Optimization of Thermal and Mechanical Properties of Unsaturated Polyester Resin as a Binder in Polymer Concrete for Manufacturing Precision Tool Machine Bases

Haddad H* and Sbarski I
Swinburne University of Technology, Australia

Abstract
This study investigates the effect of unsaturated polyester resin chemical composition on the coefficient of thermal expansion, damping properties, flexural strength, tensile strength and hardness. The resin is used as binder in polymer concrete for manufacturing the bases of precision tool machines in previous work published by the authors. Resins of various ratios of styrene-ARAPOL and methyl methacrylate (MMA)-ARAPOL were made and their curing kinetics was studied using viscosity measurements and exothermic reaction temperature profiles. The resins were studied using dynamic mechanical analysis and in-house thermal expansion measuring devices. It was found that ARAPOL–MMA (60:40) has the highest damping factor of 5.46%, and the thermal expansion coefficient of 7.98 × 10^-5/°C. This composition also has the optimum flexural and tensile strengths at 128 MPa and 58.6 MPa.

Keywords: Polymer concrete; Resin binder; Thermosetting polymer; Precision tool machine bases; Coefficient of thermal expansion; Damping factor

Introduction
Unsaturated polyester resins (UPEs) are thermosetting materials used as the binding matrix in polymer concretes (PCs) and other composite materials [1,2]. UPEs cure via the radical copolymerization of a monomer and the low molecular weight unsaturated polyester liquid when an initiator and an accelerator are added at ambient conditions [3-6]. UPE curing is an exothermic reaction accompanied with viscosity growth due to molecular weight increase to form a three-dimensional cross-linked network [7-11]. The mechanical properties of the resin and its adhesion to aggregates in PC are the main sources of the advantageous mechanical properties of PC for its application in precision tool machine bases [12,13], where PCs (polymer concretes) are used due to their high damping properties and their ability to absorb unwanted system vibrations [14].

Several strategies to improve UPE properties have been reported. When a rubber phase is introduced into a polymeric matrix, the mobility of the rubber molecules enhances the dissipation of vibration energy in the resin [15-17]. Synthetic and natural rubbers and elastomers in solid and liquid forms have been applied to improve UPE damping properties. Rubbers such as natural rubber latex (NRL) [16,18] and styrene-buta diene rubber (SBR) latex [19,20], and functional elastomers such as hydroxyl-terminated polybutadiene, deoxidized natural rubber, hydroxyl terminated natural rubber, and maleated nitrile rubber [15] have been used to enhance UPE damping properties. Also Polyoxypropylenetriamine (POPTA) has also been employed, combined with temperature during curing, to optimize the damping factor and mechanical properties of UPE [21]. In addition polyhedral oligomeric silsesquioxanes (EA-POSS) has been used to improve the damping behaviour and other mechanical properties of UPE [4,22]. These modifications increase the toughness and tensile strength of UPE resin. The dissimilarity of the rubbery and resin phases results in miscibility problems which researchers have attempted to solve using copolymerizing terminal groups [23] and dispersants and solvents [16].

Copolymers of UPE and polyurethanes [24,25], polyureas, polysiloxanes, polyimides or polyglycols also produce resins with improved damping properties [26]. Butadiene as a vinyl monomer has also been employed to modify UPE resin’s mechanical properties [27].

Curing and processing conditions also have significant effects on UPE’s mechanical properties [28]. Research literature suggests that varying the resin curing rate via curing temperature [29] or initiation mechanism or post-curing heat treatment of the resin affect UPE resin damping properties. Li et al. [30] studied the effect of high temperature curing and post-curing heat treatment on the microheterogeneity of UPE and its effect on its mechanical properties. Kim et al. [31] used UV initiation curing of UPE and found that the type and the amount of photo initiator affect the level of improvement in mechanical properties.

*Corresponding author: Header Haddad, Swinburne University of Technology, Australia, Tel: +61 3 9214 8000; E-mail: headerhaddad@swin.edu.au

Received November 06, 2017; Accepted November 14, 2017; Published November 24, 2017

Citation: Haddad H, Sbarski I (2017) Optimization of Thermal and Mechanical Properties of Unsaturated Polyester Resin as a Binder in Polymer Concrete for Manufacturing Precision Tool Machine Bases. J Material Sci Eng 6: 395. doi: 10.4172/2169-0022.1000395

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Sanchez et al. [32] showed that the styrene ratio in UPE pre-polymerization mixture affects the phase continuity of resin after curing due to the limited miscibility of polystyrene in UPE. This phase separation can be affected dramatically by curing temperature [33].

