



High performance pressure sensitive adhesives by miniemulsion photopolymerization in a continuous tubular reactor

Vesna Daniloska^a, Paula Carretero^a, Radmila Tomovska^{a,b}, José M. Asua^{a,*}

^a POLYMAT and Departamento de Química Aplicada, Facultad de Ciencias Químicas, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, Donostia/San Sebastián 20018, Spain

^b IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain

ARTICLE INFO

Article history:

Received 5 May 2014

Received in revised form

13 August 2014

Accepted 15 August 2014

Available online 28 August 2014

Keywords:

Miniemulsion photopolymerization

Pressure sensitive adhesives

Polyurethane/acrylic hybrids

ABSTRACT

High solids content PU/(meth)acrylics latexes for application as pressure sensitive adhesives (PSAs) were successfully synthesized by miniemulsion photopolymerization in a continuous tubular reactor at room temperature. It was shown that the process is very flexible and the polymer microstructure can be widely changed by simply controlling the radical initiation using different photoinitiator types and concentrations and varying the incident light irradiance. PSAs presenting a whole spectrum adhesive properties were obtained, some of them having the desired and unusual combination of high work of adhesion and maximum shear adhesion failure temperature (SAFT > 210 °C). The adhesive properties were analyzed in terms of the molecular weight distribution of the whole sample measured by asymmetric flow field flow fractionation.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Pressure sensitive adhesives (PSAs) are unique subset of adhesives with exceptional properties: aggressive and permanent tack, immediate adherence with no more than finger pressure, sufficient ability to hold onto an adherent and sufficient cohesive strength to be removed cleanly from the adherent [1,2]. Materials that function well as PSAs are polymers designed and formulated to exhibit the requisite of microstructure and viscoelastic properties, which result in a desired balance of tack, peel adhesion, and shear holding power. PSAs usually compose of a soft component that provides adhesivity, i.e., the soft polymers (n-butyl acrylate, 2-ethylhexyl acrylate and iso-octyl acrylate) and a hard component that provides desired mechanical properties (methyl methacrylate, styrene, vinyl acetate) [1]. Acrylic PSAs had the fastest growth in commercial applications because of the balance between end-product properties, compatibility with additives, processability, competitive cost, and oxidative ultraviolet resistance [3]. However, they have shown poor performance at high temperatures [4]. As an answer on this drawback, hybrid polymer–polymer PSAs have been synthesized, by addition of polyurethanes (PU) into acrylic polymers [5–9]. This have resulted in increase of the shear strength, which is usually low

in waterborne PSAs [2,3], particularly at high temperatures [10]. However, the results have show that the increase of shear strength is accompanied with a decrease in the tack adhesion [5,6,11], and a compromise should be found.

Very suitable technique for synthesis of these complex polymer–polymer hybrid materials is miniemulsion polymerization [12–20]. The hybrid PU/acrylic polymer is produced by free radical polymerization of acrylic monomers and addition polymerization of PU pre-polymer, resulting in crosslinked structure formation. Both processes occurred simultaneously, when performed at higher temperatures in thermally initiated miniemulsion polymerization [5,6]. Recently, it has been demonstrated that the miniemulsion photopolymerization performed in a continuous tubular reactor (CTR) and initiated by UV light is a quite flexible process [21]. On one hand, the narrow diameter CTR ensures decreasing the effect of the limitation of penetration depth of the UV light, associated with the photopolymerizations usually performed in batch reactors [22–31]. On the other, it offers opportunity of design of the hybrid polymer microstructure only by varying the reaction parameters (photoinitiator (PI) concentration, incident light irradiance and residence time) [21]. This study was performed under relatively low solids content (20 wt%) and attempts to perform synthesis of higher solids content latexes for investigation of adhesive properties, resulted in reactor clogging. This happened due to the preferable interactions of the monomer droplets (containing PI) with the reactor wall that led to formation of polymer on the wall under

* Corresponding author. Tel.: +34 943018181; fax: +34 943017065.

E-mail addresses: jm.asua@ehu.es, qpasgoj@sq.ehu.es, jmasua@sq.ehu.es (J.M. Asua).

UV irradiation. This problem was overcome by using a reactor composed of two sections. The first one was made of low surface energy material to avoid the preferable interaction with the monomer droplets. The residence time of the first part was such that a monomer conversion of about 45% was reached. The second part of the reactor was made of a material highly transparent to UV (quartz tubes) where the high conversion could be achieved. In this way, the photopolymerization of the higher solids content miniemulsions was accessible [32].

Recently, it has been found that the microstructure of the PU-acrylics synthesized by miniemulsion photopolymerization in a CTR at room temperature evolves during storage at room temperature [33]. The evolution was due in part to the formation of urea groups from the NCO that did not react in the CTR because of the short residence time. This process led to an increase in the molecular weights and to the formation of highly branched chains during the first eight days of storage. In addition, physical interactions (likely hydrogen bonding) led to a further assembly of macromolecules and to the formation of nanogels over a period of several months [33].

In this work, a high solids content (~46 wt%) miniemulsion photopolymerization of PU/(meth)acrylic monomers carried out in a CTR was studied. The effects of the photoinitiator type and concentration, incident light irradiance (ILI), and residence time (τ) on the polymerization rate, polymer microstructure and adhesive and viscoelastic (linear and nonlinear) properties were investigated. The adhesive properties were also measured after 229 days of storage, a period of time in which the microstructure of the polymer reaches its final configuration [32]. The flexibility of the photopolymerization process provided the opportunity to synthesize a wide variety of PSAs, some of them having the desired and unusual combination of high work of adhesion and maximum shear resistance at high temperature. The adhesive properties were analyzed in terms of the MWD of the whole PSA determined by asymmetric flow field flow fractionation.

