European Polymer Journal 108 (2018) 507–516

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Estrogenic activity research of a novel fluorinated bisphenol and preparation of an epoxy resin as alternative to bisphenol A epoxy resin

Hao Jiang[a], Lin Sun[b], Yurong Zhang[b], Fanting Meng[b], Wanxi Zhang[a,*], Chengji Zhao[b,*]

[a] College of Materials Science and Engineering, Jilin University, Renmin Street 5988#, Changchun 130022, PR China
[b] Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Qianjin Street 2699#, Changchun 130012, PR China

ARTICLE INFO

Keywords:
Estrogenic activity
Epoxy resin
Fluorinate
Alternative

ABSTRACT

A low estrogenic activity bisphenol 3,5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ) and its corresponding epoxy resin (BTFMEP) were synthesized via a multi-step procedure including the Meerwein arylation reaction, and followed by nucleophilic reaction. The chemical structures of two monomers were confirmed by their ^{1}H NMR spectra. After curing, the properties of this fluorinated epoxy resin were measured and compared with the commercial epoxy resin diglycidyl ether of bisphenol A (DGEBA). As the result, BTFMEP exhibited good dimensional stability, excellent hydrophobic and low dielectric properties. Furthermore, BTFMEP showed a high glass transition temperature of 142 °C and a lower coefficient thermal expansion (CTE = 55.03 ppm/°C) than that of DGEBA (CTE = 60.71 ppm/°C). Moreover, BTFMEP exhibited the contact angle of 99.6°, which satisfied the standard of hydrophobic material. In addition, BTFMEP showed lower dielectric properties than DGEBA, because the introduction of side groups with high fluorine content into the material improved the electronegativity of epoxy material and reduced the polarizability of molecules efficiently. Herein, we believe the novel epoxy resin (BTFMEP) has a wide application prospect as the alternative to DGEBA.

1. Introduction

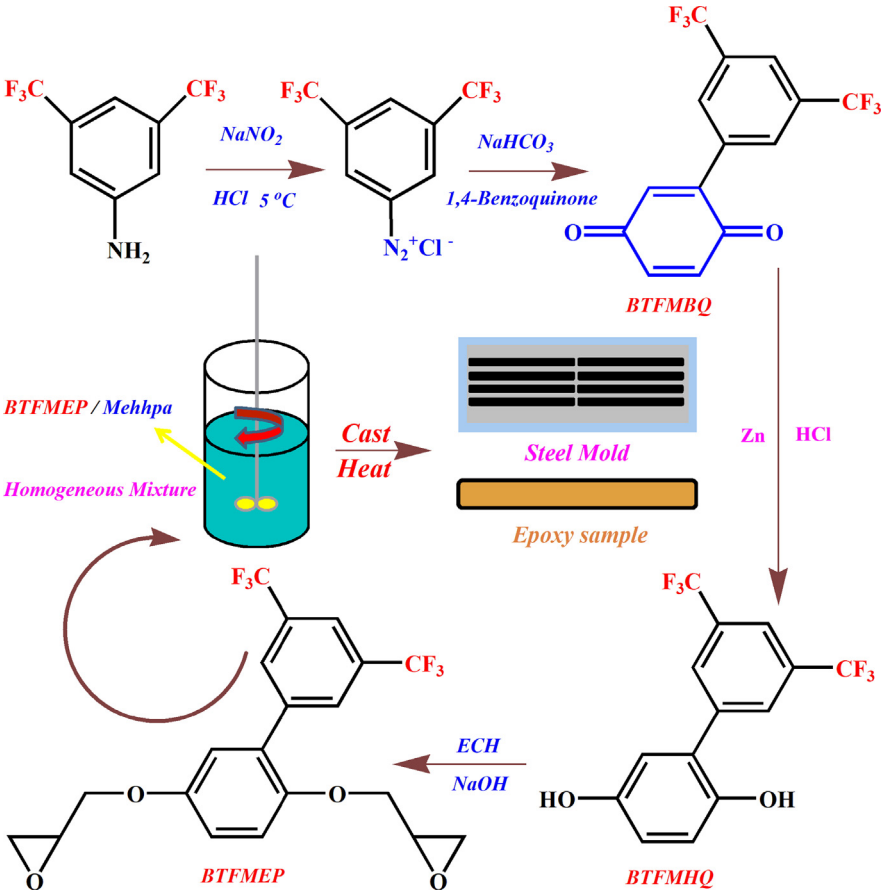
Epoxy resin, as one of the most important thermosetting materials, has been widely used in coating, adhesives, aerospace and electronics industry due to its outstanding adhesion, lower density, high strength, good durability, excellent chemical resistance [1–11]. As one of conventional epoxy resins, diglycidyl ether of bisphenol A (DGEBA) has been found in over 90% of thermosetting epoxy resins worldwide, in a market with a global production currently exceeding 2 million tons per year [12,13]. However, there are two main problems to restrict the application of DGEBA in human daily lives. The one problem is the properties of DGEBA could not satisfy the demand for advanced materials, such as good thermal stability, excellent hydrophobic, flame retardance and dielectric properties. The other one is bisphenol A (BPA) as the precursor of DGEBA possesses the similar structure to estrogens, which has been recognized as an endocrine disruptor. The estrogenic activity of BPA could increase the risk of reproductive disorder and cancer [14,15]. In addition, a small amount of BPA can still release from the epoxy resin with time due to its not completely stable chemical bonds. Therefore, the trace residual of BPA is usually detected in foods and liquids stored containers made from or lined with BPA-containing materials [16,17]. As the result, it is necessary to maintain a strict monitoring of the release of BPA from DGEBA, and the application of DGEBA has been restricted in many countries.

