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Temperature-triggered release of a liquid cross-linker micro-encapsulated in a glassy polymer for low temperature curing

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ABSTRACT

In order to prevent a liquid epoxy cross-linker from premature, Arrhenius-law predicted, reaction with an acid-functional polyester resin, the liquid cross-linker has been physically separated from the resin by encapsulation while release is only possible by a temperature-controlled trigger. The glass transition temperature T_g of the polymeric encapsulant was used to trigger the softening of the polymeric capsule.

Epoxidized linseed oil (ELO) cross-linker was encapsulated as 0.1 μm diameter droplets in 16 μm diameter microparticles (poly(N-vinyl)pyrrolidone) (PVP) by means of spray-drying. The resulting nanocomposite microparticles were used to cross-link the acid functional polyester in a powder coating.

It was found that below T_g the encapsulation considerably slows down the (premature) cross-link reaction. Beyond T_g also a slowdown was found but in this case it was caused by the mere presence of PVP rather than by the state of encapsulation of the cross-linker: PVP as a strong hydron bond acceptor slows down the reaction of epoxy with the acid groups of the polyester.

In conclusion, the T_g of the encapsulant was successfully used as a temperature trigger for realizing the controlled release of a liquid reactant in a reactive polymer matrix.

1. Introduction

More and more severe environmental regulations have provided an impetus for developing alternatives for solvent-borne paints. Among these, powder coatings are known to be environmentally friendly because they are 100% solvent free and their volatile organic emissions are virtually zero. Powder coating formulations essentially contain a resin, a cross-linker, pigments and several additives. These ingredients are melted, typically at 90–110 °C, and homogeneously mixed by means of an extruder. After extrusion, the melt is cooled to ambient temperature, ground and sieved. The powder coating obtained in this way is ready to be applied by spraying electrostatically on the object to be coated. The process is completed when the applied powder melts and cures. This is done by heating the object to a temperature usually between 150 °C and 200 °C [1].

The current trend in powder coatings is to use formulations which cure at temperatures lower than 140 °C. Such powder coatings can be used on heat-sensitive substrates like wood, plastic and MDF (medium density fiberboard) [2]. In order to enable low temperature curing, a sufficiently high reaction rate at temperatures lower than 140 °C is required. However, as the kinetics of curing of a thermosetting powder coating follows a classical Arrhenius equation, a higher curing rate at lower temperature also implies a chemically less stable system during melt extrusion and upon storage [3], conflicting with requirements on chemical stability in processing and storage of powder coatings. Note that also the physical storage stability, not discussed in this paper, is an important aspect of a powder for powder coating, especially its ability to prevent premature sticking or aggregation of the powder particles and retain its free-flowing properties [4].

Powder coatings are based on either a thermoplastic or a thermosetting resin. The thermosetting polyester resins are based on carboxyl or hydroxyl functional polyesters [5]. A widely used system which offers good exterior durability is based on acid-functional polyester (APE) and triglycidyl isocyanurate (TGIC). Unfortunately, TGIC has been shown to be highly toxic and carcinogenic. Given the need to find an environmentally friendly and less toxic alternative cross-linker, the use of aliphatic oxirane compounds has been explored [6]. These compounds are obtained by epoxidizing vegetable oils, e.g. olive and linseed oils. The epoxy

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derivative of the latter, epoxidized linseed oil [7] (ELO), and other aliphatic oxiranes are liquid compounds, which can act as plasticizers and lower the glass transition temperature T_g of the resin. The plasticizing effect might compromise the physical and chemical stability of powders for powder coatings upon storage.

In this paper, our aim is to demonstrate that microencapsulation of a liquid reactive component of the powder coating formulation (i.e., a liquid cross-linker) can improve the chemical and physical stability of the powder. Microencapsulation is a process in which liquid droplets, particles or gas bubbles are enclosed in a continuous film of polymer (the encapsulant). Spray drying is one of the most commonly used microencapsulation techniques because it is environmentally friendly, straightforward and relatively inexpensive [8,9]. In [10] we reported a Design of Experiment approach for the processing aspects of the microencapsulation (by means of spray-drying) of the liquid cross-linker ELO. The microencapsulation converts the liquid ELO into a solid particle. Poly (N-vinyl-2-pyrrolidone) (PVP) was used as encapsulant because it is a water soluble polymer with good film forming and emulsifying properties. In addition, PVP has a T_g which varies from 54 °C to 175 °C depending on molecular weight and the amount of absorbed water [11]. The T_g of the encapsulant is a key factor for the efficacy of the encapsulation: it should be high enough to guarantee good protection upon storage and melt extrusion, but low enough to allow the release of the cross-linker upon curing.

For the preparation of microparticles containing ELO, we used the optimized conditions as reported earlier 10 and characterized the microparticles in terms of amount of encapsulated ELO, particle size and morphology. Finally, we show the benefits of using encapsulated ELO in a powder coating formulation by oscillatory shear rheometry and differential scanning calorimetry.

