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Thermal Characteristics of Oxazolidone Modified Epoxy Anhydride Blends

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Abstract

Oxazolidone modified epoxy resin blends can be prepared with dianhydrides to form thermosets with higher thermal stability. Curing the oxazolidone modified resin is an addition reaction, which offers better thermal properties and improved chemical resistance. Chemical reactions that take place during cure, determine resin morphology and properties of cured thermosets. Such epoxy resin systems are used for various reinforcements because they offer significant advantage over metals in area of weight saving and corrosion resistance and for use in glass fabric reinforced flame retardants.

Keywords: modified epoxy resin, oxazolidone, diianhydrides, epoxy anhydride blends, thermogravimetric analysis, thermal stability

1. Introduction

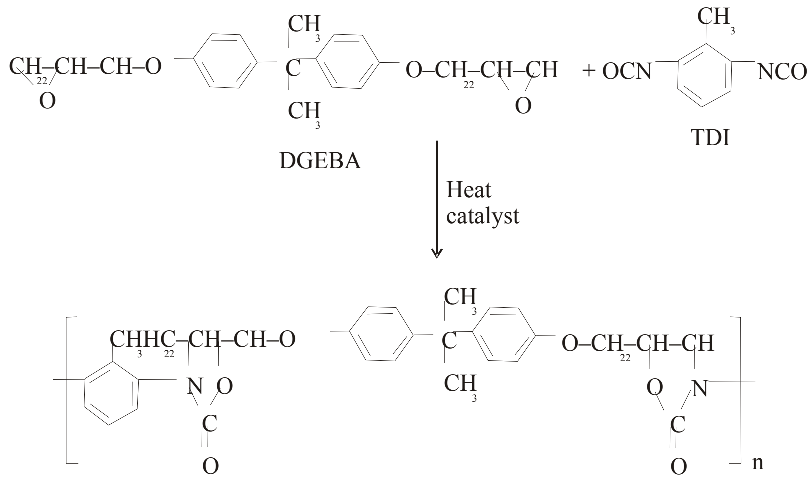
Oxazolidones are synthesized by polyaddition reaction between di isocyanates and di epoxies, forming linear thermoplastic polymers (Hong & Wu, 2000). In this work, Diglycidal Ether of Bisphenol A (DGEBA) was modified using Tolylene 2,6 Diisocyanate (TDI) to give oxazolidone modified epoxy. Oxazolidone incorporated linear epoxy resins were cured with Benzophenone Tetracarboxylic Dianhydride (BTDA) to obtain high temperature resistant thermosets (Santoshi & Shinichi, 2001). The crosslinking of these linear thermoplastic oxazolidones with dianhydrides results in the formation of insoluble and infusible cross linked thermosets which possess better thermal stability (Jamshldi & Talemi, 2006; Javni, Guo, & Petrovic, 2003; Chan & Yi, 2001).

Anhydrides today are a major class of curing agents for epoxies because epoxy-anhydride systems exhibit low viscosity and long pot life, low exothermic heats of reaction and little shrinkage when cured at elevated temperatures, hence anhydride curing systems are used for curing epoxies to obtain higher thermal stability.

The properties of oxazolidone modified epoxies can be tailored by the choice of suitable amount of curing agents, as a result, the ratio of the epoxy to the anhydride becomes an important factor in deciding the final material performance. Temperature is a major influence on cure conditions.

2. Materials & Methods

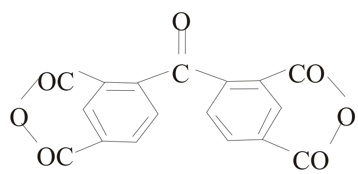
Cycloaddition of diisocyanate to diepoxies results in the formation of linear oxazolidone modified epoxy resin (Petrovic & Javni, 2002; Callie, Pascault, & Tighzert, 1990; Merline, Reghunadhan Nair, Gouri, Sadhana, & Ninan, 2007; Frisch, Sendijarevic, & Sendijarevic, 1987; Dušek, 1986).



