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An efficient method for the output of new self-repairing materials through a reactive isocyanate encapsulation

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ABSTRACT

An efficient method for the preparation of stable microcapsules with an industrially relevant core material was investigated for future use in self-repairing coatings. Microcapsules filled with isophorone diisocyanate (IPDI) were synthesized with different polymeric shells: polyurethane PU, poly(urea–formaldehyde) PUF and bi-layer polyurethane/poly(urea–formaldehyde) PU/PUF. Changing the encapsulation process by adding more shell wall monomers and pre-polymers allows the modulation of physical and mechanical properties of microcapsules. The thickness of microcapsules shell walls can be tuned for coating thicknesses and chemical environments. The effect of diverse process parameters and ingredients on the morphology of the microcapsules was observed by scanning electron microscopy (SEM) and optical microscopy (OM). Different techniques for the characterization of the chemical structure and the core content were considered such as Fourier transform infrared spectroscopy (FT-IR) as well as the characterization of thermal properties by differential scanning calorimetry (DSC). High yields of free flowing powder of spherical microcapsules were produced. The application of a liquid phase IPDI in self-healing polymer composite is studied. Diisocyanates, being reactive with water, introduce the possibility of achieving a really autonomous self-healing system in an aqueous or moisture-sensitive environment.

1. Introduction

The self-healing coatings have been studied and exploited extensively in the last decade to protect materials, in a better way, from the effects of environmental exposure [1–6]. During normal use, the coatings undergo stresses that can cause cracking, and this leads consequently to mechanical failure. Self-healing materials should be able to retain functionalities, to restore structural integrity autonomously after an eventual damage caused by a mechanical injury or by corrosion, to extend the lifetime of the material [7,8].

Several thermosetting polymeric formulations based on mechanical, thermal, photo-, electrical or other external stimuli [9–12], have been developed with the ability of initiating a healing process, only if assisted by a catalyst. Till now to create self-healing polymeric coatings and adhesives have been used microencapsulated reactive chemicals and matrix embedded catalysts [2,13,14]. When a propagating crack breaks the embedded microcapsules, the released mending agent polymerises and repairs the damage in the presence of the catalyst.

In truth the high-cost catalytic systems, generally employed for these purposes, hinders a wide spread for large-scale applications. Hence, clever approaches to reduce the healing catalyst loading in self-healing polymers are of great interest. In particular, considerable attention is given to the possibility of creating self-healing coatings that automatically repair themselves and prevent corrosion of the underlying substrate *via* a truly independent healing process [1,15–17]. One of the possible approaches to free catalyst self-healing systems is to use microcapsules filled with isocyanates, widely used in abrasion and

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UV-resistant coatings, because of their high reactivity with water. Indeed the isocyanates introduce the possibility of planning a really autonomous self-healing system in an aqueous or moisture-sensitive environment (Fig. 1).

The preparation of durable microcapsules discloses some difficulties, and the stability of the capsules is very sensitive to the parameters of the encapsulation process. Microcapsules are prepared by several methods, which include self-assembly, phase separation, polymerization, and templating synthesis. Each method offers different advantages according to the specific applications adapted and to the variety of capsule characteristics [18–22].

In the recent past, the encapsulation of isocyanates has been limited to the solid state or blocked form [23,24]. Only two reports have appeared in the literature concerning the encapsulation of liquid isocyanates in the polyurethane shell walls by oil-in-water (O/W) emulsion method. For the first time, Sottos et al. [25] described the synthesis of PU microcapsules filled with IPDI. Then Yang et al. reported microencapsulation of more reactive hexamethylene diisocyanate (HDI) [26] in the polyurethane spheres again. Although the endurance of polyurethane was a required characteristic to encapsulate reactive healing agents such as isocyanates, the capsule shell wall material must ensure a good adhesion to the matrix in which the microcapsules will be incorporated to make the new self-repairing composite. Since the capsule adhesion to the matrix affects the self-healing success, the goal of the modification is to improve dispersion and adhesion in spherical particle and to reinforce composites [27].

