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International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Influence of hydrogen bond on rheological properties of solventless UV crosslinkable pressure sensitive acrylic adhesive prepolymers

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ARTICLE INFO

Article history:

Accepted 30 October 2013

Available online 19 December 2013

Keywords:

Pressure-sensitive

Solventless

Rheology

ABSTRACT

A rheological characterization of 100% solid UV crosslinkable acrylic pressure sensitive adhesive with respect to different amounts of acrylic acid (AA) comonomer is presented. The reaction mixture consisted of three acrylic monomers (2-ethylhexyl acrylate, acrylic acid and t-butyl acrylate), azobisisobutyronitrile initiator, chain transfer agent n-dodecylmercaptan, and unsaturated UV photoinitiator 4-acryloyloxy-benzophenone. The amount of AA in the prepolymer formulation was varied from 0 to 9 wt%. All experiments were conducted on Anton Paar MCR 301 Rheometer with parallel plate sensor system. In the first part of the study, the influence of AA on prepolymer viscosity and loss and storage moduli during the bulk polymerization process was investigated. The second part of the study was focused on the temperature and shear rate dependency of rheological properties of synthesized prepolymers. During polymerization, viscosity and both moduli of all tested reaction mixtures gradually increased due to increasing average molecular weight of reaction mixtures. Storage modulus remained lower than loss modulus throughout the prepolymer synthesis process. Already a small amount of AA significantly amplified viscosity and moduli increases, what was attributed to intermolecular hydrogen bonds formation. Viscosity and moduli values of obtained prepolymers strongly depended on AA amount. The rheological properties of synthesized prepolymer without AA were independent of shear rate in the investigated range of shear rates. However, when the prepolymer contained AA, the properties became shear rate dependent. At higher shear rates hydrogen bonds breakage occurred resulting in lowered viscosity and moduli values. The viscosity and moduli values of synthesized prepolymers decreased with increasing temperature. Larger decreases for prepolymers containing AA were observed because of hydrogen bonds breakage.

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1. Introduction

UV crosslinkable solventless acrylic pressure sensitive adhesives (PSA) may be considered as a perspective new type of pressure sensitive adhesives [1–4]. Their main advantage is relatively low viscosity at room temperature, which enables coating using conventional roll coating equipment. The prepolymers are synthesized by highly exothermic bulk polymerization process, using different types and amounts of acrylic monomers [5,6]. The final formation of adhesive coating with sufficient cohesivity is achieved in final stage of the coating process, when coated film is exposed to UV light source. For UV induced crosslinking process, an unsaturated photoinitiator is added in the monomer mixture prior to polymerization process and because of its nature, the photoinitiator is incorporated in polymer backbone [7,8]. Selection

of monomers and their ratios plays an important role in adjustment of adhesive properties. Normally, a reaction mixture consists of three basic acrylic monomers: 2-ethylhexyl acrylate (2-EHA), acrylic acid (AA), and t-butyl acrylate (t-BA). 2-EHA is the basic monomer, whose homopolymer has a low glass transition temperature. Addition of t-BA influences the prepolymer viscosity due to steric effect of bulky t-butyl side group [6]. Lastly, AA comonomer governs the adhesive properties mainly via formation of hydrogen bonds between adhesive and the substrate [5]. However, the formation of intermolecular hydrogen bonds increases the prepolymer viscosity, what may be regarded as a negative effect. Beside the monomers, also modified montmorillonite clays may be added in monomer mixture. Clay type and amount also influence the prepolymer viscosity [9].

Rheology of 100% solventless prepolymers is important from industrial point of view, as the rheology parameters determine the in and out of phase response of a fluid to an applied stress or deformation and its related to the structure of viscoelastic material. The rheology properties govern the selection of appropriate