TDI modified oxazolidone

This reaction was conducted in solution, using N,N Dimethyl Formamide (DMF) as solvent and the product was characterized by Fourier Transform Infra Red Spectroscopy (FTIR) Figure 1. FTIR of the synthesized polymer shows characteristic peak for oxazolidone at 1754 cms^{-1} whereas the peak for DGEBA at 915 cms^{-1} is almost nonexistent, indicating that all the epoxy groups have been consumed. Peak for isocyanate at 2270 cms^{-1} is also absent, indicating that all the isocyanate has reacted with epoxy to produce oxazolidones.

1) Benzophenone Tetracarboxylic Di anhydride (BTDA)



BTDA

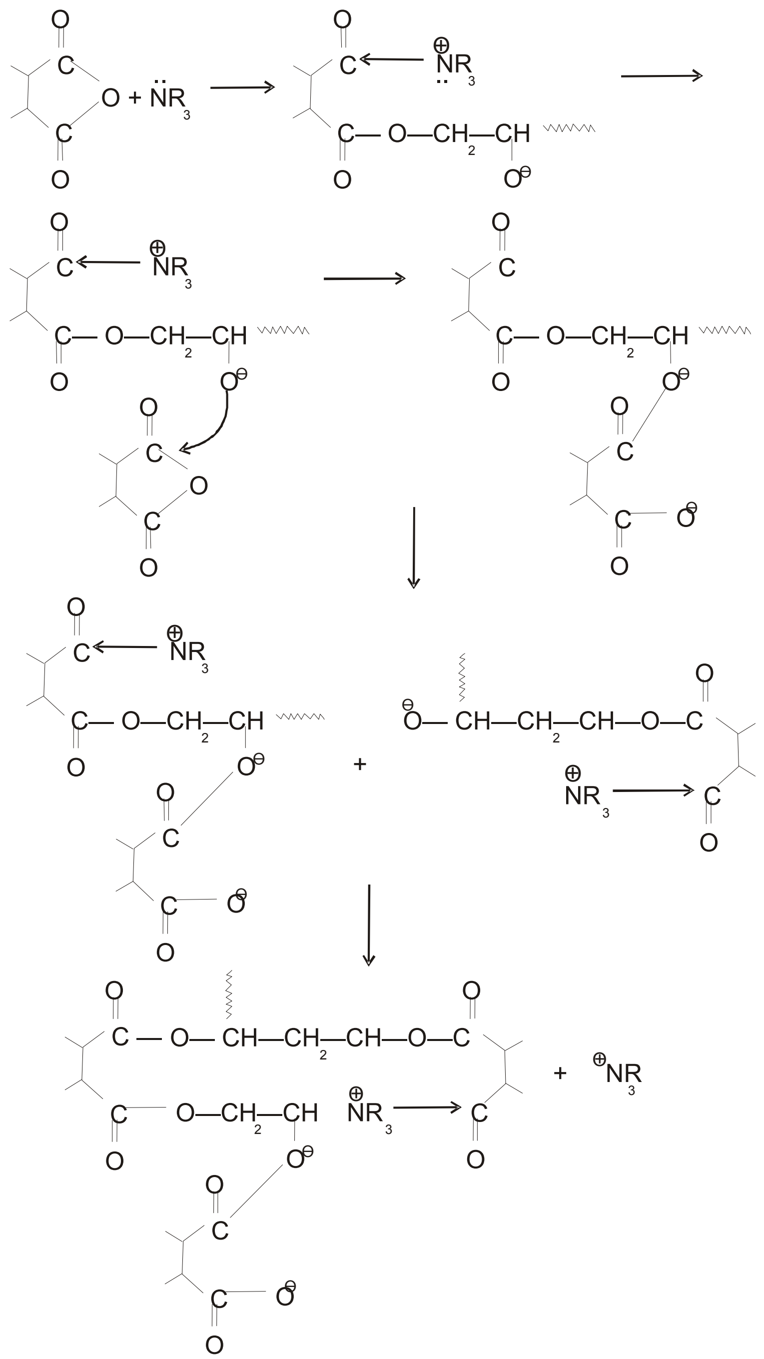
2.1 Preparation of Anhydride Blends Using Benzophenonetetracarboxylic Dianhydride (BTDA)

