CertBond
COST Action CA18120

WG1: Validation of new solutions for sustainable and REACh compliant adhesives

Report with the validation of new solutions for sustainable and REACH compliant adhesives and surface treatments (deliverable #10)

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Isocyanate microencapsulation as a safe alternative for the use of isocyanate based crosslinkers for high performing adhesives

We have developed microcapsules (MCs) containing isocyanate encapsulated, which are intended to substitute the current crosslinkers used in polyurethane (PU) and polychloroprene (PCP) adhesives that are currently supplied as two-component (2K) formulations composed of a polyol OH prepolymer and a crosslinker, usually isocyanate based. The microencapsulation of the isocyanate reduces or eliminates the risk associated with its handling, and at the same time offers control over its triggered release.
The MCs respond to the stimuli of pressure and/or temperature applied during the adhesive joint preparation, which leads to the isocyanate release and cure of the adhesive.
Although the developed MCs already proved to be efficient crosslinkers for this application, reported at Attaei et al., 2018, a smaller size distribution would lead to a more homogeneous and reproducible adhesive joint, as different sized MCs might contain different amounts of encapsulated content [1].

1) Emulsion stabilization studies for microcapsules optimization

We have developed work aimed at reducing the MCs´ size and size distribution, but mainly to understand the impact of the emulsion stability on the control of the MCs final morphology. The innovation of this work relies on the fine-tuning of the final MCs' size and size distribution, by developing an efficient O/W emulsions stabilization system. For that, the effect of a polysaccharide, a surfactant and a polymer, and combinations between them were studied. GA, the polysaccharide, was the stabilizer used in previous studies and is here used as reference [1-3]. Partially hydrolyzed PVA, a non-toxic and biodegradable water-soluble polymer, is used to function as a thickening agent [4]. DC193 is a non-ionic silicone surfactant and was chosen based on its HLB value and its low surface tension. The stabilization system was intended to enable: (i) the production of a stable emulsion with a small size distribution; (ii) a minimum variation between the size of the initial emulsion droplets and that of the final MCs, which will enable the control of the MCs' final morphology; (iii) the production of MCs with a good encapsulation efficiency and shelf-life.

Rheology modification (by PVA) was found to be the most effective strategy to stabilize O/W emulsion systems for the MCs´ synthesis. The increased viscosity of the continuous phase, achieved with PVA at 2 wt% in the aqueous phase of the emulsion, is an effective strategy to reduce gravitational separation phenomenon (droplet sedimentation) and to finely control the size of the final MCs, resulting in relatively small MCs (size distribution peaked at 40.9 µm)

with 46 wt% of encapsulated isocyanate and, therefore, acceptable for the envisaged application as solid crosslinkers for mono-component adhesives (Fig. 1).

Paper published in the scope of this work: Mónica V. Loureiro, António Mariquito, Mário Vale, João C. Bordado, Isabel Pinho and Ana C. Marques, "Emulsion Stabilization Strategies for Tailored Isocyanate Microcapsules", *Polymers*, 15 (2023) 403. https://doi.org/10.3390/polym15020403