The operational drawbacks of PC when used as bases of precision machines include its coefficient of thermal expansion (CTE), high shrinkage [34,35] and low creep resistance [36]. According to Valore [37], the CTE is high in PCs containing UPE resin in comparison to cast iron and other metal inserts. Precision machines have a complex combination of metal inserts and connecting plastic pipes for fluids in the PC base [31]. This leads to a non-uniform distribution of thermal expansion for the base during operation. It has been reported that reduction of the resin-to-aggregate volumetric ratio in the PC reduces its CTE [31]. Achieving a CTE for the PC as close as possible to that of the precision machine metal components can enhance the distribution of thermal expansion of the base.

The main purpose of this study is to optimize the resin binder through its chemical composition to achieve the lowest CTE and highest damping properties combined with good mechanical properties. The study also considers the manufacturing conditions of PC, including the low initial viscosity of UPE resin to obtain good wetting of aggregate particles during the initial mixing process. A low curing temperature of UPE resin is required for this application to reduce the thermal stresses. The resin is used as binder in polymer concrete for manufacturing the bases of precision tool machines in previous work published by the authors [12].

**Experimental Section**

**Materials**

The UPE resin was made from a commercial unsaturated polyester AROPOL (67% unsaturated polyester dissolved in 33% styrene) obtained from Huntsman Chemical Company (Australia), methyl methacrylate (MMA) from Degussa (Australia), cobalt octoate and dimethyl aniline (DMA) from Alfa Aesar (USA), and methyl ethyl kenton peroxide (MEKP) NR20 from Nuplex Industries (Australia).

**Specimen preparation**

A typical resin sample was produced by mixing a volumetric 3:2 ratio of UP to MMA by hand. To this mixture, 0.8% cobalt octoate (promoter), 0.2% DMA (accelerator) and 2% (v/v) MEKP (initiator) were added and mixed respectively. The mixture was cast in a high density polyethylene (HDPE) mould dimensions were 55 mm × 15 mm × 10 and cured in ambient conditions for 24 hours.

**Kinetics**

A Brookfield RVDV-II+Pro viscometer (USA) was used to determine the copolymerization mixture’s viscosity during the reaction. Gel time was determined for the resin according ASTM D 2471-99. The reaction mixture temperature profile was measured using a thermocouple (SE00 type K thermocouple, Pico Technology, UK).

**Mechanical measurements**

The three-point bending flexural test was carried out on resin samples using a Zwick Z010 (Germany) machine to evaluate tensile and flexural strength. The specimen dimensions were 50 mm × 10 mm × 2.5 mm. A Zwick 3130/3131 (Germany) machine was used to measure the Shore D hardness of the resin samples. Dynamic oscillatory measurements were conducted using Dynamic Mechanical Analysis (DMA) (TA Instruments, SDT 2960, USA) to evaluate the specimens’ damping ratio (tan δ) using a dual cantilever measuring system.

**Thermal expansion measurements**

The coefficient of thermal expansion (CTE) was measured using a custom-built device. Samples were cylindrical, 10 mm in diameter and 70 mm in length. The device includes a heating chamber (Thumler Model number TH2700-26, Germany) with two displacement probes attached to a digital display unit (SYLVAC DSOS, Switzerland) and a thermostat connected to temperature control microprocessor. The UPE resin sample temperature was obtained using a data acquisition system connected to a computer, as illustrated in Figure 1.

Two rods made of Invar were used in this set-up. Invar is a 36% nickel-iron alloy with the lowest CTE among metal alloys in the 20-230°C range, αi=1.2 × 10^-6/°C. One of the rods was used as a reference and the other was placed above the PC sample. The expansion of the reference rod and the sample with the second rod is monitored by the probes on the top of the heating chamber. Figure 1 shows this arrangement. The UPE resin sample had a hole in the centre in order to place the thermocouple sensor (SE00 type K thermocouple, Pico Technology, UK) to monitor and control the temperature inside the
Results and Discussion

Resin curing kinetics

PCs containing polymethyl methacrylate as a binder show a high modulus of elasticity [38] and very low CTE [39] making MMA a good candidate to control and balance both the mechanical and CTE characteristics of the binding polymer in PC. The PC damping properties can be modified using the styrene component of the resin due to the low miscibility of polystyrene in UP and phase separation [32]. In this research program, several compositions of UP: styrene: MMA were prepared to study various aspects of the curing process and mechanical properties of the binding resin.

