

Inline characterization of dispersion formation of a solvent-borne acrylic copolymer by Photon Density Wave spectroscopy

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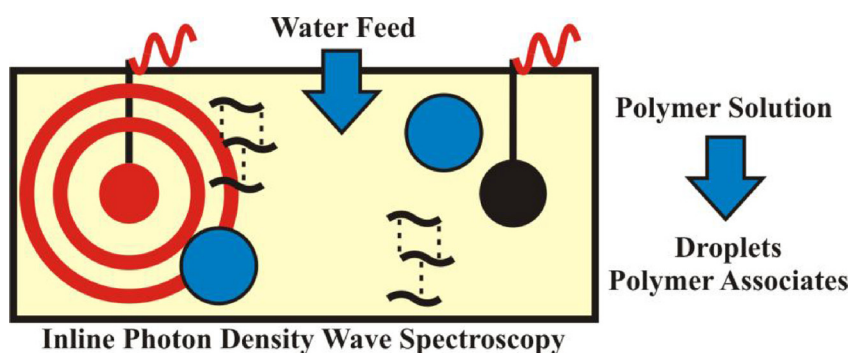
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GRAPHICAL ABSTRACT



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ABSTRACT

Most investigations on phase inversion (PI) of resins upon addition of water have been carried out by dynamic light scattering (DLS), torque, and viscosity measurements. The main problem, however, is analytic discontinuity due to sample removal and a changing matrix due to dilution during the preparation of the aqueous resin dispersions. This work presents Photon Density Wave (PDW) spectroscopy as a tool for the inline characterization of the acetone process for an acrylic copolymer with high acrylic acid (AA) content. PDW spectroscopy revealed different trends for optical properties compared to torque during water feed. Also the absence of PI due to dissolution of copolymer in the solvent/water mixture is observed by PDW spectroscopy. PI for the investigated copolymer did not occur during water feed but during removal of solvent. Different feeding rates of water gave similar trends while a change in temperature and degree of AA neutralization led to changes in optical properties and torque. Thermal processing showed that the optical properties of mixtures prior and after removal of solvent were completely different caused by changes of solubility.

1. Introduction

Much research in recent years has focused on phase inversion (PI) of resins as this process determines the properties of dispersions such as

particle size distribution (PSD) [1–6]. In general, PI is a result of addition of water to a hydrophobic liquid (or vice versa) until the added phase becomes the continuous phase [5]. The process of PI for alkyd resins and other resins such as epoxy resins is driven by surfactants

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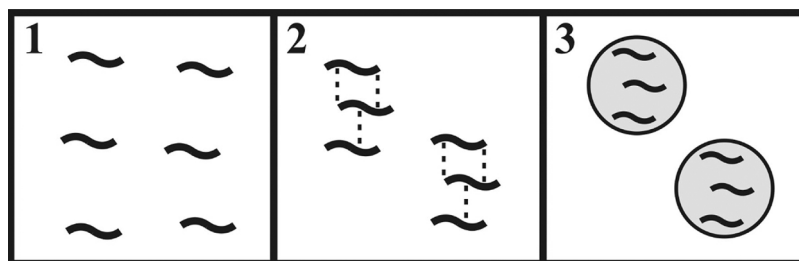
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Scheme 1. Acetone process of polyurethanes. Part of the carboxylate groups of a polyurethane dissolved in an organic solvent is neutralized (1). Water is added to the solution and leads to formation of hydrophobic associates (2). Upon further water addition, phase inversion and dispersion formation occurs (3).

which provide amongst others emulsification of water droplets until water is the continuous phase [5,7]. PI during the acetone process of polyurethanes (PU) is caused by the loss of solvation sheath and solubility for a partially neutralized solvent-borne polymer and leads to formation of hydrophobic associates until the associates form particles (Scheme 1) [8]. The acetone process consists of three steps: First, a solvent-borne polymer with carboxylic acid groups is prepared. Second, the solvent-borne polymer is partially neutralized with a base and water is added to the polymer solution until PI takes place which gives polymer particles in a solvent/water mixture. Third, the organic solvent is removed under reduced pressure leading to an aqueous dispersion.