Over the past years, a lot of researchers have been focused on the preparation of novel epoxy resin to replace the DGEBA. As is well known, almost all of the epoxy resins are produced via the reaction of bisphenol monomer and epichlorohydrin. Thus, it is confirmed that the structure of bisphenol has a direct influence on the properties of epoxy resin. Numerous alternative BPA-free precursors have been reported and intended to promote the properties of epoxy resins and satisfied the demand of the advanced materials. For instance, Liu et al. [18] synthesized a novel bisphenol with $-CF_3$ side chains as the precursors of the fluorinate epoxy resin. The results showed the highest T_g of materials was 135 °C, 15 °C lower than DGEBA . Lin et al. [19] synthesized 2, 6-dimethyl phenol-dicyclopentadiene and aimed to obtain a low dielectric constant epoxy resin. The results exhibited that novel epoxy material possessed dielectric properties was 2.8 at 1 MHz, which was lower than DGEBA. Na et al. [20] synthesized a novel 2, 6-Naphthalenediol containing 4-fluorobenzoyl side chains and furtherly prepared its corresponding epoxy resin. The epoxy material showed a remarkably higher T_g = 170 °C than DGEBA. It also possessed a lower dielectric constant (2.97 at 1 MHz) than DGEBA .

There are many similar reports about designing the functional

* Corresponding authors.
E-mail addresses: zhangwx@jlu.edu.cn (W. Zhang), zhaochengji@jlu.edu.cn (C. Zhao).

https://doi.org/10.1016/j.eurpolymj.2018.09.020
Received 1 August 2018; Received in revised form 5 September 2018; Accepted 12 September 2018
Available online 14 September 2018
0014-3057/



Scheme 1. The synthetic route of BTFMHQ and BTFMEP.

structure of bisphenol as the precursor and then obtaining the high performance epoxy resins as the alternative to DGEBA [16,21,22]. Unfortunately, few researchers estimated the estrogenic activity of the functional bisphenol or examined the degree of toxicity between the novel bisphenol and BPA. It is necessary to consider whether there is a real significance of alternating DGEBA only in performance but ignore the potential harm of human health.

According the research and our previous work [23–25], we find that the introduction of fluorine groups into epoxy monomer could promote the properties of the epoxy resin thoroughly. Therefore, we synthesized a novel fluorinated bisphenol monomer 3, 5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ) as the precursor of the epoxy resin with a rigid 3,5-bis(trifluoromethyl) biphenyl structure via Meerwein arylation reaction (Scheme 1). Meanwhile, we focused on the estrogenic activity of BTFMHQ and compared with estrogen and commercial bisphenol (bisphenol A and bisphenol F) by a methylthiazolyldiphenyltet-razolium bromide (MTT) assay using MCF-7 (human breast adenocarcinoma cell line) as an estrogen receptor . Furthermore, we researched the relationship between the structure and the properties of the novel 3, 5-bis(trifluoromethyl)phenylhydroquinone epoxy resin (BTFMEP) obtained by introducing both stiff and fluorinated groups into the backbone. For this purpose, the synthesis and characterization of BTFMHQ and BTFMEP were firstly described and the properties of the cured BTFMEP materials, including thermal stability, glass transition temperature (T_g), coefficient thermal expansion (CTE) and dielectric properties, as well as contact angle were studied in detail and compared with the commercial DGEBA epoxy resin. We believed that this research would provide a way to obtain a series of high performance epoxy resins for alternating DGEBA thoroughly.

2. Experimental

2.1. Materials

Benzimidazole, 1,4-benzoquinone and sodium bicarbonate were purchased from Beijing Chemical Company (Beijing, China). Epichlorohydrin (ECH) was obtained from TCI Shanghai Development Co., Ltd. DGEBA (KDS-8128) was purchased from Kukdo Chemical (Kunshan) Co., Ltd. Methylhexahydrophthalic anhydride (Mehhpa), 3,5-bis(trifluoromethyl)aniline, bisphenol A (BPA) and bisphenol F (BPF) were obtained from Energy Chemical. Co. Sodium hydroxide (NaOH), sodium nitrite ($NaNO_2$) and tetrabutylammonium bromide were purchased from Sinophram Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis of monomer 3,5-bis(trifluoromethyl) benzoquinone (BTFMBQ)

3,5-Bis(trifluoromethyl)aniline(114.56 g, 0.5 mol) and 200 mL of deionized water were added into a 1000 mL three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer. The mixture was kept at the temperature below 5 °C with ice bath. Then, hydrochloric acid (168 mL, 11.8 M) was added into the solution dropwise. The sodium nitrite solution (124.5 g) with a concentration of 27.7% was added from a dropping funnel to a well stirred mixture into the flask. The mixture was stirred at 5 °C for 1 h and a transparent solution was obtained. The resulting solution was filtered and added dropwise into a mixture of 1,4-benzoquinone (54 g, 0.5 mol), sodium bicarbonate (126 g, 1.5 mol) and deionized water (200 mL). The reaction mixture was stirred at 8–10 °C for 3 h, and then kept at room