Polymer Testing 28 (2009) 296–300

Contents lists available at ScienceDirect

Polymer Testing

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

Material Behaviour

Effect of UV radiation on some polymeric networks based on vinyl ester resin and modified lignin

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ARTICLE INFO

Article history:
Received 11 November 2008
Accepted 5 January 2009

Keywords:
Vinyl ester resin
Lignin
Semi-IPNs
Photochemical stability

ABSTRACT

Some semi-interpenetrating polymer networks (semi-IPNs) based on vinyl ester resin (VER) and ammonium lignosulfonate (ALS) modified lignin were synthesized and characterized using Fourier transform-infrared (FT-IR) spectroscopy, optical microscopy (OM) and differential scanning calorimetry (DSC) techniques. VER was synthesized starting from an epoxy resin in reaction with acrylic acid. The cross-linking reaction was initiated by UV radiation. The synthesized networks showed good compatibility, due to some possible interactions between the functional groups from VER and ALS components (OH, especially). A slight effect of photostabilization of the VER was noticed, due to the ALS structures which were incorporated into the resin matrix.

1. Introduction

Vinyl ester resins (VERs), very well known thermoreactive polymers, are obtained from the reaction between α,β-unsaturated acids and epoxy resins. They are characterized by the presence of the double bonds as the end groups, which are derived from the acid structure. The existence of the double bonds in VER structures is a way to obtain cross-linked networks by initiation with free radicals. Due to their excellent mechanical properties, thermal stability and high corrosion resistance, VERs are the polymer matrices used for manufacturing high performance composites intended for marine, aerospace, transportation, building, construction and biomedical applications [1–6].

VERs and their compositions are widely used as protective films for various materials. Unfortunately, their use as surface coatings in outdoor applications is limited by the sensitivity to photo-oxidative degradation [7]. Blending of VERs with other synthetic and/or natural polymers provides a means of producing new materials which combine the useful properties of all the constituents [8,9]. Interpenetrating polymer networks (IPNs) are ideally compositions of two (or more) chemically distinct polymeric networks held together exclusively by their permanent mutual entanglements [10]. This definition has been generalized to include semi-IPNs, when only one of the components forms a network [11].

Lignin is an abundant amorphous natural polymer, readily available and relatively inexpensive. Because of its structure and macromolecular properties, lignin is an interesting material for use as a component in polymer blends [12], being used as stabilizer (antioxidant) for plastics and rubber, as well as in the formulation of dispersants, adhesives and surfactants [13,14]. Due to its phenolic structures, lignin is an excellent light absorber.

Ammonium lignosulfonate (ALS), a soluble derivate of lignin, is a by-product of the acid sulfate pulp-making process. Like lignin, ALS has very complex macromolecular structure, with negatively charged sulphonate, hydroxyl, phenolic and carbonyl groups.

Also, VERs are considered as corrosion resistant materials, but their use in outdoors is strongly limited by sensitivity to visible and ultraviolet domains. Lignin and its derivative (ALS) can be used as antioxidant agents in the compositions with VER resin. In the presence of UV radiation, VERs undergo severe degradation with changes in the

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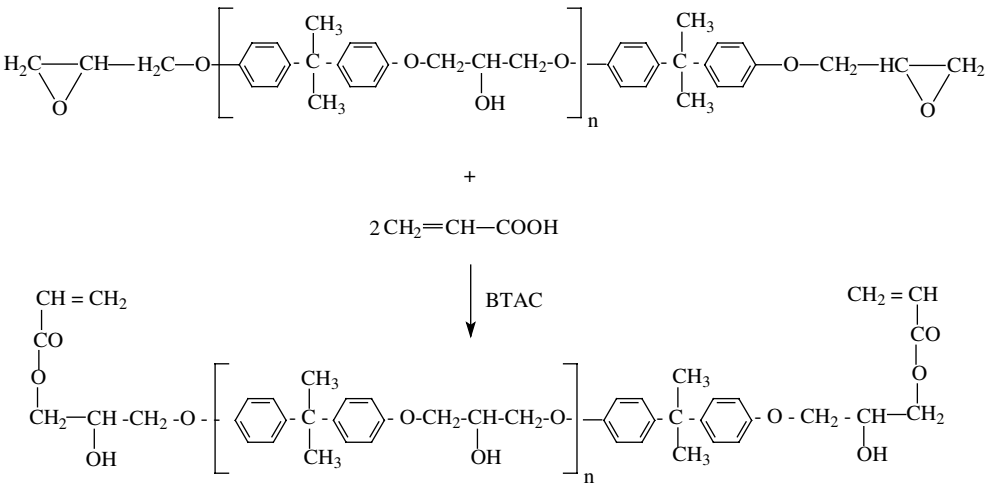
doi:10.1016/j.polymertesting.2009.01.004



