



Examining the effects of storage on the initiation behaviour of ionic liquids towards the cure of epoxy resins



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ABSTRACT

Four structurally related ionic liquids (1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium thiocyanate) are examined for their storage characteristics and the effect on their ability to initiate the cure of epoxy resins. At ambient temperature, epoxy formulations containing 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate display marked colour changes to yield dark red samples with greatly increased viscosity after one day; after six days both samples have undergone vitrification. The epoxy formulation containing 1-ethyl-3-methylimidazolium acetate continued to polymerise even at sub-zero temperatures. Storage in dark bottles retarded the reaction during the 30-minute period that the sample is removed from the freezer prior to an aliquot being taken, but once the autocatalytic low temperature reaction has started, the dark glass no longer provides effective protection. Samples of 1-ethyl-3-methylimidazolium dicyanamide/epoxy were also stored and sampled in the same manner, but no differences were exhibited between the samples in clear and dark brown glass bottles. Infrared and nuclear magnetic resonance studies confirmed that the hygroscopic ionic liquids pick up water readily (coordinating to the H atom at the 2-position on the imidazolium ring), but once dried the initiating ability is lost.

1. Introduction

Epoxy resins are especially interesting to the composites industry due to their design versatility and the wide variety of chemical compounds that can effect cure [1], making it possible to tailor the level of cross-linking and the temperature at which the reaction is carried out [2]. Imidazoles have been demonstrated to catalyse the homopolymerisation of epoxide groups [3,4] and compositions of imidazoles and epoxy resins yield adhesives and coatings with very good mechanical properties and superior physical properties [5] such as better heat resistance [6], lower tensile elongation, and higher modulus. Imidazole formulations can offer a wider range of cure temperatures compared with amine-cured systems [7], but the reactivity of the imidazole can limit the processability of the formulations with relatively short processing windows. Ramis et al. [8] employed 1-methylimidazole to accelerate the Jeffamine-cured polycondensation of the

diglycidylether of bisphenol A, but found that differences in reactivity (with diethylene triamine or hyper-branched poly(ethyleneimine)s) meant that the 1-methylimidazole was unsuitable for use in mixed formulations requiring sequential curing steps. A variety of strategies have been examined to control their reactivity, including the formation of coordination compounds [9]. Structurally related imidazolium-based ionic liquids [10] are relatively easily prepared [11] and offer good stability of the ring in oxidative and reductive environments. From the perspective of processing, ionic liquids act as catalysts to enhance both the rate of reaction and the reaction yield, but also offer low viscosity formulations.

The ability to display cure latency (*i.e.* to mix an epoxy monomer with a curing agent, hardener and store it at ambient or sub-ambient temperature without advancement of the reaction [12,13]) is a key feature of a one-pot formulation allowing ease of processing, ease of storage, cost reduction, and customer convenience. Kowalczyk and

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Spychaj [14] examined the use of 1-butyl-3-methylimidazolium tetrafluoroborate as an initiator for a commercial epoxy (Epidian 6) and additionally, a formulation comprising the two components could be stored for a period of 6 months at ambient temperature without any change in viscosity. Rahmathullah et al. [15] explored the use of 1-ethyl-3-methylimidazolium dicyanamide as an initiator for epoxy resins and, moreover, determined that it could be used as a latent initiator which was miscible with another commercial epoxy (Epon 828) and exhibited long-term stability at room temperature. The stability of the formulation was tracked through monitoring the characteristic epoxy ring absorbance band in near-infrared spectroscopy and it was suggested by the authors that the mechanistic route may involve reaction between the cyanamide and epoxy groups and not the nitrogen atoms in the imidazolium cation directly.

Maka et al. also reported the use of imidazolium-based ionic liquids as initiators for epoxy resins based on both 1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions [16]. It was suggested that, in these cases, thermal decomposition of the ionic liquid could proceed via a highly stabilised N-heterocyclic carbene structure, which, in turn, would result in generation of imidazole or 1-alkyl derivatives. The interaction of the pyridine-type nitrogen atom in the imidazole ring with an epoxy group to form a 1:1 adduct was concluded as the most likely anionic polymerisation route. The stability of the formulations stored at room temperature was examined and revealed that samples comprising tetrafluoroborate exhibited a storage period of 20 days irrespective of the cation size, the viscosity of the 1-decyl-3-methylimidazolium chloride/diglycidylether of bisphenol A (DGEBA) system remained almost unchanged after a storage period of 30 days at room temperature; no influence of alkyl chain length on the storage time was identified. In a further study, Maka et al. found that the initiation of the epoxy polymerisation reaction with 1-butyl-3-methylimidazolium thiocyanate proceeded via thermal decomposition products including imidazole and alkyl derivatives resulting from the ionic liquid [17]. Soares et al. reported that N,N'-dioctadecylimidazolium iodide successfully initiated the polymerisation of DGEBA and also suggested that the mechanism proceeded via thermal decomposition of the ionic liquid at high temperatures to yield imidazole, N-alkylimidazoles and imidazole moieties linked by a methylene bridge which were capable of initiating the polymerisation reaction [18].

