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Protected *N*-heterocyclic carbenes as latent organocatalysts for the low-temperature curing of anhydride-hardened epoxy resins

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ABSTRACT

Epoxy resins based on commonly used epoxy compounds, various anhydrides and CO_2-protected *N*-heterocyclic carbenes (NHCs), which combine the favorable properties of fast curing at low reaction temperatures, pot life in the range of hours to days and full homogeneity in the form of low-viscosity liquids, are presented. These characteristics are achieved by careful tuning of the components. 1,3-Dimethylimidazolium-2-carboxylate (**5u-Me-CO_2**) as a thermally latent organocatalyst offers facile one-step preparation and robustness towards atmospheric conditions as well as the high reactivity required once the polymerization is "switched on" by heating. A systematic screening of several epoxy compounds and 14 different anhydrides is conducted to identify the monomers that are suited best for rapid monomer consumption and thus for low curing temperatures. From these experiments, more than 15 different systems were found where a homogeneous liquid can be formed in the absence of further additives (no solvent or reactive thinner). Several of these one-component mixtures were investigated more detailed by in-situ DSC and rheology measurements. In general, the combination of aliphatic epoxides and low-melting or liquid anhydrides delivers the fastest polymerization under the mildest conditions, while maintaining a very low initial viscosity (< 100 mPa·s at room temperature), thereby offering access to sprayable precursor systems. Full curing within minutes, as evidenced by DSC experiments, is achieved at T = 100–120 °C, depending on the composition of the resins.

1. Introduction

Arguably, *N*-heterocyclic carbenes (NHCs) constitute the most versatile and successful class of organocatalysts established in recent time [1–4]. Their key beneficial properties include structural variability, high nucleophilicity and Brønsted-basicity as well as the intriguing chemistry of the carbene reactive center itself, which has enabled challenging chemical transformations like *Umpolung* reactions or the addition to double bonds, among many other examples [5–10]. Polymer chemistry has profited solidly from these advances in organic chemistry: NHC-triggered organopolymerization [11–13] can nowadays be applied to prepare polymers via ring-opening polymerization (lactones [14–18], lactams [19,20], epoxides [21–23], cyclosiloxanes [24–27] and others), by conjugate addition [28,29] (including a wide range of acrylic monomers) but also by condensation reactions [30–33]. In many cases, NHCs provide these services with additional benefits, such as increased polymerization rates, excellent control of end-groups or advantageous polymer architectures such as cyclic structures [11–13,34].

However, the transition from laboratory use to commercial, large-scale applications has so far been hampered by some inherent problems that come with the use of NHCs. The main difficulties can be identified as (a) sensitivity to protic compounds/impurities

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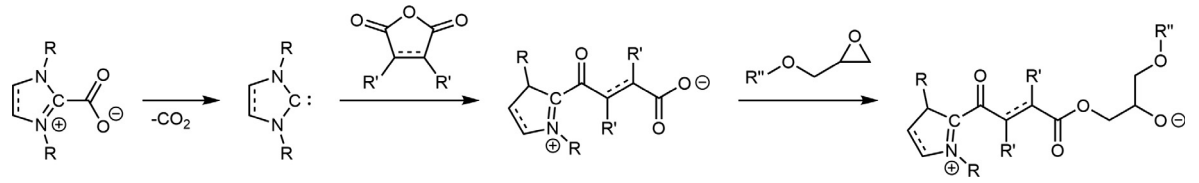

Fig. 1. Proposed initiation step for curing of anhydride-hardened epoxy resins by thermal deprotection of the catalyst and alternating, anionic copolymerization of the monomers [35].

(water), (b) limited storability and (c) synthetic requirements, which can be prohibitive for use in polymer industry.