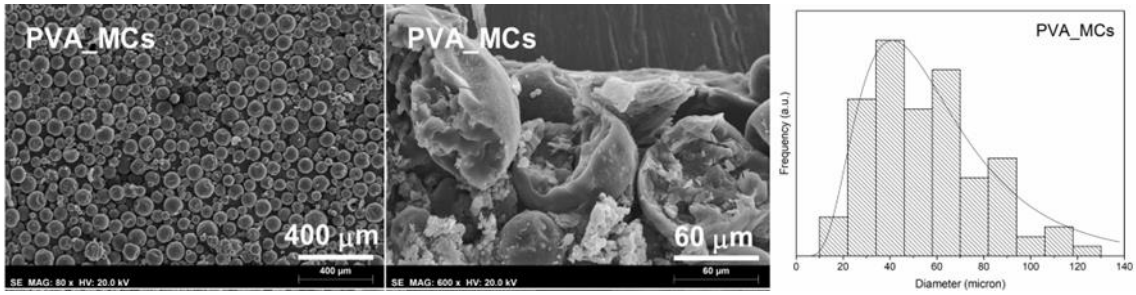


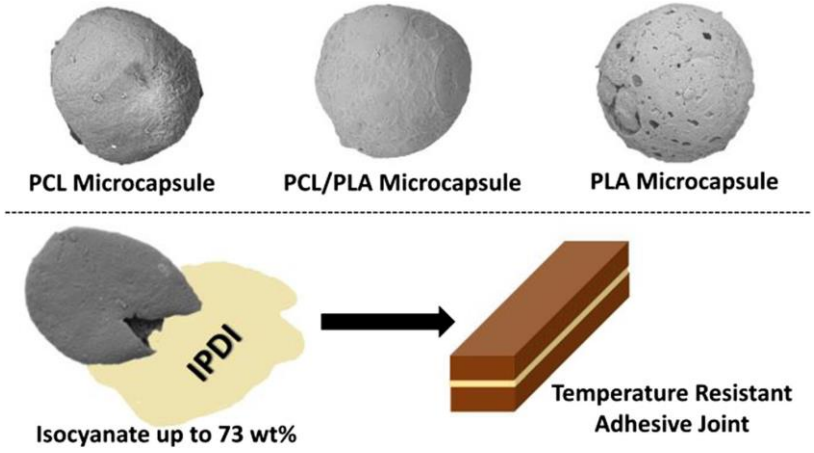
Fig. 1. SEM images of the obtained MCs at 80x amplification (at the left). SEM images of isolated MCs' cross sections, deliberately crushed (obtained at different magnifications). MCs' size distribution (at the right).

2) PCL/PLA biodegradable microcapsules for adhesives

We developed a straightforward and efficient process to encapsulate isophorone diisocyanate (IPDI) using biodegradable polymers by an emulsion system combined with the solvent evaporation method. Spherical, disaggregated, and core–shell MCs using poly(e-caprolactone) (PCL), polylactic acid (PLA), or PCL/PLA blends as shell materials, were produced. As far as we know, it is the first time that isocyanate species are encapsulated by PLA or PCL/PLA blends. Our process leads to a production yield of 70–74% and an encapsulated isocyanate content up to 73 wt% of the MCs. All MCs showed very good isocyanate protection, especially when stored in low-moist environments. Their use as cross-linking agents for harmless, eco-innovative, and high-performance adhesive formulations for footwear was tested, for the first time, according to the specifications of industry standards, in collaboration with an adhesives company, CIPADE SA. This serve as a basis for other industries testing protocols. The peel tests of the adhesive's joints revealed peeling strength values between 3.45 and 6.09 N/mm which is higher than the minimum required by the company (3 N/mm). The creep tests demonstrated that the use of MCs with encapsulated IPDI improves the heat resistance of the adhesive joints. Therefore, the MCs revealed an effective isocyanate release and very capable adhesive joints with no negative effects from the polymeric shell, validating the employment of these cross-linking agents in the footwear industry. Although PCL MCs were the ones with the highest IPDI content, the best adhesive formulations were produced with MCs with a high amount of PLA, due to their smaller size, good dispersibility and better distribution at the substrate. MCs with PCL/PLA at 93/7 promoted strong

and efficient joints, with an average peel strength of 5.37 N/mm and displacement of only 0.28 cm at 90 ºC. The herein presented MCs are a potential solution for ‘‘solid’’ cross-linking agents for safer, eco-innovative, and high-performance adhesive formulations.

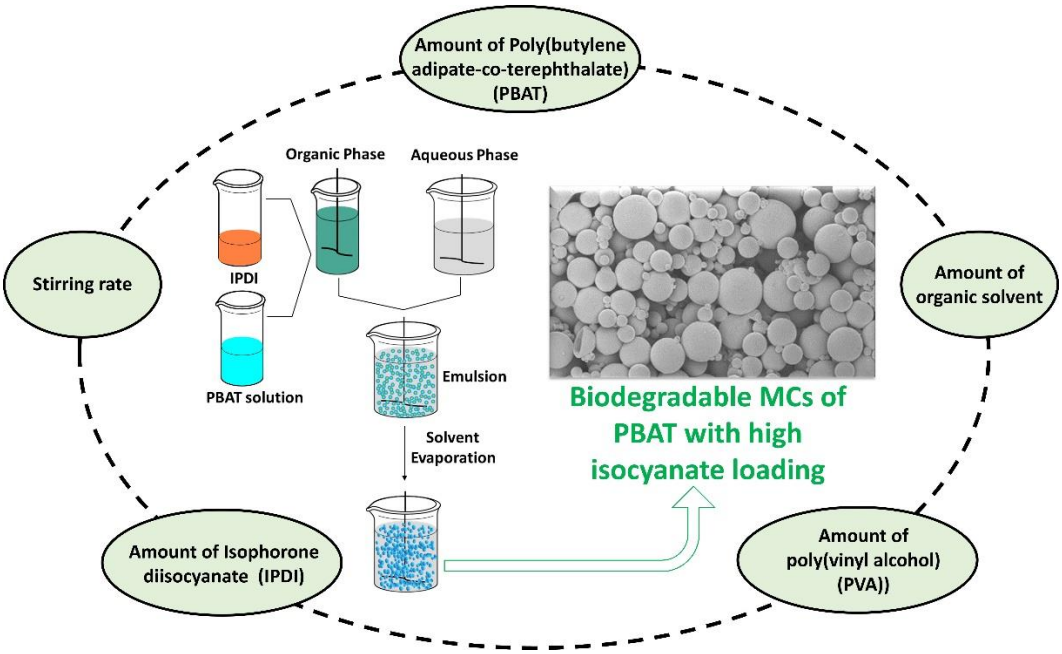
Paper published in the scope of this work: António Aguiar, Mónica V. Loureiro, Isabel Pinho, Ana C. Marques, “Efficient encapsulation of isocyanates in PCL/PLA biodegradable microcapsules for adhesives”, *J Mater Sci* (2023). https://doi.org/10.1007/s10853-023-08160-9



