

Processability of one Tri-A Polyimide for Resin Transfer Molding

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Abstract

This paper explored the processability of one Tri-A polyimide for resin transfer molding. Its melt viscosity was lower than 1Pa.sec over 15min and 10Pa.sec for two hours at 280°C. Cure reaction was fast only above 350°C, but cure should be more than 30min at 370°C. The cured resin exhibited T_g above 330°C, the weight loss is below 2.5% up to 500°C in argon gas. The combination of processability and heat resistance showed great potential for fabricating large and complex high quality aerospace parts.

Introduction

High temperature-stable, high-performance resins are potential for aerospace composite structures in high speed aircraft and reusable launch vehicles needed for serious service environment throughout the operational lifetime. Most of resins are fit for fabricating composites by traditional prepreg containing solvent and conventional autoclaves. The relatively higher voidage reduces properties of resultant composite. More attention was paid on such low-cost and flexible fabrications as resin transfer molding (RTM) and resin infusion (RI) for large and complex structures with good surface quality, better parts integration and excellent dimensional stability. Therefore, the fitful resins were widely explored, among which polyimide is the focus with unique property combinations.

Recent years, developments in the area of phenylethynyl-containing imide oligomer of polyimides have been used to produce tough, ductile and solvent resistant thermosets. The molecular weight was lowered by offsetting the molar ratio of the amine monomer versus dianhydride and by terminating the resin with a monofunctional monomer. Furthermore, the asymmetric monomer structure was found to introduce the chain flexibility for low melt viscosity and the rigidity for high glass transition temperature (T_g) of the cured [1]. The typical resins are referred as PETI-298 and PETI-330 as well as PETI-375 in NASA, and Tri-A PI (amorphous, asymmetric and addition-type polyimide) by Ube Industries Ltd [2-4]. Incorporating high stoichiometric offset in molecular morphology resulted in wide molecular weight distribution in favoring of lowering melt viscosity. These oligomers have wide processing window between T_g and T_{cure} without volatiles evolved during curing. This paper was aimed to explore the processability of one Tri-A imide oligomer for thermosetting composite by RTM.

Experimental

The used polyimide is one one version for resin transfer molding (RTM) provided by Ube Industries,Ltd. The isothermal and non-isothermal DSC were performed on one SII Exstar 6000 calorimeter, Seiko Instruments Inc. The sample was contained in aluminum pan with one empty pan for reference. The cured sample was investigated in argon atmosphere in SII Exstar 6000 thermo gravimetric analyzer (TGA), Seiko Instruments Inc. The compression molding powder or films was tested in Fourier transform infrared spectrometer FTIR-610, JASCO Co. Its dynamic rheological properties were tested by one AR2000 Advanced Rheometer with parallel-plate fixture, TA instruments Inc. The compacted sample disks were sheared under 1.5mm thickness between two 25mm parallel discs with frequency 1.0Hz and 5% strain

Results

The non-isothermal DSC traces of the Oligomer and the cured polymer are shown in Fig.1(a). The glass transition (T_g) of the oligomer was 145°C . The cure exotherm moved to higher temperature with heating rate. The principal cure occurred after 290°C . No doubt, the cure rate should be lower or cure time should be longer for higher cure degree. Fig.1(b) shows that cure reaction was quickened with temperature and reached ca. 80% at 415°C in cure at $15^\circ\text{C}/\text{min}$. The cure degree rises linearly to 2% before 290°C . Thus, this work lies focus on the reaction above 290°C . T_g of the cured polyimide was ca. 330°C when cured at $5^\circ\text{C}/\text{min}$ while it was 338°C at $1^\circ\text{C}/\text{min}$. In slower heat cure, the cure crosslink network became denser and T_g of the cured polyimide arose.