2. Experimental section

2.1. Materials

Technical grade monomers, 2-ethylhexyl acrylate (2EHA, Quimidroga), methyl methacrylate (MMA, Quimidroga), methacrylic acid (MAA, Aldrich) and 2-hydroxyethyl methacrylate (HEMA, Fluka), were used as received. N-octadecyl acrylate (SA, Aldrich) was used as a reactive costabilizer in order to prevent Ostwald ripening [34,35]. An aliphatic isocyanate terminated polyurethane (PU) prepolymer, Incorez 701 (Incorez Ltd.), specially designed for adhesive applications was used without further purification. The equivalent weight of the prepolymer is 1050 g/equivalent. Dibutyltin dilaurate (DBTDL) (Aldrich) was used as catalyst for the polyaddition reactions. Dowfax 2A1, (alkyl diphenyloxide disulfonate, DowChemicals) was used as surfactant to prepare the miniemulsions, and sodium dodecyl sulphate (SDS, Aldrich) was added after the miniemulsification to improve the miniemulsion stability. Both were used as received. Three types of photoinitiators (PI) were used, two oil soluble (non-photobleaching 1-hydroxycyclohexyl phenyl ketone (HCPK, Aldrich) and photobleaching photoinitiator commercial mixture of 2-hydroxy-2-methyl-1-phenyl-propan-1-one and 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide (D4265, BASF, Germany)), and water soluble, non-photobleaching (2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-prop-anone (I2959, BASF, Germany)). All of them were used as received. Sodium bicarbonate (NaHCO_3 , Aldrich) was used as a buffer. Gel-permeation-chromatography grade tetrahydrofuran (THF, Schar-lau) was used as solvent. Oxygen-free grade nitrogen was used for

purging the feed. Double deionized water was used throughout this study.

2.2. Synthesis of the PU/Acrylic hybrid latexes

45 wt% solids content miniemulsions were prepared based on the formulation shown in Table 1.

First, the organic phase was prepared by dissolving the Incorez 701 in the monomer mixture (2EHA/SA/MMA/MAA/HEMA). The oil soluble photoinitiator (HCPK or D4265) was also dissolved in the organic phase, while I2959 was dissolved in the water phase. Then, the organic phase was mixed with an aqueous solution of the surfactant (Dowfax 2A1) and NaHCO_3 under intensive magnetic stirring (15 min at 1000 rpm) to create an emulsion. The resulting coarse emulsion was sonicated for 15 min at 9 output control and 80% duty cycle with a Branson 450 (Danbury, CT). Although the miniemulsion was placed in an ice bath, the temperature at the end of sonication was around 68 °C.

In the miniemulsification, droplets result from the interplay between droplet break-up and droplets coalescence. When the internal viscosity of the droplets is low (as it is the case in this work due to the low content of PU prepolymer) the droplets are easily broken and the final size is determined by the availability of the surfactant [36,37]. This means that after miniemulsification, the droplets presented a limited stability. Therefore, in order to improve the miniemulsion stability, SDS was added. SDS was used because its adsorption-desorption mobility increases its availability to stabilize the interfaces [38]. After the addition, the miniemulsion was cooled down to room temperature under agitation (approximately 2 h).

The polymerizations were performed in a continuous tubular reactor composed of a 740 mm silicone tube (2 mm inner diameter) and 7 quartz tubes connected with each other with 6 semicircular silicone bends (2 mm inner diameter). Each quartz tube had a length of 400 mm, an inner diameter of 1 mm and an outer diameter of 3 mm. These two materials were used for the design of the reactor in order to avoid clogging of the reactor [31]. A UV chamber (model BS 03, Dr. Gröbel UV-Elektronik GmbH) equipped with 20 UV lamps giving UV light in the range from 315 to 400 nm with a maximum at 368 nm was used. The incident light irradiance was measured using a radiometer UV sensor. A gear pump (model 305, Gilson) was used to feed the miniemulsion (that was kept under stirring at 450 rpm) to the reactor. Prior to be fed to the reactor, the miniemulsion was purged with nitrogen for about 30 min. The latexes analyzed were obtained under steady-state

Table 1
45 wt% solids content PU/(meth)acrylics miniemulsion formulation. Reaction temperature: 25 °C.

Component	Amount (g)	Weight %
2EHA	196.43	91.5 ^a
SA	12.5	5.8 ^a
MMA	3.04	1.4 ^a
MAA	2.03	0.9 ^a
HEMA	1.01	0.4 ^a
PU	22.5	10 ^b
DBTDL	0.11	500 ppm ^c
PI	0.202–1.01	0.09–0.48 ^a
DDI-water	270.05	—
Dowfax 2A1	9	2 (45 wt% active) ^b
NaHCO_3	0.46	0.02 M ^d
SDS	2.25	1 ^{b,e}

^a Weight based on monomer weight.

^b Weight based on organic weight.

^c ppm based on organic phase.

^d Based on water phase.

^e Post miniemulsification addition.

Download English Version:

<https://daneshyari.com/en/article/5180961>

Download Persian Version:

<https://daneshyari.com/article/5180961>

[Daneshyari.com](https://daneshyari.com)