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coating system. As in many other cases also in the case of acrylic based prepolymers, the prepolymer rheology properties are strongly influenced by prepolymer molecular weight and by selection of different acrylic monomers and thereby connected intermolecular forces. Most of the published studies deal with correlation of polymer rheological properties, its microstructure and adhesive performance. It was found that the PSAs performances, such as peel strength, tack and shear resistance, are greatly dependent on the viscoelastic properties of the bulk PSAs [10–12]. Recently, a special interest has been paid to rheological properties of hot melt or 100% solid adhesive systems. Park et al. [13] investigated rheological properties of ethylene vinyl acetate (EVA) copolymers of various melt indexes, when blended with aromatic hydrocarbon resin in the molten state. They found that the storage and loss moduli of the blends decreased with increasing temperature, while $\tan \delta$ increased. The influence of secondary comonomers, such as hydroxyethyl acrylate, methyl methacrylate and acrylic acid, on the adhesion properties and on adhesive rheological properties has been investigated as well [14]. It was found that the change of moduli and adhesion properties occurred as a consequence of different monomer ratios in reaction mixture. In a study published by Baron et al. [15] rheological behavior of polyurethane graft copolymers containing poly(*n*-butyl acrylate) and the description of their morphology relating to tack were discussed. They have found a qualitative link between rheological behavior and adherence properties. Similar correlations between adhesion and rheological behavior were established also in the field of emulsion based PSAs [16,17]. An empirical relationship between the viscoelastic parameters and the PSA peel properties has been developed by Jensen et al. [18]. The relationship was developed by considering the viscoelastic behavior during debonding process. It was found that the resistance to peel is proportional to the peel strip dimensions and to the dissipated energy during deformation and thus to the loss modulus at the peel frequency. Effect of crosslinking density on rheological properties of solvent based acrylic pressure sensitive adhesives was investigated by Zhang et al. [19]. A review on mechanical properties of pressure sensitive adhesives was published by Sun et al. [20]. They correlated the mechanical/adhesive properties of PSAs (tack, shear resistance and peel strength) with bulk viscoelastic properties of adhesive system.

However, not a lot of interest was devoted to prepolymer rheology during the bulk synthesis process and to the influence of different parameters, such as temperature or shear rate, on the rheology properties of obtained prepolymer. The goal of this study was to investigate the influence of AA comonomer on the viscosity and loss and storage moduli of solventless UV crosslinkable pressure sensitive acrylic adhesive prepolymer during the synthesis. Since the prepolymer rheological behavior is extremely important and crucial for the selection of appropriate coating system and its operating parameters, the second part of the study was focused on the temperature and shear rate dependency of rheological behavior of synthesized prepolymers containing

different amounts of AA and thus different concentrations of intermolecular hydrogen bonds.

2. Experimental procedure

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), unsaturated photoinitiator 4-acryloyloxybenzophenone (4-ABF – Chemitec Company) were used in the commercially available form without further purification.

2.2. Preparation of reaction mixture

Four different formulations were prepared, each with different amounts of acrylic acid in range from 0 to 9 wt%. Formulations noted from UV X PSA 01 to UV X PSA 04 are gathered in Table 1.

An amount of 50 g of reaction mixture was prepared. All components were stirred for 30 min using a magnetic stirrer and were also purged with N_2 in order to remove unwanted oxygen.

2.3. Determination of prepolymer viscosity under destructive conditions

Viscosities of prepolymers during synthesis were determined on Anton Paar MCR 301 Rheometer with parallel plate sensor system. The plate diameter was 50 mm and the gap between plates was set to 1 mm. The reaction mixture was added between the plates, all of the excessive material was removed and then the convection oven was mounted on the apparatus. Different types of measurements were performed for each formulation. The first experiment under destructive conditions was performed to monitor the viscosity increase during the prepolymer synthesis (polymerization phase). The sample was kept at 80 °C and constant shear rate of 1 s^{-1} for 60 min in order to achieve the highest possible overall monomer conversion (as normally performed in a batch polymerization process [5,6]). All four formulations were subjected to equal testing parameters. After the polymerization phase, also the dependency of synthesized prepolymers viscosity on temperature under destructive conditions was investigated. From industrial point of view, temperature is an especially important parameter because heating of the coating system may reduce high prepolymer viscosity. First, the samples were heated from 20 to 100 °C with heating rate of 5 °C/min at constant shear rate of 1 s^{-1} . Next, the shear rate viscosity dependency of

Table 1
Reaction mixtures formulations.

Material	UV X PSA 01		UV X PSA 02		UV X PSA 03		UV X PSA 04	
	W (wt%)	m (g)	W (wt%)	m (g)	W (wt%)	m (g)	W (wt%)	m (g)
2-EHA	88.4	44.2	85.4	42.7	82.4	41.2	79.4	39.7
AA	0	0	3	1.5	6	3	9	4.5
<i>t</i> -BA	10	5	10	5	10	5	10	5
AIBN	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05
CTA	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25
4-ABF	1	0.5	1	0.5	1	0.5	1	0.5

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