Scheme 1. Synthesis of VER.

surface chemistry, morphology and structure [15]. The aim of this study was to investigate the behaviour of some semi-IPNs based on VER and ALS to UV radiation.

2. Experimental part

2.1. VER synthesis

The chemical reactions used for synthesis of VER are shown in Scheme 1.

The VER based on bisphenol A was obtained by the procedure described elsewhere [16]. The synthesis was carried out using commercial Ropoxid 501 resin (Policolor SA Bucharest, Romania) and acrylic acid, in the presence of benzyltributylammonium chloride (BTAC) as catalyst. Ropoxid 501 resin, with epoxy equivalent value 0.525 equiv. 100 g^{-1} and number-average molecular weight ($\overline{M_n}$) of 381 g mol^{-1}, was obtained by reaction of bisphenol A with epichlorohydrin (EPI). The synthesized VER, soluble in dimethylformamide (DMF), is characterized by $\overline{M_n}$ = 525 g mol^{-1} and melting point 53 °C.

2.2. ALS characterization

ALS is a by-product of the acid sulfate pulp making process, with characteristics as follows: amount of solid substances, between 45 and 48 wt%; OCH_3 groups, 8.5–9.2 wt%; COOH groups, 6–18 wt%; elemental analysis: C, 45.05%; H, 5.5%; N, 3.6%; S, 6.5%. UV-VIS spectra recorded for ALS water solutions evidence the presence of three absorption maxima, which are positioned at wavelengths lower than 300 nm (λ = 201.7 nm, A = 1.4472; λ = 262.85, A = 0.1746; λ = 280.85, A = 0.2159).

Table 1
VER and VER–ALS semi-IPNs.

Sample	VER content (%)	ALS content (%)
VER	100	–
VER–ALS-1	99	1
VER–ALS-2	97	3
VER–ALS-3	95	5
VER–ALS-4	93	7

2.3. VER–ALS semi-IPNs preparation

The VER–ALS semi-IPNs were prepared by a sequential procedure of mixing VER and ALS solutions in DMF. Bis(2,4,6-trimethylbenzoyl)phosphine oxide, in concentration of 0.25 wt% against the VER mass, was added to the mixture as photoinitiator. The VER–ALS composites were obtained by casting the mixtures onto glass slides and, subsequently, drying in air and then in vacuum at 110 °C for 3 h. The solvent was completely removed and the films were cross-linked in the presence of UV radiation.

2.4. Irradiation and analysis

The UV irradiation of the obtained VER–ALS semi-IPNs was carried out by means of a medium-pressure

Table 2
IR characteristic bands of VER–ALS-3 semi-IPN sample.

Wavenumber (cm^{-1})	Main assignment
3320	νOH associated
3036	νCH of the aromatic ring
2960/2929/2871	νCH; νCH_2; νCH_3
1889	γCH aromatic ring
1712	νC=O
1635	νC=C double bond
1591	νC=C aromatic ring
1488	δCH2 or/and δCH3
1467	Aromatic ring stretch
1382	δCH2 or/and δCH of the double bond
1293	νC–O
1224	νC–O–C
1160	νC–CO–O
1090	δCH aromatic ring
940	δCH double bond
812	Polyhydroxyether backbone
750	γCH aromatic ring