Benzophenone tetracarboxylic dianhydride (BTDA) is a multifunctional anhydride for use in high temperature applications (Hong & Wu, 2000). Diglycidal ether of Bisphenol A (DGEBA) was heated to 80 ℃ and a weighed quantity of oxazolidone was added with continuous stirring and temperature was increased to 100 ℃ till the oxazolidone dispersed completely in the epoxy. The anhydride was added gradually, along with 1 phr of the amine – Benzyl dimethyl amine (BDMA) as a catalyst. After stirring to get an evenly dispersed solution, the blends were poured into preheated and pretreated moulds. Curing was carried out at 130 ℃ for 4 hours. Post curing was carried out at 200 ℃for 6 hours (Cole, 1991; Jan-Eric et al., 2007; Steven, Guy Van, Vuchelen, & Bruno, 2005; Wei & Delmar, 2004; Woo, & Seferis, 2003; Min, Stachurski, Hodgkin, & Heath, 1993; Min, Stachurski, Hodgkin, & Heath, 1993; Min, Stachurski, Hodgkin, & Heath, 1993).

Theoretically, a cross-linked thermoset polymer structure is obtained when equimolar quantities of resin and hardener are combined (Poisson, Lachenal, & Sautereau, 1996). However, in practical applications, epoxy formulations are optimized for desired performance rather than to complete stoichiometric cures. In this work, blends were prepared using 1 %, 5 %, 10 %, 15 %, 25 %, and 50 % of oxazolidone and the cured sample was then evaluated for thermal stability using Thermogravimetric Analysis (TGA) (Miren Blanco, Angeles, Carmen, Riccardi, & Iñaki Mondragon, 2005; Min, Stachurski, & Hodgkin, 1993; Poisson et al., 1996).

3. Results and Discussions

In epoxy-anhydride curing reaction, less than stoichiometric ratios of curing agents are used because of significant homopolymerization. The epoxy terminated oxazolidone is converted by means of a crosslinking reaction into a three dimensional hard thermoset (Younes, Wartewig, Lellinger, Strehmel, & Strehmel, 1994).



The ring opening mechanism governs the reaction between the epoxy and the anhydride (Unnikrishnan, Thachil, & Eby Thomas, 2006). The mechanism of anhydride cure is complex and both etherification and esterification can occur. The anhydride must first be converted into its monoacid/monoester for the reaction to occur. Secondary alcohols from the epoxy backbone react with anhydride to give a half ester which in turn reacts with an epoxy group to give the diester. Tertiary amines are used in small amounts to accelerate the curing (Pham & Marks, 2004). During cure, the lone pair of electrons on the nitrogen atom of amine, help in the ring opening of the anhydride group to form a complex. This in turn reacts with the epoxy group to form an ether linkage.

3.1 Thermogravimetric Analysis (TGA) of the Oxazolidone Anhydride Blends

Thermal stability of oxazolidone modified epoxy with stoichiometric amounts of dianhydrides was determined by recording TG/DTG traces in N_2 atmosphere at a constant heating rate of 10°/min. TGA studies were carried out in HIResTGA-2950 Thermogravimetric Analyser and weight loss Vs temperature plots were obtained and are shown in Figure 2-7.

Table 1, shows the TGA analysis data of anhydride epoxy blends, it is evident that the onset, midpoint and T_{end} are of the same order for almost all the blends. It was observed that the char yield progressively increases as the percentage of oxazolidone increased in the blend because of the presence of increased heterocyclic groups in the oxazolidone blends. However, the presence of 50 % oxazolidone in the blend shows a decrease in the char yield, probably because of the splitting of the oxazolidone and anhydride in the blend.

Data obtained during the thermogravimetric studies on various blends was carried out at constant heating rate of 10°/min.

The TGA thermograms show a single sharp degradation for all the oxazolidone-anhydride blends, irrespective of the amount percent of oxazolidone used, indicating compatibility of the system. The above thermograms show a single sharp degradation peak in the region 380-386 ℃ which is also indicative of the homogeneity in the networks formed during cure.

4. Conclusions

Synthesized linear oxazolidone modified epoxy can be successfully cured using anhydride-BTDA. Anhydride-cured epoxies can be of much use in high temperature resistant polymers and they also exhibit better aqueous acid resistance. Hence, oxazolidone epoxy-anhydride blends can be termed as the polymer of the future in the field of high temperature resistant polymers because in the modern world of plastics, polymers having higher thermal resistance find a very important and significant place.

TGA studies showed that 15 % of the oxazolidone in the blend was sufficient to give maximum increase in thermal stability and that 0.05 mole of catalyst (BDMA) was sufficient.