3) New PBAT biodegradable microcapsules for adhesives

In this study, we demonstrate the encapsulation of isocyanate (IPDI) using poly(butylene adipate-co-terephthalate), PBAT, as biodegradable shell material. These novel MCs present a regular surface, without holes or cracks, a very thin shell, and high isocyanate loading, up to 79 wt%. We also demonstrate that the PBAT shell protects IPDI from air moisture, a critical feature for a long shelf-life.
In addition, we systematically studied the impact of the production parameters on MCs size, morphology, and IPDI loading. The increase of different parameters such as stirring rate (1000 rpm), amount of emulsion stabilizer PVA (2.5 g), or organic solvent (27.5 g) leads to smaller MCs. On the contrary, the increase of PBAT amount (4.75 g) leads to larger MCs. In this way, we can produce rounded PBAT MCs with tailored mean diameters between 36 µm and 521 µm (median 34–523 µm). Throughout this study, the IPDI loading was obtained as theoretically expected, and apart from a few extreme variations, the polymerization extension of IPDI, in the form of PUa, represented only 1 or 2 wt% of the MCs. This study provides valuable information for future works since it presents the first report on PBAT MCs loaded with isocyanate, and it explains several correlations that greatly impact the size and quality of these MCs. This was followed by validation in the industry (CIPADE SA), which shows that encapsulated isocyanate by PBAT shell microcapsules leads to better results in the creep tests and adhesion peeling tests than non-encapsulated, presenting an extra benefit of sustainability and safety in the adhesive joints preparation.

Paper published in the scope of this work: António Aguiar, António Mariquito, Diogo Gonçalves, Isabel Pinho, Ana C. Marques, "Biodegradable Microcapsules of Poly(Butylene Adipate-Co-Terephthalate) (PBAT) as Isocyanate Carriers and the Effect of the Process Parameters", *Polymers* 15 (2023) 665. https://doi.org/10.3390/polym15030665



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"BEYOND ECOBOND – Development of new monocomponent, self-reactive adhesives, through
microencapsulation techniques". The authors work within the Technology Platform on Microencapsulation and Immobilization (https://web.tecnico.ulisboa.pt/ana.marques/SiteTPMI/) Application of Atmospheric-Pressure Jet Plasma in the Presence of Acrylic Acid for Joining Polymers without Adhesives of CERENA (Strategic Project FCT-UIDB/04028/2020).

Other works on sustainable and REAch compliant adhesives

The synthesis and characterization of novel eco-epoxy adhesives was carried out by elements of the WG1 of this COST Action [5, 6, 7, 8], as well as the synthesis of polyurethane bio-based adhesives resulted from the depolymerization of lignocellulose biomass, and their characterization [9]. A review on the topic of non-formaldehyde, bio-based adhesives for use in wood-based panel manufacturing industry was also prepared by the group [10].
In what regards surface treatment, the group has reported on the surface modification using MAPLE Technique for improving the mechanical performance of adhesive joints [11] and has delivered an e-course on this topic. An alternative tecnhique for joining polymers without adhesives was also developed and reported in [12], based on the application of atmospheric-pressure jet plasma in the presence of acrylic acid.
Finally it should be stated that a compilation on adhesives and surface treatments for structural applications was done and reported in co-authorship by the WG1 in [13], where the recent developments on sustainability and implementation for metal and composite substrates are described. This work has been elected Editor's choice in the journal Materials.

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