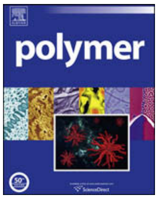
Polymer 50 (2009) 1654–1670

Contents lists available at ScienceDirect

Polymer

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



Control of adhesive properties through structured particle design of water-borne pressure-sensitive adhesives

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ARTICLE INFO

Article history:
Received 23 October 2008
Received in revised form
22 January 2009
Accepted 24 January 2009
Available online 30 January 2009

Keywords:
Emulsion polymerisation
Morphology
Adhesives

ABSTRACT

The concept of using structured particles and the mechanism of film formation from latexes to produce pressure-sensitive adhesive (PSA) films with controlled sub-micron and nanometre scale morphology has been investigated with the objective of enhancing adhesive performance. Structured particle acrylate-based latexes were synthesised by seeded semi-continuous emulsion polymerisation procedures. Aliquots removed at intervals during the polymerisations were analysed for conversion and *z*-average particle diameter; the results confirm that the particles grew without secondary nucleation or coagulation. Three-layer particles were studied first and comprised a core whose composition was the same for all particles, an interlayer between core and shell which was crosslinked during synthesis (using 1,6-hexanediol diacrylate, HDDA) and a shell which contained diacetone acrylamide (DAAM) repeat units that provided for interfacial crosslinking between particles during film formation by reaction with post-added adipic acid dihydrazide (ADH). The three-layer latexes produced adhesive films with high shear resistance when ADH was added, but peel adhesion was generally low and further reduced by increasing either the thickness or HDDA concentration of the interlayer. Thus two-layer latexes with shell layers containing DAAM but no pre-crosslinked interlayer were the main focus of the study. The effects of core:shell ratio and amount of DAAM on adhesive performance were optimum with a core:shell ratio of 80:20 and 2 wt% DAAM in the shell copolymer, for which interfacial crosslinking using the stoichiometric amount of ADH led to a marked increase in shear resistance with only a slight reduction in peel adhesion. Increasing the level of *n*-dodecylmercaptan (DDM) chain transfer agent used in synthesis of the core increases peel adhesion and reduces shear resistance in the absence of ADH, but high shear resistance can be recovered through interfacial crosslinking with ADH. Adhesive performance can be optimised by using a high DDM level in the core and a low DDM level in the shell, a combination that enables both high peel adhesion and shear resistance to be achieved with the addition of ADH. The results from this study define guiding principles for development of commercial water-borne PSAs that can compete with solvent-borne PSAs in high-performance applications.

1. Introduction

Pressure-sensitive adhesives (PSAs) are viscoelastic materials which adhere to substrates on the application of slight pressure over short periods of time. The largest proportion of the PSA market is now held by water-borne acrylic systems based on latexes prepared by emulsion polymerisation [1]. The monomers typically used to produce the commercial PSA latexes are *n*-butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) which produce high molar mass, permanently tacky polymers (*i.e.*, with a very low glass transition temperature, T_g) [2]. Carboxylic acid containing monomers, such as methacrylic acid (MAA) and acrylic acid (AA), are included at low levels because, after neutralisation, the acid groups enhance latex colloidal stability, facilitate stronger bonds to polar substrates and provide physical crosslinking via ion clustering. Such water-borne PSA latex systems have gained market share at the expense of flammable, environmentally unfriendly solvent-borne acrylic PSAs not only because they replace solvents with water but also because the latexes can achieve much higher solid contents at low viscosity which brings further benefits in formulation, transport and coating.

There are, however, some PSA applications for which current water-borne PSAs cannot match the performance of, and thus replace, solvent-borne acrylic PSAs. Such applications typically require high cohesive strength whilst retaining high peel and tack performance and/or bonding to low energy surfaces, such as

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0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.01.054

polyethylene and polypropylene. The latter substrates are inherently difficult for water-borne PSAs because latexes are, by nature, hydrophilic and do not easily wet such hydrophobic surfaces and also because, even though the acrylic polymer may be highly hydrophobic, the latex particle surfaces are hydrophilic due to functional groups and ionic charges derived from surfactant, initiator and functional comonomers. The challenge of enhancing the adhesive performance of water-borne PSAs such that they can compete with solvent-borne PSAs in high-performance applications was central to the 'NsHAPe Project' (see Acknowledgements), some of the results from which are presented in this paper.

The objective of the work reported herein was to establish whether the mechanism of film formation from latexes, which leads to retention of particle structure/morphology in the adhesive films [3,4], can be used to advantage to achieve both sub-micron and nanometre scale control of adhesive film morphology (inaccessible using solvent-borne adhesives) combined with manipulation of fundamental parameters known to modify adhesive performance in order to enhance the performance of water-borne PSAs. This approach had been tried before [5,6], but the lack of control of polymer architecture led to application properties which were inferior to the homogeneous systems. Through careful design and synthesis of latexes with structured particles that facilitate simultaneous control of film morphology and the properties of the phases in the film, it has been possible to relate chemical and particle design parameters to adhesive performance and, thereby, define principles for enhancing the performance of water-borne PSAs.

