



New biobased epoxy hardeners: Thiol-ene addition on oligobutadiene

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ABSTRACT

We report the synthesis and characterization of oligobutadienes functionalized with primary amine groups and their use as hardeners for epoxy resins. The functionalization of polybutadiene (with 59% of 1,2 double bonds) was carried out by the addition of 2-amino-3-mercaptopropanoic acid (cysteamine) in different ratios through thiol-ene coupling. The thiol-ene addition was performed in tetrahydrofuran solvent with 2,2'-azobis(2-methylpropionitrile) as radical initiator at 70 °C. The ratio polymer/cysteamine was varied in order to obtain several number of amine functions per polymer chain and to compare the reactivity of thiol onto 1,2 and 1,4 double bonds of polybutadiene. The different characterizations of synthesized polymeric amines allowed us to identify the quantities of amine groups grafted onto 1,2 and 1,4 double bonds, the cyclization side reactions of 1,2 double bonds and the unreacted 1,2 and 1,4 double bonds. These polymeric amines were mixed with epoxy resins (BADGE) and led to materials with glass transition temperatures between 20 °C and 60 °C depending on the polymeric amines functionalities. The thermal properties of synthesized resins are similar to the ones measured on epoxy resins obtained with commercial hardeners (cycloaliphatic amine and 1,10-diaminododecane).

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1. Introduction

Epoxy resins are one of the most important groups of thermosetting polymers. They are able to react with various curing agents to form solid, crosslinked materials with considerable strength and adhesion. This transformation is generally referred to as curing or hardening. The polyaddition reaction is the most commonly used type of reaction for the cure of epoxy resins. The curing agents used in this type of reaction have an active hydrogen compound, and they include amines, amides, and mercaptans. The curing reaction proceeds through the ring-opening of oxirane rings of the epoxy component [1–5]. Etherification reaction depends on reaction temperature [6] and on basicity of the diamine [7]. Indeed, reactivity of both primary and secondary amines is generally different. Therefore kinetic constant ratio k_2/k_1 has an important influence on this reaction.

The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions that can be used for the curing and different properties that result of such resins [8,9]. This kind of chemistry is rather unique among the thermosetting resins. Furthermore, the knowledge of the chemistry involved allows the user to cure the resins over a wide range of temperatures and to

control the degree of crosslinking [10], which has a crucial influence on the physical properties. Depending on the chemical structure of hardener and on the curing conditions, it is possible to obtain different properties for the resins: chemical resistance, heat resistance, toughness, mechanical properties from extreme flexibility to high strength and hardness... Uncured, the resins have a wide range of physical forms, from low-viscosity liquids to solids. As a result of their versatility, these products have found use in protective paints and coatings, adhesives for most substrates, flooring, foams, potting and encapsulation compounds, low-pressure molding resins, and glass-reinforced plastics [8,9,11,12]. Different amines are used as hardeners for epoxy resins. The diamines the most used in industry are methylenedianiline (MDA) and diaminodiphenylsulfone (DDS) (Scheme 1a). However, DDS is toxic and DMA is a CMR (carcinogenic, mutagenic and reprotoxic) chemical. Therefore their use is very harmful and should be avoided.

Others amines are also used as epoxy resin hardeners, such as isophorone diamine and N-aminoethyl piperazine, but these amines remain toxic for human and environment (Scheme 1b and c).

New amines were designed in order to improve reactivity of curing reaction or final properties. Thus, Maity et al. designed new amines for bisphenol A diglycidyl ether (BADGE) curing [13]. Their work is based on the synthesis of amine functional aniline

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Ref	Name	Formula
a	Methylenedianiline, (R=CH ₂) Diaminodiphenylsulfone, (R=SO ₂)	
b	Isophorone diamine	
c	N-aminoethyl piperazine	
d	AFAFC (R=H) and AFCFC (R=Cl) (ref 13)	
e	Polymeric mercaptoamine hardeners with R1, R2: hydrogen or methyl. R4, R3: ethylene group R5: alkyl radical (ref 14)	
f	Polymeric amines with R1, R2, R3, R4: hydrogen, alkyl or aminoalkyl (ref 15)	

Scheme 1. Amine hardeners commercial or reported in literature.

formaldehyde condensates (AFAFC) and amine functional chloroaniline formaldehyde condensates (AFCFC) (Scheme 1d). AFAFC and AFCFC can be used as effective curing agents for BADGE. Curing kinetic study reveals the first order of these two curing reactions. The activation energy, rate constant and T_g value show that AFCFC formulations exhibit lower reactivity than AFAFC formulations. Moreover, concerning mechanical properties, AFAFC cured epoxy networks have higher rigidity than AFCFC cured epoxy matrix. The amine cured epoxy networks are thermally stable up to around 230–240 °C.

Generally, new amines designed as epoxy hardener are low molecular weight amines. Authors have also worked on polymeric amines. For example, Fischer et al. [14] have patented new polymeric mercaptoamine hardeners (Scheme 1e) in order to improve chemical resistance of synthesized resins. The cured resins produced therefrom exhibit by a high degree of flexibility and good viscoelastic properties combined with good hardness values.

New polymeric amines based on phenol were also patented by Mill as hardeners and/or accelerators in curing reactions (Scheme 1f) [15].

The polydienes functionalization was already studied extensively. First of all, studies were based on telechelic oligomers [16], then homopolymers [17], statistic copolymers [18] but also block copolymers [19]. Various chemical functionalizations were performed onto double bonds, such as glycidyl group formation [20]. But thiol-ene coupling has been the most used reaction, by thermal or photochemical initiation, since Serniuk et al. [21] in

1948, Pascault et al. [22] or Priola et al. [23] in 80s, our own team [16,24,25] in 90s and more recently Schlaad [17,19] in years 2000. Table 1 summarizes thiols used and applications targeted by these polymers.

These studies have demonstrated that even if vinyl double bonds (1,2 units) are the most reactive, chain double bonds (1,4 units) can also react totally. In case of polybutadienes, the thiol addition always occurs owing to anti-Markownikoff addition. This is different from the additions observed by Boileau on silicones bearing vinyl groups [30] where until 5% of reverse addition with pyridylthiol was identified by ¹H NMR analysis.

Lotti reported the thiol-ene coupling of amino acid derivatives of L-cysteine onto polybutadiene. Moreover, the grafted polymer obtained is a chiral polymer, starting from a non-chiral polymer, confirming that thiol-ene reaction is a viable approach to synthesize optically active polymers from a chiral molecule [31].

Furthermore, Brummelhuis et al. [26] worked on polydienes with high content in 1,2-double bonds and showed that different reactions occurred, based on the two neighboring double bond cyclization (Scheme 2).

This cyclization content depends on steric hindrance of thiol and tends to reduce functionality of polymer from 18% to 48%. Both MALDI TOF, NMR and elemental analysis techniques allowed determining this secondary reaction. This side reaction was already described by Ren et al. [27], who studied the addition of C₆F₁₃I onto 1,2-polybutadiene with boranes as initiators. This cyclization reaction has been evidenced from ¹³C NMR (CH₂I shifts) technique.

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