and 73 wt% micrometer size silver particles. Further ink component tuning and study of alternative photo-initiators compatible with silver should follow in future work.

4. Conclusion

The synthesis described above has been found to be suitable for the incorporation of UV-curable acroloyl groups into ethylcellulose. So far, in the terms of constant amounts of acroloyl groups in the cellulose, a disadvantage of the synthesis has been its low repeatability. Although the synthesis was always carried out using exactly identical experimental conditions, the acroloyl group content varied between 1.1 and 2.4 mmol/g in the products. The formulations contained ethylcellulose acrylate, solvent and photo-initiator cured after UV exposure due to the polymerization reaction. This was established by rheological measurements.

This described reaction offers a possibility to use modified ethylcellulose instead of reactive solvent or diluent in UV-curable ink compositions applied by the gravure offset printing techniques. This gives environmental benefit because low boiling monomers and volatile organic solvents are absent.

Acknowledgements

This research was supported by Brite/Euram project ‘Development of a high-resolution printing process for cost-effective production of ultra-fine line electronic circuitry’ (BE 97-4607). Project partners were Philips CFT, Gwent Electronic Materials Ltd, Max Simmel GmbH., Thales Airborne Systems and Coates Electrographics.

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