Resins with ARAPOL: styrene or MMA ratios varying between 25:75 and 68:32 were prepared. The curing rate in the formulations studied shows a decrease with increasing MMA or styrene ratios. The curing rates for compositions with MMA decrease further in comparison with compositions containing styrene. This is an indication that the reactivity ratio of styrene is higher than that of MMA in the UP radical copolymerising system. Figure 2A and 2B show the rate of viscosity increase of ARAPOL: styrene and MMA during the curing process.

Increasing the MMA and styrene ratios decreases the initial
viscosity of the polymerising mixture. The initial viscosity of the polymerising mixture is also important in the processing of PC. Lower initial viscosity enhances the mixing efficiency with the initiator and promoter and allows for more efficient diffusion of the binding resin in the space between the aggregate particles in the concrete.

Figure 2C and 2D show the temperature profile of the curing exothermic process for the above-mentioned compositions. Peak temperature reduces from 124°C at 22 min in 25% styrene to 84°C at 41 min in 40% styrene in ARAPOL. Higher ratios of styrene do not produce a temperature peak. Similar behaviour was observed in ARAPOL:MMA compositions. Peak temperature reduces from 122°C at 178 min in 25% MMA to 117°C at 243 min in 32% MMA in ARAPOL.

The decrease in the curing rate and lowering the peak temperature of the mixture during the curing process is essential to produce a homogeneous resin with no residual thermal stresses that may form a fatigue point in the structure. A slow curing rate and longer fluid initial stages allow for better wetting, more efficient diffusion in pores and spaces between aggregates and time to remove bubbles in the PC mix [40]. The gel time of the above-mentioned resin compositions of UP, styrene and MMA was measured using the ASTM D 2471-99 method. In this method a wooden stick dipped in the resin sample and the resin collected by the stick indicate the gel point. When the adhered resin to the wooden stick is starting to obtain a certain thinness this may record as a gel time. The results of gel time are shown in Figure 3. The gel time increases from 1 to 28 min in ARAPOL: styrene with increasing styrene ratio. In comparison, in this system, MMA as a monomer with a lower reactivity ratio reduces the curing rate of the resin, increasing the gel time from 6 to 210 min 41. This may be the reason for the ARAPOL: MMA composition possessing better mechanical properties in comparison to ARAPOL: styrene 27.

**Flexural strength**

As the resin is the backbone of PC composites, the risen binder forms a high percentage of the flexural strength of PC. Figure 4D illustrates the effect of styrene and MMA volume fraction on maximum flexural strength. ARAPOL/MMA compositions seem to have a higher strength than the ARAPOL/styrene compositions. The addition of MMA increases the flexural strength of ARAPOL:MMA from 73.7-128 MPa when it reaches the maximum at 40% ARAPOL: MMA then it deceases, even though the strength is still higher than that of the ARAPOL: styrene compositions. The reactivity coefficient for MMA is lower compared to styrene which is used initially to reduce the initial reaction mixture viscosity and reduce the curing rate of the resin [41,42] this situation enhance mixing initiator and promoter with the composition, this can be the reason for ARAPOL/MMA composition to have good mechanical properties compared to ARAPOL/Styrene composition [27].

**Tensile strength**

Tensile strength was tested for different resin compositions. Tensile strength is higher for ARAPOL/MMA than the ARAPOL/styrene compositions at the maximum. The tensile strength of ARAPOL/MMA follows similar behaviour to flexural strength. The highest strength is reached at 40% ARAPOL/MMA 58.6 MPa, as shown in Figure 4B. The strain is higher for ARAPOL/MMA compositions than for ARAPOL/styrene, as shown in Figure 4A. The maximum strain is reached at the same resin composition where maximum strength is reached. The modulus of elasticity was calculated. ARAPOL/MMA compositions demonstrate a higher level of modulus of elasticity than the ARAPOL: styrene compositions. Increasing ARAPOL or decreasing MMA increase the modulus of elasticity at various levels of ARAPOL/MMA composition. An increase in the ARAPOL increases the modulus of elasticity of the ARAPOL: styrene compositions, except for the last point in the 75% ARAPOL/styrene composition, which descends rapidly as it is the lowest, as shown in Figure 4C.

**Hardness**

Hardness was measured for a variety of resin compositions. Figure 5 illustrates the relationship between ARAPOL volume fraction and Shore D hardness. It is reasonable to say that an increase in the ARAPOL volume fraction decreases the hardness in the ARAPOL/MMA composition except with 60% ARAPOL/MMA as shown in Figure 5A. An increase in the ARAPOL volume fraction does not indicate a trend in the Shore D hardness for the ARAPOL/styrene compositions, as shown in Figure 5B.