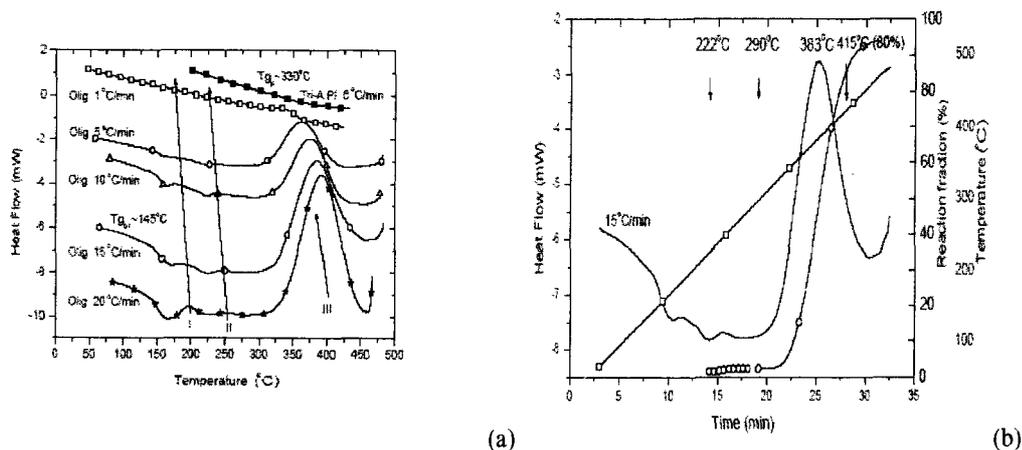


Fig.1. DSC curves of oligomer and the cured polyimide and the reaction fraction in cure at $15^\circ\text{C}/\text{min}$

Further, the isothermal cure was conducted at 356°C - 389°C (Fig.2). The peak cure time was ca. 40min in cure at 350°C , which seemed to be accepted in industry. The cure was quickened with temperature. The cure peak time decreased to 30min for isothermal cure at 370°C and 15min at 389°C .

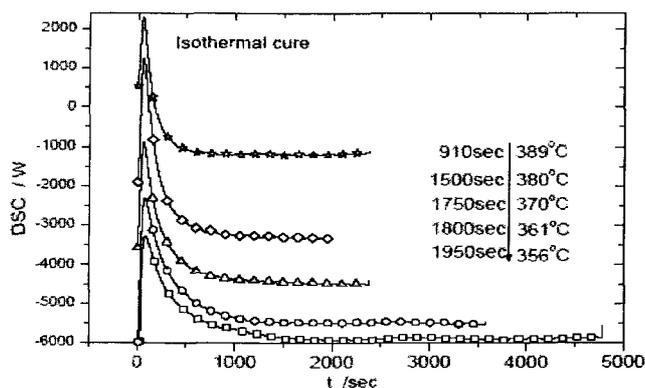


Fig.2. Isothermal cure traces of the oligomer

Fig.6 shows the FTIR spectra of the oligomer and the polyimide cured to different degree. The absorbance at 2210cm^{-1} is that of phenylethynyl $\text{C}\equiv\text{C}$, 1780cm^{-1} of imide carbonyls $\text{C}=\text{O}$. The major reaction progress corresponded to the change in peak area of $\text{C}\equiv\text{C}$ absorbance. Obvious crosslinking and termination did neither occur ever up to 375°C if heated fast, nor did at 280°C for 2 hours. However, termination almost completed after 1hour at 370°C .

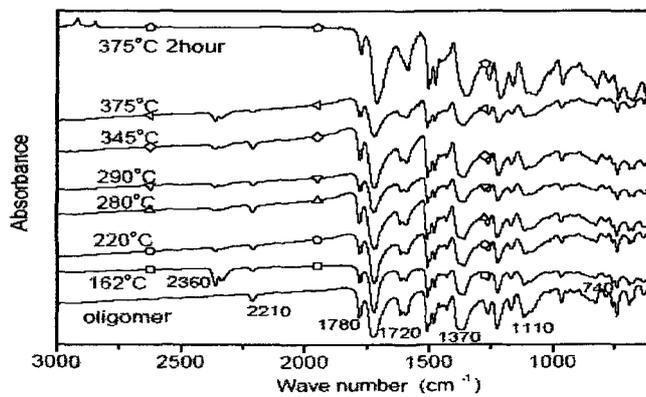


Fig. 3. FTIR spectra of oligomer and cured polymers.

The oligomer melt viscosity was shown in Fig.3. It can be seen that the viscosity dropped quickly until reaching the minimum viscosity. After that, the viscosity increased abruptly for quick cure under continuous heating. If the viscosity in high temperature RTM was permitted up to 10Pa.sec, then the oligomer possessed wide processing window. However, both the minimum viscosity and the needed time decreased with heat rate. The viscosity was reduced below 1Pa.sec only when heat rate was above 3°C/min. i.e., the short term before melting is necessary so that the initial cure degree was sufficiently low for subsequent flow.