2. Experimental

2.1. Materials and methods

Epoxidized linseed oil used in the present study has a mass per equivalent (mass in g of sample containing one mol of epoxy groups) of 167.5 and was provided by DSM Resins BV, Zwolle, The Netherlands. Poly (N-vinyl-2-pyrrolidone) (Povidone K30) with M_w of about 40,000 g/mol and sodium dodecyl sulphate (SDS) were obtained from Aldrich. Carboxyl-functionalized polyester (APE), with an acid number of 24 mg (KOH)/g (resin), alkali-metal catalyst (Uranox P7121, masterbatch with 20% active ingredient), degassing agent (benzoin), flow agent (Resiflow PV5) and anti-oxidants (ADK stab LA63-hindered amine and stabilizer P43-phenolic antioxidant) were also obtained from DSM Resins BV.

2.2. Preparation of the encapsulated cross-linker

The microencapsulation of ELO by spray drying was carried out using optimized conditions as established by a Design of Experiment method [10]. The carrier solution containing PVP was prepared by dissolving 60 g of PVP in 120 g distilled water containing 1 wt% of SDS. Once the polymer had been dissolved, 20 g of ELO was added to the solution and the dispersion was stirred, by means of a magnetic bar for 2 h. The total amount of additives (PVP, ELO and SDS) in water was 40 wt%, with an ELO to PVP ratio of 1 to 3. After that, the pre-emulsion was homogenized using a sonicator (Sonic VCX, 750 W, 29 Hz) equipped with a 13 mm tip high intensity horn. The ultrasound probe was immersed at a depth of about 1 cm and placed centrally in 200 g pre-emulsion in a 5 cm diameter glass bottle. Emulsions were prepared at a power amplitude of the sonicator of 80%, which results in an input in the emulsion of 70–80 W, during 90 s. Subsequently, the fine emulsion was spray-dried using a BÜCHI B290 mini spray-drier. Operational conditions of the spray-drying were: air inlet temperature: 150 °C; air outlet temperature: 100 °C; feed rate: 10 mL/min; air flow: 40 m^3/min; spray-flow: 500 L/h. Powders were stored at room temperature in tightly closed bottles in a desiccator (silicagel).

2.3. Characterization of the spray-dried powder

The ELO droplet size distribution and the spray-dried particle size distribution were measured using a Light Scattering Particle Size Analyzer (Coulter LS230). This instrument is able to measure a wide particle size range (0.4 up to 2000 μm) when equipped with the Small Volume Module (SVM), as it combines classical laser light diffraction with polarization intensity diffraction in its scattering cell. To measure the droplet size distribution of the ELO emulsion a few droplets (2–3 mL) of the emulsion were directly poured into the SVM module containing water as dispersing medium. In order to measure the particle size distribution of spray-dried powder (SDP), 0.5 mg of SDP was dispersed in 5 mL of 2 wt% solution of Span 80 in n-heptane. The dispersion was stirred for 1 min with an ultrasound processor equipped with a micro-tip horn. A few drops of this dispersion were added into the module which used n-heptane as dispersant medium. In addition, 0.2 g of spray-dried powder was dissolved in 1.8 mL of water by gently stirring with a magnetic bar. The droplet size distribution of the resulting emulsion (reconstituted emulsion) was measured also by light scattering.

The internal and external structure of the spray-dried particles (SDP) was studied by Scanning Electron Microscopy (Jeol JSM840A). For the study of the outer structures of the microparticles, the particles were attached to a specimen holder by a double carbon coated tape and then sputtered with a layer of gold. For studying the inner structure, at first, a double-coated carbon tape was fixed on the sample holder and covered with a certain amount of microparticles; thereafter a second carbon coated tape was added on the top of the sample. Subsequently, the upper tape was pulled off fiercely in order to induce mechanical fracture of some of the microparticles.

The payload of ELO, defined as mass percentage of ELO in the powder as based on the total powder mass, was evaluated via Differential Scanning Calorimeter (DSC, PE Pyris 1). The instrument was calibrated with indium and lead standards. Samples were placed in 10 μL Al pans and hermetically sealed to minimize the effect of water loss and possible PVP decomposition on the measurement of T_g for ELO and for PVP. The sample mass varied between 5 and 10 mg. Samples were first cooled down from 30 °C to −110 °C at 20 °C/min, then heated up to 40 °C at 20 °C/min and cooled down again at 30 °C/min to eliminate an endothermic peak of crystallization, which complicates the measurement of the T_g of ELO. Finally, the sample was heated again at 20 °C/min and the T_g was measured as the midpoint of the heat capacity transition. The DSC thermogram of the pure ELO showed a T_g at about −56 °C. Considering that the ELO and the PVP are immiscible, we can quantify the amount of ELO in the SDP as payload [12]:

$$\text{Payload} = \frac{\Delta C_p(\text{SDP})}{\Delta C_p(\text{pure})} \cdot 100$$

where $\Delta C_p(\text{SDP})$ is the change in specific heat of the SDP at the T_g of ELO and $\Delta C_p(\text{pure})$ is the change in specific heat of pure ELO at its T_g.

The amount of surface ELO (free ELO) was evaluated by washing 0.5 g of spray-dried powder (w_1) with 20 mL of a diethyl ether/petroleum ether mixture (1:3). This solvent mixture is able to dissolve any free ELO, but not the PVP polymer and therefore not the encapsulated ELO. The dispersion was gently stirred for 10 min, and then filtered on a paper filter and washed for three times with 10 mL of ether solution. The solution was collected in a 70 mL