We have already reported our findings on the proposed initiation mechanism involving 1-ethyl-3-methylimidazolium acetate [19], and found that it degraded at 150 °C to yield dealkylated products including methyl acetate and ethyl acetate as well as 1-methylimidazole and 1-ethylimidazole. The dealkylated imidazole ring was proposed as a route for initiation of the epoxy ring. Adduct formation between 1-ethyl-3-methylimidazolium acetate and benzaldehyde at room temperature was observed leading to the proposal of the generation of a carbene species as a route for initiation of the epoxy ring in formulations with the acetate anion. At elevated temperatures, a second, competing reaction, involving deprotonation of the imidazolium ring, also becomes

active. We have now extended the investigation into the ability of formulated epoxy/ionic liquid formulations to be stored at room temperature and at sub ambient temperatures is an important step to determine how this affects subsequent polymerisation reaction kinetics and mechanism. The present paper addresses the influence of initiator structure and storage temperature on latent cure capability.

2. Experimental

2.1. Instrumentation

Infra-red spectra were obtained using an Agilent Technologies Cary 600 Series Fourier Transform Infrared spectrometer. A golden gate accessory with a diamond crystal was used for all ATR-IR spectroscopy analyses. A background spectrum consisting of 32 scans with the golden gate *in situ* was run before all analyses. The resulting spectrum for each sample was taken from an average of 32 scans which were recorded in absorbance mode over a spectral range of 600–4000 cm^{-1} . The samples were placed directly on the sapphire platform and good contact between the diamond crystal and sample was checked prior to commencement of analysis. The data were processed using Agilent Resolutions Pro.

^1H NMR spectra comprising of 16 scans, conducted on a Bruker 300 MHz nuclear magnetic resonance (NMR) spectrometer at room temperature. The samples for analysis (80 mg) were mixed with D_6 -acetone (0.6–0.7 ml) and transferred to a NMR tube.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples (5.0 ± 0.5 mg) in hermetically sealed aluminium pans. Experiments were conducted at a heating rate of 10 K/min from 10 °C to 200 °C (heat/cool/heat) under flowing nitrogen ($50 \text{ cm}^3/\text{min}$). DGEBA and the ionic liquid were mixed by hand in glass scintillation vials. The samples were immediately analysed after mixing and the remaining mixture placed in the freezer. DSC analysis was also performed to study the differences in exothermic profile between freshly-mixed formulations and those which had been exposed to various storage periods and conditions. All analyses were performed at a scan rate of 10 K/min under a heat/cool/heat temperature programme from 0 to 200 °C.

Dynamic oscillatory rheology was performed using an Anton Paar MCR-300 rheometer with a 25 mm peltier plate and disposable aluminium pan set up. DGEBA and the ionic liquid were combined in a speed mixer pot (100 g) and subjected to two consecutive mixing periods of 2 min at 2500 rpm. The rheometer was operated in oscillation mode and samples were subjected to a temperature ramp from 25 °C to 200 °C at 5 K/min with the collection of data set to a frequency of 0.2 min. The strain was held constant at 0.5% and the normal force programmed to remain at 0 N.

2.2. Materials

The four ionic liquids (1-ethyl-3-methylimidazolium acetate, 1-

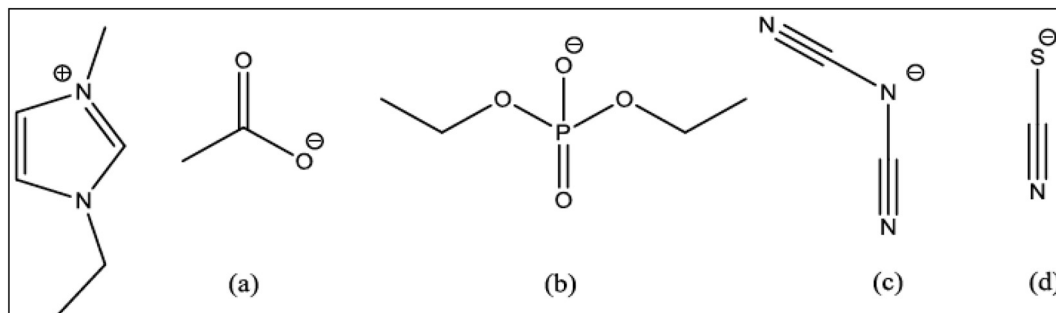


Fig. 1. Structures of 1-ethyl-3-methylimidazolium (a) acetate, (b) diethyl phosphate, (c) dicyanamide, (d) thiocyanate.

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