Thermal studies also prove that thermal stability of the blends containing 15 % of oxazolidone in the blend was better as compared to other ratios and showed minimum rate of degradation in the system. Hence in our study, 15 % of the oxazolidone modified epoxy is optimum for maximum thermal stability of the thermoset.

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Table 1. TGA analysis of BTDA cured oxazolidone modified resins

Exp. No.	Composition Epoxy/Oxz.	Onset Temp. ℃	DTG Maxima	T_{end} ℃	Char. yield at 600 ℃
1.	Neat Resin	384.30	386.74	390.00	30 %
2.	5 %	379.77	383.12	396.62	32 %
3.	10 %	382.69	385.49	390.00	34 %
4.	15 %	370.61	379.85	390.93	43.2 %
5.	25 %	370.11	383.10	400.10	44.10 %
6.	50 %	373.21	381.64	395.73	43.09 %

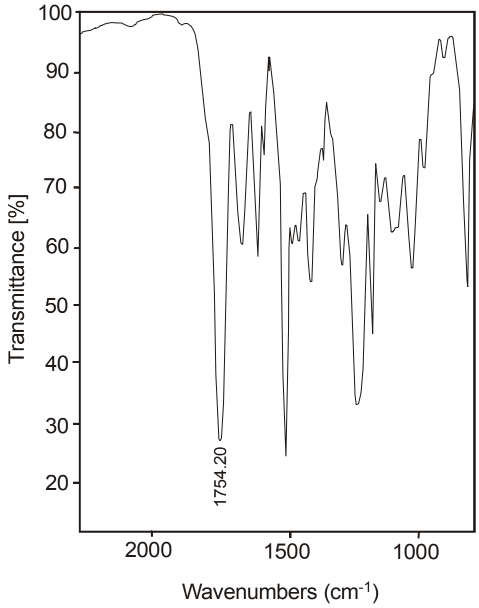

Figure 1. FTIR of the synthesized oxazolidone modified epoxy resin

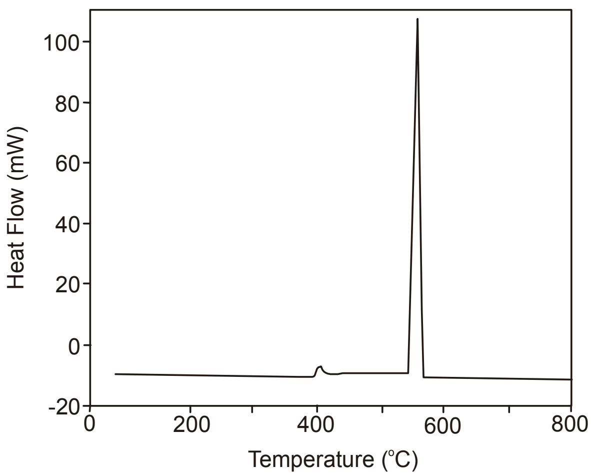

Figure 2. TGA of 1 % oxazolidone in the oxazolidone-anhydride blend

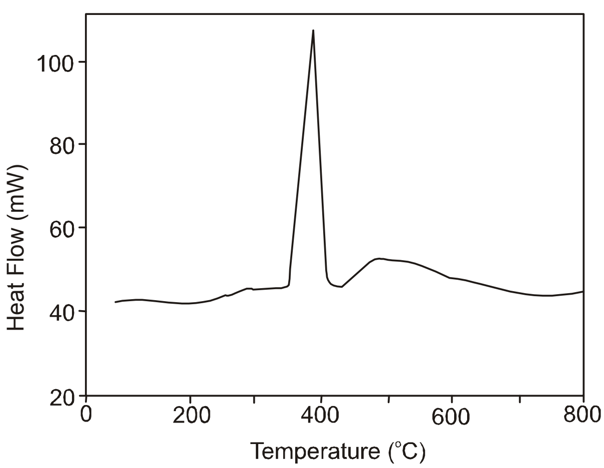

Figure 3. TGA of 5 % oxazolidone in the oxazolidone-anhydride blend

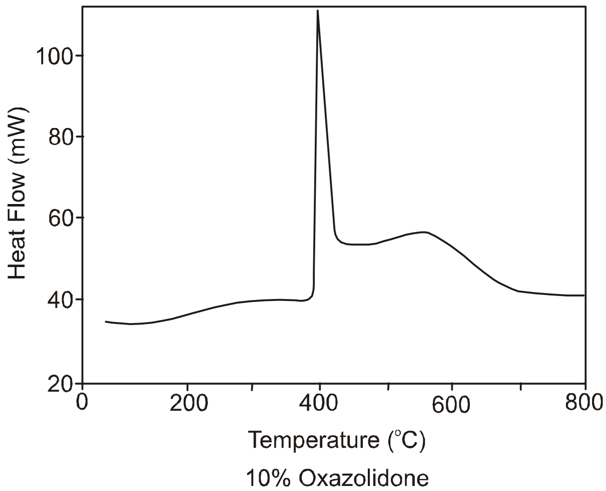

Figure 4. TGA of 10 % oxazolidone in the oxazolidone-anhydride blend

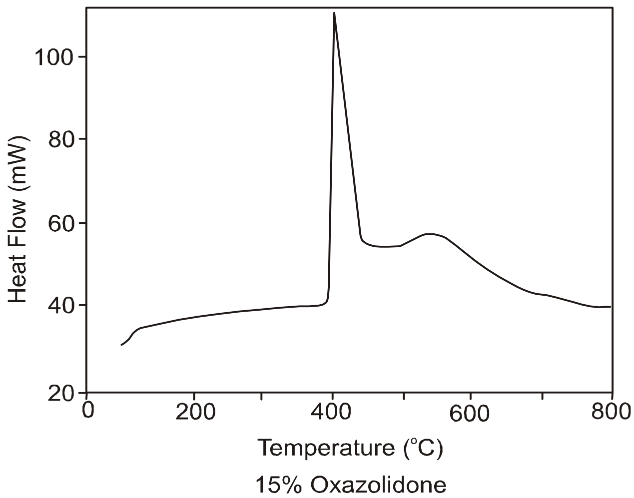

Figure 5. TGA of 15 % oxazolidone in the oxazolidone-anhydride blend

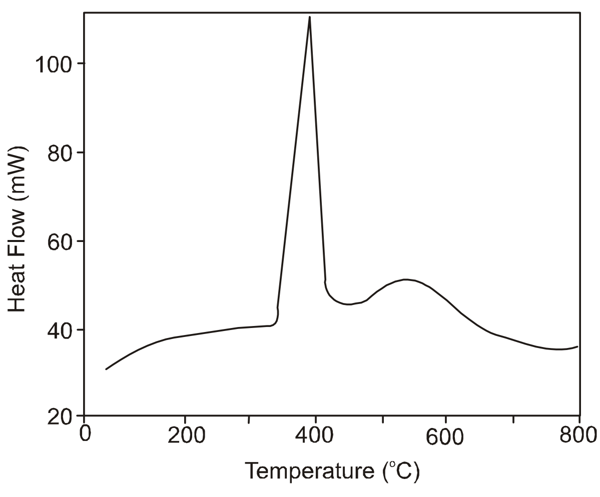

Figure 6. TGA of 25 % oxazolidone in the oxazolidone-anhydride blend

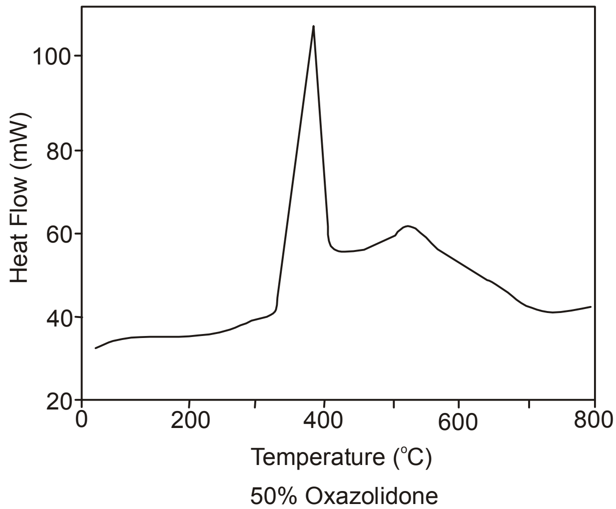

Figure 7. TGA of 50 % oxazolidone in the oxazolidone-anhydride blend