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Curing kinetics of epoxy-deep eutectic solvent mixtures

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ABSTRACT

A deep eutectic solvent (DES) based on choline chloride and urea (ChCl-U) was used to prepare epoxy compositions based on low molecular weight diglycidyl ether of bisphenol A (DGEBA) resin. Fourier transform infrared (FTIR) spectroscopy, rheometry and differential scanning calorimetry (DSC) were, then, used to investigate the curing mechanism of epoxy mixtures as a function of the DES content. The results confirmed that the eutectic mixture of choline chloride and urea was able to initiate the reaction of chain homopolymerization in the absence of the hardener, thus acting as a biodegradable and sustainable catalytic curing agent for epoxy resins.

Nonisothermal reaction kinetics was modeled with the results obtained by ICTAC Kinetic Project confirming the role of the analyzed deep eutectic solvent in accelerating the homopolymerization of epoxy groups.

1. Introduction

Ionic liquids (IL) are salts that typically contain organic cations and inorganic anions with unique and tunable physio-chemical properties, such as low melting temperature (<100 °C), wide liquid phase range, high thermal stability and very low vapor pressure [1,2]. The ionic liquids with best performance are those in which the cations and anions do not act as ion pairs but rather as interpenetrating structures [3]. However, the poor biodegradability and high costs of ionic liquids still limit their widespread diffusion. In the last ten years a new class of ILs, called deep eutectic solvents (DES), has emerged. DESs are defined as a mixture of two or more components which, at a particular composition, form an eutectic with a much lower melting point than those of the individual components [4,5]. DESs share many characteristics of conventional ILs (e.g., they are not reactive with water and non-volatile), offering at the same time certain advantages, since they are: (i) cheap; (ii) easy to prepare, since DESs are obtained by simply mixing two components, thus by-passing all problems of post-synthesis purification and waste disposal generally encountered with ILs; (iii) biodegradable in many cases; (iv) biocompatible and non-toxic [6–11]. Thanks to their low ecological footprint and attractive price, DESs are becoming of growing interest, both at academic and industrial levels, and the number of publications dedicated to the use of DESs is now rapidly increasing in the current literature [5,6,12,13].

Over the past two decades, both ILs and DESs have gained great attention from the scientific community as “designer solvents” for different applications [14–17]. Very recently, ILs have been proposed also as latent curing agents and/or modifying components for epoxy resins [18–23]. Latent curing agents are designed to remain inactive at ambient temperature and to undergo controlled reaction upon exposure to elevated temperatures [19]. The desired inertness increases storage and handling capabilities. ILs can overcome the major drawbacks of commercial latent curing agents, i.e., a possible inhomogeneous cure due to a difficult dispersion of these solid compounds in the resin, especially in the case of a fiber composite matrix. The control of the composition of epoxy systems with new curing agents or catalytic components is a topic of considerable interest due to the great versatility of epoxy resins for different applications, including coatings, electric and electronic devices, fiber-reinforced composite materials [24], structural adhesives [25,26], polymer nanocomposites [27], and many others [28,29].

The possibility to use a low-cost, biodegradable and sustainable catalytic component in the epoxy resins opens up new usage scenarios for DESs and, at the same time, is of crucial importance for reducing the environmental impact of epoxy resin applications. The application of DESs as cross-linker promoters of epoxy resins is still largely unexplored, apart from the work of Spychay and coworkers [30–32]. To the best of our knowledge, the curing kinetics of these systems have been so far not considered.

The aim of the research reported in the present paper is to analyze the possible role of the eutectic mixture of choline chloride and urea (ChCl-U), belonging to the class of DESs, as a biodegradable catalytic curing agent for epoxy resins. Being

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ChCl-U a type of ammonium salt, it is expected to promote epoxy cross-linking [42]. The choice of this type of deep eutectic solvent system is based on its popularity imparted by its green character, low cost and wide range of applications [33,34]. Choline chloride is produced in mass as a vitamin supplement and is, therefore, readily available in bulk and at relatively low costs [35].

Epoxy mixtures based on low molecular weight diglycidyl ether of bisphenol A (DGEBA) resin and choline chloride/urea were prepared and characterized. The curing kinetics of epoxy-ChCl-U blends was modeled in accordance with the results obtained by ICTAC Kinetic Project [36,37].

2. Experimental

A diglycidyl ether of bisphenol A (DGEBA) with the commercial name EC 01, supplied by Elantas Italia S.r.l., was used as received. The resin had an epoxy equivalent weight in the range 184–190 g/mol and a viscosity in the range of 12–15 Pa s at 23 °C.

The investigated DES was based on choline chloride (ChCl) and urea (U), both supplied by Iolitec GmbH. Choline chloride (2-hydroxyethyl-trimethylammonium chloride) had a molecular weight of 139.62 g/mol, a purity higher than 97% and a melting point of 302 °C. Urea (carbonyldiamine) had a molecular weight of 60.06 g/mol, a purity higher than 99.5% and a melting point of 133 °C. The eutectic mixture was formed by stirring choline chloride and urea (1:2 molar ratio) at 90 °C until a homogeneous colorless liquid was formed. This eutectic mixture remained liquid at ambient temperature (melting point = 12 °C). The chemical formula of the materials used is reported in Scheme 1.