**Damping factor**

A high damping factor is the primary reason why thermoset resin is used as a binder in PC for the bases of precise tool machinery [43]. This property constructs the functionality to damp vibration generated from servo motors in the precision tool machinery [44]. The damping factor was measured for all compositions of ARAPOL/styrene and ARAPOL/MMA using DMA, except for the 25% ARAPOL/styrene resin composition, because of the unsuitability of the resin for making a sample. An isothermal frequency sweep for dual cantilever was conducted in the range of frequency of 1-200 Hz, in considering the precise tool precision machine work in the range of 60-6000 RPM [45] and the base structural design, which is a simple supported beam similar to the DAM structural experimental design. Figure 6A and 6B illustrate the DMA analysis of the results for the damping factor versus frequency for all compositions.

The composition with the highest damping factor (Tan Delta), which is almost constant with frequency sweep, is 40% ARAPOL/MMA, reaching a damping factor of 0.0546. Each composition has its own behaviour, and most are a function of frequency. The most constant damping factor and the highest is produced by the 40% ARAPOL/MMA composition.
Coefficient of thermal expansion (CTE)

The first order approximation of CTE in PC, as a composite, can be obtained using the mixing rule [46].

\[ \alpha_c = \alpha_f \phi + \alpha_m (1 - \phi) \]

Where \( \alpha_c \), \( \alpha_m \), and \( \alpha_f \) are the CTEs of the composite, matrix resin and filler aggregate, and \( \phi \) is the volume fraction of the aggregate.
In PC, the CTE of the mortar resin is usually 7 to 10 times higher than the CTE of the aggregate [12]. Lowering the resin CTE to come closer to that of the aggregate and other components in PC bases of precision tool machines, produces a more homogeneous composite with uniform thermal expansion and less thermal stress. Figure 7 shows that the MMA-containing UPE resins have lower CTEs compared to the styrene-containing resins, in the 25-60°C temperature range. This is consistent with reports of low CTE for PC with poly methyl methacrylate as binding resin [39]. The CTE increases with increasing ARAPOL ratio.

The higher thermal expansion of the styrene-rich resin may be due to molecular packing factor of these resins, leaving only a small space for molecular expansion at increasing temperatures. The inclusion of MMA in the resin composition increases the spatial disorganization and lowers the molecular packing factor, allowing for the polymer chain expansion to be accommodated in the free space existing in the cross-linked network of the resin. This phenomenon can be studied by following the resin shrinkage during the curing process which was successfully reduced by adding montmorillonite filler in composite material [47].

Conclusion

The composition with the highest damping factor of all the resins is achieved with 40% ARAPOL/MMA, which has a damping factor of 5.46%. The highest flexural strength is reached by the same composition with 128 MPa and a low strain of 10.4%. The highest tensile strength is achieved by this composition. The lowest CTE is achieved by 25% ARAPOL/MMA (6.93 × 10⁻⁵ 1/°C), followed by 40% ARAPOL/MMA (7.98 × 10⁻⁵ 1/°C). The module of elasticity of the 40% ARAPOL/MMA is 759 MPa. The highest Shore D hardness for 25% ARAPOL/MMA is 86.6 and 85.5 for 40% ARAPOL/MMA. The result of the mechanical properties shapes the focus for the rheological analysis of the ARAPOL/MMA compositions whilst not ignoring the ARAPOL/styrene compositions. The effects of the UP/styrene in the ARAPOL/styrene and UP/MMA/styrene ratios in ARAPOL/MMA composition were studied. It is concluded that the ARAPOL/MMA compositions are more suitable for consideration, since the mixing efficiency with the initiator and the promoter produce a more uniform solid resin. In addition, it may enhance the mixing of the aggregate with the liquid resin as well as by giving more time while the polymerizing mixture is still a flowing liquid. The exothermic temperature profile is relatively lower in the ARAPOL/MMA compositions than the ARAPOL/styrene composition. The lowest composition in terms of exothermic temperature and viscosity is the 25% ARAPOL/MMA, followed by the 40% ARAPOL/MMA. The mechanical properties of 25% ARAPOL/MMA are very low compared to the 40% ARAPOL/MMA. This results in the nomination of the 40% ARAPOL/MMA as the optimum binder for PC to be used in the manufacture of bases for precision tool machines, because it complies with most categories of the optimisation criteria at a good level.

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