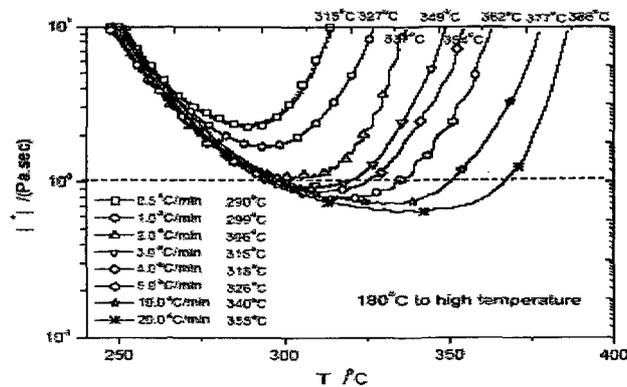


Fig. 4. Melt viscosity versus temperature

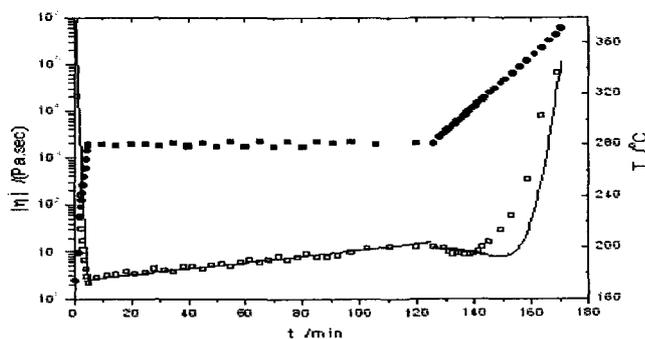


Fig.5. One typical cure viscosity of the Oligomer

To test if the viscosity could remain enough time (>2 hours) for complex RTM operations, one typical cure rheological behavior was measured: temperature ramp from 180°C to 280°C at 4°C/min; time sweep at 280 °C for 2h; temperature ramp from 280°C to 370°C at 4°C/min, and time sweep at 370 °C. The result was shown in Fig. 5. It is seen that the viscosity arose linearly within two hours but below 10Pa.sec, and could dropped a little when increased temperature and then abruptly increased when continuous heating for higher cure degree. It is also noticed that the viscosity could be further reduced by shortening the intermediate isothermal stay and by increasing temperature a little in the later injection of injector or in resin-permeating fabric preform in mold. So, processing time is completely enough for RTM.

For pure resin, its cured polyimide exhibited the excellent thermal stability as seen from Fig.6. The weight loss is below 2.5% for all conditions up to 500°C. The weight loss is only 5% at 550°C. The final remaining weight could be above 70% depending on the cure conditions. The cure degree was higher for longer cure. The cure did not completely finish even after one hour at 370°C in one typical molding cycle, so the cured resin or composite could appropriate toughness.

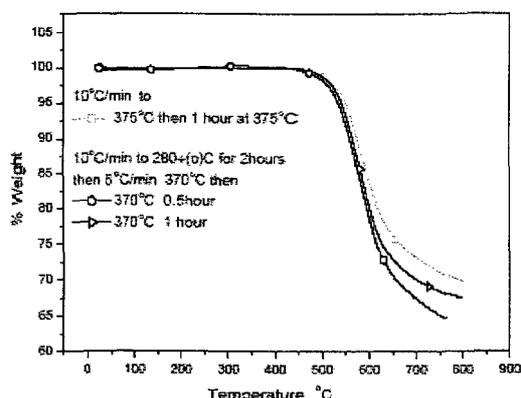


Fig. 6. Thermo-gravimetric curves of the cured polyimide from different cure conditions

Conclusion

In general, the phenylethynyl-containing imide oligomer was of the stable and low viscosity for RTM to fabricate composites. Robust process window was wide, the melt viscosity was lower than 1Pa.sec over 15min and 10Pa.sec for two hours at 280°C. The cure reaction was fast only above 350°C, but the cure time should be more than 30min at 370°C to obtain higher mechanical properties. Tg of the cured resin was above to 330°C, the weight loss is below 2.5% up to 500°C in argon gas.

Acknowledgement

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References

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