It is generally accepted that acquisition of torque and viscosity profiles are suitable parameters for the inline characterization of PI during the emulsification of alkyd resins and the preparation of PU dispersions [1,3,5,9,10]. Unfortunately, these profiles reveal only the temporal state of the PI but lack information on the particle size distribution (PSD). Often, dispersions are characterized by DLS, which requires sampling and significant dilution. While DLS works well for the determination of the PSD of PU during PI [11], it is not applicable for alkyd and other resins due to changes of the PSD upon dilution. However, DLS for PSD measurements of alkyd resins works well after completed PI [1]. To understand in more detail the particle formation process, there is a need for an efficient method that can detect PI and PSD simultaneously without sample dilution during PI also in larger production-relevant scales.

Here, Photon Density Wave (PDW) spectroscopy [12–16] is presented as an inline process analytical tool (PAT) to detect optical properties during the acetone process of a solvent-borne acrylic copolymer. The basis of PDW spectroscopy is transport theory for photon migration in multiple light scattering environments. If intensity-modulated light is inserted in a strongly light scattering and weakly absorbing material, a PDW is created. The amplitude and phase of the wave are influenced by the absorption and scattering properties of the investigated material. In PDW spectroscopy, the shifts of amplitude and phase are characterized as function of emitter/detector-fiber distance and modulation frequency (cf. section 2.5 for technical details), allowing, as a main result, for the independent and calibration-free determination of the absorption and the reduced scattering coefficient (μ_a and μ'_s , respectively). They are the absolute optical properties of the turbid material. The theoretical background of the approach used here is described in detail elsewhere [17].

Due to its fiber-optical inline process probe, PDW can in principle be implemented in lab, pilot, and production scale. On basis of the Mie theory and theories for so-called dependent light scattering, the reduced scattering coefficient can be analyzed with respect to particle size [12]. In this work, the focus was put on the evaluation of the suitability and sensitivity of PDW spectroscopy for understanding the PI process based on the optical coefficients, not yet on PSD determination.

The investigated copolymer was found to behave different during the acetone process as described above. PI did not take place during water feed due to increased solubility of copolymer in the solvent/water mixture. Removal of solvent led to PI because of decreased solubility of copolymer in the aqueous phase.

2. Materials and methods

2.1. Materials

2-ethylhexylacrylate (2-EHA, > 99% purity, BASF, Ludwigshafen, Germany), acrylic acid (AA, > 99% purity, BASF, Ludwigshafen, Germany), azobisisobutyronitrile (AIBN, > 98% purity, AkzoNobel Functional Chemicals, Arnhem, Netherlands), dimethylethanolamine (DMEA, > 99% purity, GB Chemie, Messel, Germany), methyl ethyl ketone (MEK, > 99% purity, BCD Chemie, Hamburg, Germany) and water (MilliQ grade) were used as supplied.

2.2. Solution polymerization

For reproducibility tests, one batch of solvent-borne copolymer being sufficient for all shown experiments was prepared by solution polymerization (Table 1). First, MEK was charged into a selfmade 25 L stainless steel reactor (related photograph: Supporting Information S-I) equipped with an U-shaped stirrer blade and condenser and heated to 80 °C (step 1). Second, a solution of MEK, monomers, and initiator was fed to the reactor within 2 h (step 2). Once the feed was completed, a further amount of MEK was added and the temperature was kept constant for 3 h at 80 °C (step 3). Finally, a solution of MEK and initiator was added and the temperature was kept constant again for 3 h (step 4). The solvent-borne copolymer solution with a theoretical solid content of 50% was then cooled down to room temperature and used for all experiments without further purification. The experimental solid content of the solvent-borne copolymer solution was 49.7%. The characterization of the solvent-borne copolymer with this monomer composition and the dispersion thereof is described in detail elsewhere. [18]

2.3. Water feed and parameter variation

The synthesized copolymer solution was partially neutralized with DMEA and water was fed to an automated 1 L lab reactor (OptiMax, Mettler Toledo, Gießen, Germany), equipped with a condenser and a PDW spectroscopy process probe. The stirrer motor of the reactor provided a relative torque (RT) trend. Water feed into the reactor was

Table 1
Preparation steps and masses for the solution polymerization for a copolymer consisting of AA and 2-EHA.

Step	Component	Mass (g)
1	MEK	6038
2	MEK	1006
2	AIBN	101
2	2-EHA	8151
2	AA	906
3	MEK	1610
4	MEK	403
4	AIBN	20

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