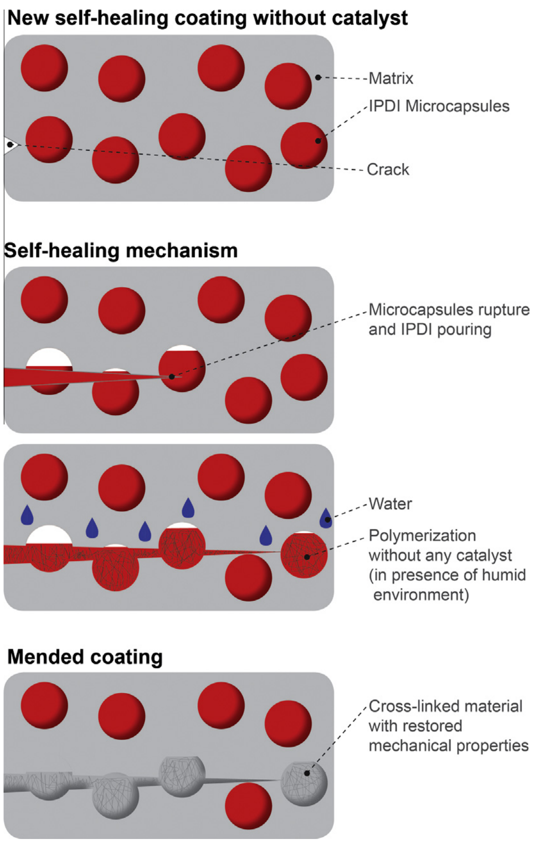

Fig. 1. Schematic of self-healing process without any intervention.

Having been inspired by the above concept, we studied the microencapsulation process of a liquid IPDI with different polymeric shell and we identified an efficient method for the preparation of stable microcapsules with a liquid IPDI in large quantities, resilient and tailored to be embedded in epoxy matrices. Here we report the new synthesis of double layered polyurethane/poly(urea–formaldehyde) (PU/PUF) microcapsules filled with IPDI in a single batch process. The encapsulation of IPDI into PU/PUF double layered shell walls brings substantial improvements to the microcapsule properties. The PUF shell wall forms a stable protective layer around the sticky PU surface so that the double-walled shell shows to be hard and able to preserve the liquid IPDI, that instead diffuse outside of single UF shell microcapsule. At the same time the inner PU layer is soft and deformable for low mechanical strength, in order to impart flexibility and tightness to the microcapsules. Therefore our microcapsules combine the high shell strength, provided by the PU/PUF double wall component, with the more effective incorporation into bulk matrices, as verified during composite manufacture. In addition the PU shell wall was obtained by using commercially available TDI based pre-polymer, with effective improvement for large scale application.

The advantages offered by isocyanate encapsulated by the present approach are an easy handling property and an easy incorporation in polymeric coatings and adhesives.

The endurance of our microcapsules made easy to embed them in a structural polymer matrix in order to obtain new coatings and adhesives with improved self-healing functionality. Furthermore the effectiveness of crack healing given by the encapsulated IPDI in epoxy coating and corrosion protection has been proved by an accelerated corrosion process in the preliminary experiments [26].

2. Experimental procedures

2.1. Microcapsule materials

Desmodur L-75 and Desmodur I (IPDI) were obtained from Bayer Materials Science. Desmodur L-75 is an aromatic polyisocyanate based on toluene diisocyanate in ethyl acetate solution with an NCO content of 13.3 ± 0.4 wt%, viscosity 1600 ± 400 MPa s @ 23 °C and equivalent weight of 315 g. Desmodur I is a monomeric cycloaliphatic diisocyanate based on IPDI with an NCO content of 37.5 wt%, viscosity 10 MPa s @ 23 °C and equivalent weigh of 111 g. Urea, ammonium chloride (NH_4Cl), gum Arabic (GA), resorcinol, formaldehyde solution (formalin, 37 w/v%) 1,4-butanediol, 1-octanol, sodium chloride (NaCl), chlorobenzene, ethylacetate, diethylenetriamine (DETA) were purchased from Sigma–Aldrich. All these products were used without further purification.

2.2. Synthesis of PU microcapsules filled with IPDI

At room temperature, 120 mL of deionised water and 13.5 g of GA as surfactant were mixed in a 500 mL flanged