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Morphological study of some epoxy resin with DOPO–based oligophosphonate S-IPNs

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There were obtained three phosphorus containing flame retardant semi–interpenetrating polymer networks (S–IPNs) having as linear component an aromatic oligophosphonate and as cured matrix an epoxy resin crosslinked with three different curing agents: 4,4'–diaminodiphenylsulfone, 1,3–bis(aminomethyl)cyclohexane and octamethylene diamine. The morphologies of the initial films were investigated in detail by scanning electron microscopy.

Experimental

Materials:. 4,4'–diaminodiphenylsulfone (DDS), 1,3–bis(aminomethyl)cyclohexane (CYDM) and octamethylenediamine ($8CH_2DA$) were purchased from Aldrich and used as received. Epoxy resin based on bisphenol A diglycidyl ether (EP), with an epoxy equivalent weight (EEW) of 0.53 equiv. per 100 g (Mn~377 g mol^{-1}; viscosity and density of 15 Pa·s and 1160 kg m^{-3} at 25 °C) was purchased from Sigma Aldrich. The S–IPNs were obtained by mixing EP with different amounts of OP under heating and stirring to reach a molecular level of mixing, followed by the curing in the presence of a suitable hardener (Table 1). DDS, CYDM and $8CH_2DA$ where used as hardeners (Scheme 1). The epoxy to amine ratio was set at 2:1 based on the assumption that each hydrogen atom on the nitrogen atoms in the curing agents reacts with an epoxide ring. The quantity of OP was calculated in order to obtain final product with 2 wt% of phosphorus. The various formulations of the pre–curing mixtures are listed in Table 1. The required quantities of EP were mixed with OP under continuous stirring at 130 °C until complete dissolution was achieved followed by the addition of a hardener and cooling of the mixture to 80 °C. The resulting mixtures were stirred homogeneously, and then poured into a Teflon coated mould to obtain the samples in the shape of plates. The formulation based on DDS was cured at 150 °C for 2 h and 180 °C for 3 h. The rest of the samples were cured at 70 °C for 4 h, 130 °C for 2 h and 150 °C for 1 h. Finally, the thermosets were cooled slowly to room temperature to prevent cracking.

Scheme 1. Obtaining of the cured matrices and S–IPNs.

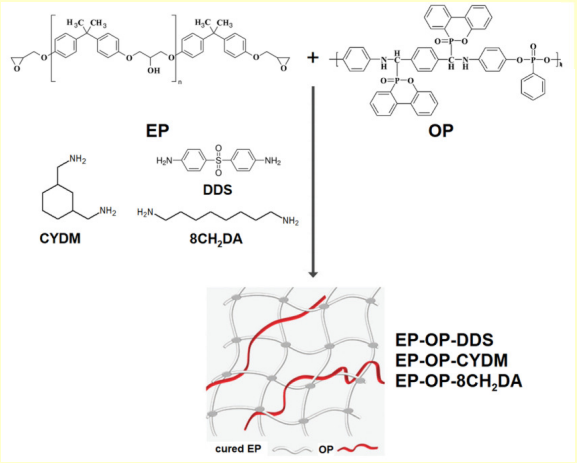

Table 1. Composition of the samples.

Sample	Hardener	Hardener (g)	Oligophosphonate(OP) (g)	Epoxy resin (EP) (g)
EP–DDS	DDS	7.45	-	22.55
EP–OP–DDS	DDS	5.99	5.61	18.36
EP–CYDM	CYDM	4.66	-	25.34
EP–OP–CYDM	CYDM	3.79	5.56	20.63
EP–$8CH_2DA$	$8CH_2DA$	4.79	-	25.23
EP–OP–$8CH_2DA$	$8CH_2DA$	3.87	5.65	20.50

Equipment

Morphological study

The morphology of the initial samples and char residue were measured by a scanning electron microscope (SEM) SEM Quanta 200 (USA), operating at 30 kV with secondary and backscattering electrons and in high vacuum mode. The SEM studies were performed on uncoated samples fixed on aluminum supports.

Results and discussions

Phase morphology

Scanning electron microscopy (SEM) is an important analytical tool both in detecting phase separation phenomena and assessing morphology–toughness correlations in multicomponent polymer systems [1]. Figure 1 shows the SEM micrographs of the samples fracture surfaces obtained after cooling in liquid nitrogen.

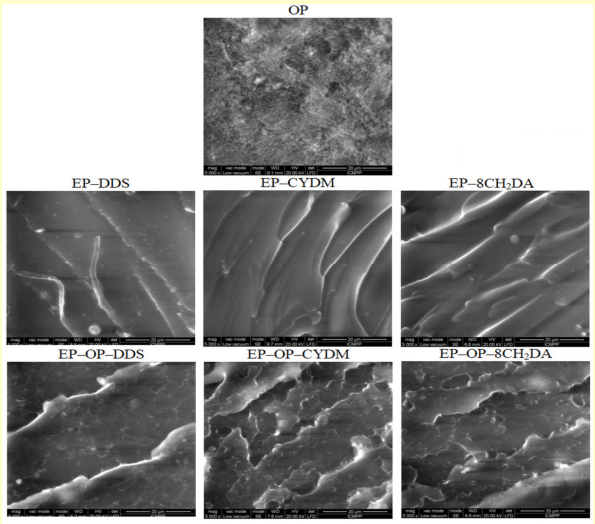

Figure 1. SEM micrographs of the samples (5000x magnification).

The cured networks show smooth glass like cracks with parallel fracture lines. This is due to the higher rigidity generated by the curing agents, hence an increased crosslinking degree and brittle character [2]. The S–IPNs present the same relatively uniform fracture lines, however showing more ridges and torsions along the cracks, owed to ductile breaking [3]. The micro fractures are spread within the whole S–IPNs sample masses, the minimal fracture area occurring through crack propagation. The uniform fractures were generated during thermal treatment by OP agglomerates, behaving as stress concentration centres [4] and indicating a good homogeneous dispersion of the OP into the cured epoxy matrices [5]. Moreover, the reactive epoxide rings of the resin are crosslinked to generate larger chains, indicating that the curing agents are well distributed within the whole matrix [2].

References

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Conclusions:

Flame retardant S–IPNs were obtained based on an aromatic oligophosphonate and epoxy resin cured with three different hardeners: 4,4'–diaminodiphenylsulfone, 1,3–bis(aminomethyl) cyclohexane and octa methylenediamine.

SEM technique showed a good miscibility of the oligophoshonate in the cured epoxy resin. Scanning electron microscope demonstrated that S–IPNs were highly compact networks.

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