The rapid epoxy curing system presented in this work is intended to minimize the above mentioned disadvantages while capitalizing on the benefits that can be derived from using NHCs. Our group has recently published the curing of anhydride-hardened epoxy resins initiated by CO_2− or metal-protected NHCs [35] (Fig. 1), a process that has also been shown to be compatible with vacuum-assisted resin infusion (VARI), thereby offering access to well-performing fiber-reinforced composite materials [36]. Reaction with carbon dioxide transforms the free NHC into a compound that is readily stored; its reactivity is blocked, but can be restored by heating, thus rendering the whole system latent with a one-time thermal "switch" to start polymerization [37,38]. It was furthermore shown that mixtures of an epoxy compound, anhydride and protected NHC can be fully homogeneous, stable under atmospheric conditions and do not require special storage conditions or purification of the monomers [35]. DSC experiments further revealed that pot times up to four weeks were possible, whereby this property was dominated by the protecting group and the chemical structure of the NHC. Since reactivity depends on both decarboxylation and inherent reactivity of the free NHC, the overall observed polymerization rates result from a superposition of these effects. In general, steric pressure facilitates the loss of CO_2, but might also hinder interaction of the free NHC with the monomer. Inversely, NHCs with small *N*-substituents have repeatedly shown to engage monomers more readily [14–18], but adducts with carbon dioxide are also more stable [37,38]. While the relative contribution of both effects remains elusive and will be different for every NHC, it was found that even over longer storage time the curing profile did not change, irrespective of the chemical structure of the NHC [35], which indicates that degradation of the protected NHC to carboxylic acid [39] or azolium hydrogen carbonate [40,41] did not occur to a significant degree. As a consequence of the high reactivity of NHCs, when released by warming, they are superior to commonly used accelerators for warm-curing epoxy resins, which allows for low catalyst loadings, fast polymerization kinetics and generally relatively mild curing temperatures. Mechanistically, initial reaction of the NHC with the anhydride was proposed (Fig. 1), on account of the relative slowness of NHC-addition to epoxides [21–23]. The anionic copolymerization of epoxides and anhydrides typically proceeds strictly alternating [42], a more complete polymerization scheme can be found in the SI (Fig. S2). Finally, it should be considered that after addition and ring-opening of the anhydride an acylazolium species forms (Fig. 1), reminiscent of the well-understood polymerization of lactones [14–18]. Hence the positively charged imidazolium moiety could be displaced from the carbonyl carbon by nucleophilic substitution, which would set the NHC free anew and render the whole process catalytic in nature. However, this analogy is not yet corroborated and still requires further investigation.

The results discussed in the following represent an extension of this system to a wide array of different epoxy compounds (Fig. 2, four examples) and anhydrides (14 examples), with the specific aim to generate compositions that are homogeneous with low viscosity (and preferentially *sprayable*) and that can be cured at low temperatures (T < 120 °C), while still maintaining useful pot times (hours to days). A range of different catalysts is investigated with emphasis on 1,3-dimethylimidazolium-2-carboxylate, **5u-Me-CO_2**, a pre-catalyst that can be synthesized in a single step from cheap starting materials and which is insensitive to atmospheric conditions [43]. We envision a low-viscosity, latent, low-T-curing epoxy resin to be advantageous for a significant number of applications, including composite preparation, restoration/repair works and the formulation of advanced adhesives. The development of powerful, yet latent, monomer or catalyst systems remains one of the hotspots of epoxy resin research [44]; notable recent innovations include application of masked amines (as hydrolysis-labile imines [45] or thermally labile carbamates [46]) for amine-hardened resins, while for warm-curing epoxide/anhydride composition the employment of photosensitive amidines [47], quaternary ammonium salts [48] and aminimides [49] has been reported. The fact that imidazoles are used as cheap and efficient accelerators in non-latent setups has inspired research efforts regarding "blocked" imidazoles [50–52].

2. Results and discussion

A range of different CO_2-protected NHCs (Fig. 3) was synthesized and tested for reactivity in a reference system consisting of bisphenol-A diglycidyl ether (BADGE, **E1**) and hexahydrophthalic anhydride (HHPA, **A1**). Reactivity was established by conducting differential scanning calorimetry (DSC) measurements on non-cured mixtures of the anhydride, the epoxy compound and latent catalyst. While onset and maximum of the observed exothermic curing process can be used to analyze curing kinetics, the integral delivers the released amount of heat and thus a measure for completeness of the reaction when compared to standard systems (see Fig. 4 for typical examples) [35,53]. ΔH values were found to be in agreement with literature data [54], strongly suggesting that full curing was achieved under these conditions. This was also underlined by DSC control heating cycles, which found no post-curing peaks; T_g was also found to be in the range typical for fully cured **E1**/**A1** resins (see Table S7, where a listing of several T_g values is given for different curing systems investigated in this work).