Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 43 (2007) 2422–2432
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Studies on the blends of cardanol-based epoxidized novolac resin and CTPB

Archana Devi, Deepak Srivastava *

Department of Plastic Technology, H.B. Technological Institute, Kanpur 208 002, Uttarpradesh, India

Received 15 January 2007; received in revised form 27 February 2007; accepted 2 March 2007
Available online 12 March 2007

Abstract

Cardanol-based novolac-type phenolic resins were synthesized with different mole ratios of cardanol-to-formaldehyde, viz., 1:0.6, 1:0.7, and 1:0.8. These novolac resins were epoxidized with molar excess of epichlorohydrin at 120 °C in basic medium. The epoxidized novolac resins were, separately, blended with different weight ratios of carboxyl-terminated polybutadiene liquid rubber ranging between 0–25 wt% with an interval of 5 wt%. All the blends were cured at 150 °C with 40 wt% polyamide. The formation of various products during the curing of blend samples has been studied by Fourier-transform infra-red spectroscopic analysis. The tensile strength and elongation-at-break of the cured samples increased up to 15 wt% in the blend and decreased thereafter. This blend sample was also found to be most thermally stable system. The blend morphology, studied by scanning electron microscopy analysis, was finally correlated with the structural and property changes in the blends.

Keywords: Cardanol-based epoxidized novolac resin; Carboxyl-terminated polybutadiene (CTPB) liquid rubber; Blends; Polyamide; Mechanical, thermal, chemical and morphological properties

---

1. Introduction

Cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production. Cardanol, a natural alkyl phenol from CNSL, a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial applications. By far the greatest amount of work on polymeric materials derived from CNSL or cardanol have been with their use in the manufacture or modification of phenolic resins [1–5]. The phenolic nature of the material makes it possible to react under a variety of conditions to form both base catalyzed resoles and acid catalyzed novolacs. The cardanol based novolac-type phenolic resins may further be modified by epoxidation with epichlorohydrin to duplicate the performance of such phenolic-type novolacs [1]. Having several outstanding characteristics, epoxy resins show low impact resistance in their cured state [6–11] which limits the applications

---

* Corresponding author.
E-mail address: deepak_sri92@rediffmail.com (D. Srivastava).

0014-3057/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2007.03.006

of epoxy resins. To alleviate this deficiency, epoxy resins are modified by the incorporation of reactive liquid rubber without significant loss in other properties, particularly mechanical properties [12,13]. In this way, carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) has been used by various workers [6–8] with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and epoxidized phenolic novolac resins. But, carboxyl-terminated polybutadiene (CTPB) is nowhere used for this purpose, particularly with cardanol based epoxy resins. Therefore, we have tried to produce the modified epoxy matrices, based on cardanol, by physical blending with CTPB and studied the effect of CTPB addition on thermal, mechanical and morphological changes in the blends.

2. Experimental

2.1. Materials

Cardanol (M/s Satya Cashsew Pvt. Ltd., Chennai), formaldehyde (40% solution), citric acid, sodium hydroxide, epichlorohydrin (All from M/s Thomas Baker Chemicals Ltd., Mumbai), polyamide (M/s Resinova Chemie Ltd., Kanpur) with amine value 240–400 mg KOH/g, and carboxyl-terminated polybutadiene (CTPB) (Hycar 2000 × 162) as gift sample from M/s Emerald Performance Materials, LLC, Hong Kong were used during the investigation.

2.2. Preparation of blend samples of cardanol-based epoxidized novolac resins and carboxyl-terminated polybutadiene (CTPB)

Cardanol-based novolac resins with mole ratios 1:0.6 (N_1), 1:0.7 (N_2), and 1:0.8 (N_3) of cardanol (C) to formaldehyde (F) were prepared using tricarboxylic acid, viz., citric acid, as catalyst by a method similar to that adopted in our previous article [14]. The initial pH of the reaction mixture was 6.0 which reduced to a value of 4.8 after 5 h of reaction at 120 °C. Free-formaldehyde content was checked after every 45 min to check the progress of the methylolation reaction [15]. These cardanol based novolac-type phenolic resins were epoxidized by a method similar to the method given in literature [21] with epichlorohydrin in basic medium for a period of 5 h at 120 °C. The resulting viscous product was stored for further analysis.

Table 1
Sample designation

S. No.	Blends of epoxidized novolacs (EN) with CTPB					
	0	5	10	15	20	25
1.	EN_{10}	EN_{15}	EN_{110}	EN_{115}	EN_{120}	EN_{125}
2.	EN_{20}	EN_{25}	EN_{210}	EN_{215}	EN_{220}	EN_{225}
3.	EN_{30}	EN_{35}	EN_{310}	EN_{315}	EN_{320}	EN_{325}

Cardanol-based novolac resin having mole ratios of cardanol-to-formaldehyde 1:0.6 (N_1), 1:0.7 (N_2), and 1:0.8 (N_3); E: respective epoxy.

The synthesized epoxy resins were mixed physically with varying concentration of CTPB ranging between 0–25 wt% with an interval of 5 wt%. All the samples were designated according to Table 1.

2.3. Characterization of blend samples

Fourier-transform infra-red (FTIR) spectra of uncured and cured samples were recorded on a Perkin–Elmer (Model 843) infra-red spectrophotometer, using KBr pellet, in the wave length range of 500–4000 cm^{-1}.

Dynamic scans were recorded with a Perkin–Elmer differential scanning calorimeter (DSC) (Model Dymaond DSC; Switzerland) at a heating rate of 10 °C / min in inert atmosphere up to a temperature of 170 °C to get the cure temperature. The curing of blend samples, without or with 40 wt% polyamide, were performed in an air oven (M/s Indian Equipment Corporation, Mumbai, India) at 150 °C.

The panels were prepared by applying the blend samples on sand-blasted steel sheet panels of sized 150 × 100 × 1.25 mm with a Bird Film Applicator (M/s Sheen Instruments Ltd., UK). These panels were sealed on three sides with molten paraffin wax. A dry film thickness of about 200 μm was maintained on all the panels. These films were then cured at 150 °C. The adhesion and flexibility of the cured films of the resin was tested by putting the prepared panels into one inch mandrel keeping the coated side downward. Then the two plates, connected to the mandrel, were readily bent. The bent portion of the panel was examined for any damage in the film. The impact resistance of the cured film samples was conducted by dropping a hemi-spherical shaped two-pound weight from 25 in. height over the panels. The tests were carried out with the uncoated side of the panel facing the