2. Experimental

2.1. Materials

Styrene (Merck, 99%), *n*-butyl acrylate (BA) (Alfa Aesar, 98%), ethyl acrylate (EA) (Aldrich, 99%) and 2-ethylhexyl acrylate (EHA) (Aldrich, 98%) were washed three times with aqueous sodium hydroxide solution (0.5 M) to remove the phenolic inhibitor, then washed three times with water and dried over calcium chloride. Acrylic acid (AA) (Aldrich, 99%) and methacrylic acid (MAA) (Aldrich, 99%) were treated immediately before use to remove most of the inhibitor by standing over silica gel for 30 min. Water was deionised using an ElgaStat Option 3 water purifier. Ammonium persulfate (BDH, AR) sodium carbonate (BDH, AR), methanol (BDH, GPR), tetrahydrofuran (BDH, GPR), hexadecane (Aldrich, 99%), 1,6-hexanediol diacrylate (HDDA) (Aldrich, tech., 80%), hydroquinone (Aldrich, 99%), *n*-dodecylmercaptan (DDM) (Aldrich), *tert*-butyl hydroperoxide (Aldrich, 70 wt% in water), hydroxymethanesulfinic acid monosodium salt dihydrate (Aldrich), diacetone acrylamide (DAAM) (Aldrich, 99%), adipic acid dihydrazide (ADH) (Sigma, 98%), Servoxyl VLA2170 (Elementis Specialities), Sipomer β-CEA (Rhodia), Rhodacal DS4 (Rhodia, 23% active), Rhodapex AB/20 (Rhodia, 29% active) and Dowfax 2A1 (Dow Chemical, 45% active) were used as received.

The acrylate/styrene copolymer seed latex used in the emulsion polymerisations was supplied by Cytec Surface Specialties SA (Drogenbos, Belgium) at 34 wt% solids (33 wt% polymer) and with a volume-average particle diameter of 46 nm determined by hydrodynamic chromatography.

2.2. Emulsion polymerisations

Reactions were performed under a flowing nitrogen atmosphere with mechanical stirring in flanged vessels contained in a water bath thermostated at 80 °C, which corresponded to a temperature of 78–79 °C in the reaction vessel. Example polymerisations are described below for the three types of latex preparation carried out, namely core particle latex, multi-layer particle latex grown from a pre-made core latex, and direct 'one-pot' synthesis of multi-layer particle latex. Details of the standard core and shell monomer compositions are given in Table 1.

2.2.1. Example 1: preparation of core particle latexes (CL1–CL5)

Note that core particle latexes CL1–CL5 were repeat preparations carried out using identical formulations, procedures and conditions, which were as follows. Sodium carbonate (3.60 g) was dissolved in water (600 g) in the reaction vessel and the solution stirred for 30 min while flushing with nitrogen and heating to the reaction temperature. A solution of ammonium persulfate (0.88 g) in water (10.60 g) was added and stirring continued for 5 min before adding seed latex (38.180 g), followed by water (60 g) which was used to ensure complete transfer of the seed latex. The reaction mixture was stirred for a further 5 min before beginning addition of: (i) a solution of ammonium persulfate (1.77 g) in water (18.88 g) over a period of 120 min using an Infors HT Predicor syringe pump; and (ii) a monomer emulsion (1096.006 g; prepared from 530.19 g EHA, 120.50 g EA, 80.327 g BA, 40.164 g styrene, 20.073 g AA, 12.055 g Sipomer β-CEA, 0.243 g DDM, 263.79 g water, 13.955 g Rhodapex AB/20 (4.047 g active), 3.045 g Dowfax 2A1 (1.370 g active) and 11.664 g Rhodacal DS4 (2.683 g active)) over a period of 120 min using a Watson-Marlow Model 505S peristaltic pump. When the additions of the initiator solution and monomer emulsion were complete, the reaction mixture was stirred for a further 60 min at 80 °C and then cooled to 60 °C. A 7 wt% aqueous solution of *tert*-butyl hydroperoxide (3.50 g) was then added, followed by addition of a 5 wt% aqueous solution of hydroxymethanesulfinic acid monosodium salt dihydrate (8.80 g) over a period of 30 min. Finally, the reaction mixture was heated at 60 °C for a further 30 min before cooling the latex to room temperature.

2.2.2. Example 2: preparation of a three-layer particle latex from a core latex (D3L5)

Core latex CL2 (420.01 g) was charged to the reaction vessel and stirred for 30 min while flushing with nitrogen and heating to the reaction temperature. Part (15.00 g) of the first monomer emulsion (prepared from 66.672 g EHA, 15.156 g EA, 10.097 g BA, 5.049 g styrene, 2.019 g MAA, 11.009 g HDDA, 0.0330 g DDM, 36.10 g water, 1.900 g Rhodapex AB/20 (0.551 g active), 0.409 g Dowfax 2A1 (0.184 g active) and 1.582 g Rhodacal DS4 (0.364 g active)) was added, followed by stirring for a further 30 min. A solution of ammonium persulfate (0.40 g) in water (4.80 g) was then added and stirring continued for 5 min before beginning addition of: (i) a solution of ammonium persulfate (0.80 g) in water (8.53 g) over a period of 150 min using an Infors HT Predicor syringe pump; and (ii) the remainder of the first monomer emulsion (135.026 g) over a period of 75 min using a Watson-Marlow Model 505S peristaltic pump. Immediately on completing addition of the first monomer emulsion, addition of a second monomer emulsion (150.036 g, prepared from 66.679 g EHA, 15.157 g EA, 10.098 g BA, 5.049 g

Table 1
Standard comonomer feed compositions.

Monomer	Core/wt%	Shell/wt%
EHA	66	66
EA	15	15
BA	10	10
Styrene	5	5
AA	2.5	–
β-CEA	1.5	–
MAA	–	2
DAAM	–	2