Different contents of ChCl-U were mixed with epoxy resin at room temperature until homogeneous mixtures were obtained. The epoxy compositions under analysis, containing different ChCl-U contents, are reported in Table 1.

For comparison purposes, some control formulations were prepared. As reported in Table 1 the neat DGEBA epoxy resin (without hardener) and the DGEBA epoxy resin mixed with triethylene tetramine were named E and E_TETA, respectively. The used aliphatic amine was supplied by Elantas Italia S.r.l. with the commercial name of IG 824-K24 and its chemical structure is reported in Scheme 1. Moreover, some epoxy-DES mixtures with TETA hardener were prepared as control too. They were named with the label E_(ChCl-U+TETA) *x* in Table 1, where *x*, varying from 1 to 7.5, specifies the ChCl-U content. In all the studied formulations using the hardener, this latter was used with a stoichiometric content of 13 part per hundred parts of resin (phr), which corresponded to a molar ratio epoxy/amine = 1:1.

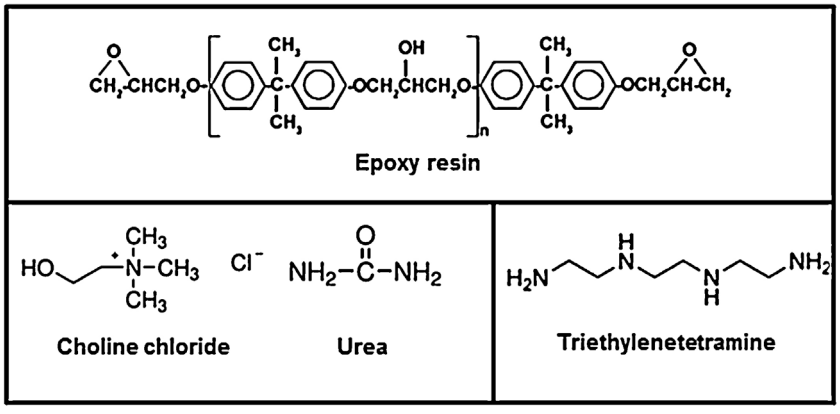
Table 1
Details of composition of the systems under analysis.

	Ionic liquid content (phr)	Curing agent content (phr)
E	0	0
E_TETA	0	13
E_(ChCl-U) 1	1	0
E_(ChCl-U) 2.5	2.5	0
E_(ChCl-U) 5	5	0
E_(ChCl-U) 7.5	7.5	0
E_(ChCl-U+TETA) 1	1	13
E_(ChCl-U+TETA) 2.5	2.5	13
E_(ChCl-U+TETA) 5	5	13
E_(ChCl-U+TETA) 7.5	7.5	13

Attenuated total reflectance (ATR) analysis was performed on thin films of uncured and cured epoxy resin without hardener (E) and epoxy/ChCl-U mixtures (E_(ChCl_U) 2.5, E_(ChCl_U) 5, E_(ChCl_U) 7.5). The cured solid samples were obtained by heating the mixtures in an oven from 30 °C to 260 °C at 5 °C/min. ATR spectra were recorded on a PerkinElmer Universal ATR spectrometer with a 4 mm diameter diamond microprism. For each measurement, 64 scans in the region between 4000 and 400 cm^{-1} were acquired with a resolution of 4 cm^{-1}. At least three spectra for each sample typology were considered.

Rheological measurements were carried out in a strain-controlled rheometer (ARES, Rheometrics Scientific) equipped with a parallel plate geometry (25 mm plate diameter) at a constant shear rate of 5 s^{-1}. The tests were conducted from 40 °C to 300 °C employing a heating rate of 3 °C/min. Rheological analysis was performed in dynamic mode to investigate the changes in viscosity at increased temperatures and, thus, determine the gelation temperature.

Differential scanning calorimetry (DSC) was, then, used to study the cure kinetics of the epoxy resin in the presence of ChCl-U, with or without the curing agent TETA. A Mettler Toledo DSC 822 calorimeter was employed to this aim, performing dynamic runs at constant heating rates in order to determine the conversion profiles and the total heats of reaction released during dynamic curing of each system. Samples of 8–12 mg were heated from 0 °C to 300 °C with different heating rates (5, 10 and 20 °C/min) in a nitrogen atmosphere. The formulations cured in a first DSC dynamic experiment were, then, subjected to a second dynamic scan between 25 °C and 280 °C to evaluate the maximum glass transitions temperature ($T_{g\ max}$) achieved by the specimens. In order to prove the repeatability of results, the calorimetric experiments were repeated at least three times and the results averaged.



Scheme 1. Chemical structure of DGEBA epoxy resin, choline chloride (ChCl), urea (U) and triethylenetetramine (TETA).