

A polymer matrix particulate reinforced composite biology essay

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material. The goal is to evaluate the importance of different factors and to suggest a well-balanced post cure mode that supports the application of the material. Polymer matrix composites are post cured at elevated temperature to increase the amount of cross linking to achieve better chemical and heat resistance and mechanical properties. Every material has an individual post cure process that depends from the raw materials. Post curing variables include temperature, duration of cure, the time between initial curing and post curing and temperature profile gradient. There are several ways to determine the cure state of a polymer. It can be evaluated based on the mechanical and physical properties, residual styrene content, glass transition temperature, residual exotherm or solvent swelling test. For the determination of the suitable post cure parameters test slabs were casted and post cured with varying time and temperature. Glass transition temperature, residual exotherm, softening in ethanol, surface hardness, flexural strength and flexural modulus were determined. It is shown that the material should be cured at 60 °C – 80 °C. With higher temperature and extended time of cure the glass transition temperature raises but the material becomes too brittle. Keywords: particulate composites, particle reinforced polymer post curing, cross linking, thermal treatment, unsaturated polyesters, glass transition temperature. 1.

INTRODUCTION*Thermosetting resins can be reinforced with continuous or short fibres or particles to form a composite material. Particulate reinforcement has many favourable properties. The addition of particles to the matrix material increases the stiffness, reduces the shrinkage and thermal expansion, lowers the cost and modifies the rheological properties

[1]. Current study investigates particulate composites that are used in building and construction industry. More precisely the material is used for fabricating laboratory and culinary bench tops, vanity tops and sanitary ware like washbasins, shower trays and bathtubs. There are a variety of resins and fillers available for such application. The most common filler materials for producing non-gel coated particulate composite products are alumina trihydrate (ATH), quartz, resin chips and recycled thermoplastics [2, 3]. To obtain pure white products ATH is the choice of filler material.

Alumina trihydrate is a non-toxic, non-corrosive, non-carcinogenic, odourless, flame retardant filler material. It is a mineral derived from bauxite. ATH has specific gravity of 2.42 g/cm³ and Mohs' hardness index of 2.5 - 3.5 [4].

Common resin systems used for producing particulate composites with this kind of application are acrylic, unsaturated polyester and unsaturated polyester modified with acrylic. Unsaturated polyester resin modified with acrylic is the best compromise between cost and properties.*

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Unsaturated polyester resin is widely used in a variety of applications. It has natural resistance to household chemicals and stains. Because of low viscosities that allow high filler content and easy casting it is the most common resin in manufacturing of engineered stone products [5]. Casting applications contribute around 20% to the overall unsaturated polyester resin usage [6]. Polyester is formed by the reaction of difunctional acid and difunctional alcohol (glycol). Properties of polyesters can be varied by using different diacids and/or glycols depending from the application. For polyester resins meant for casting sanitary ware

neopentyl glycol (NPG) and isophthalic acid (ISO) are a good choice. Neopentyl glycol provides good corrosion and weather resistance. Isophthalic acid based resins have high heat and chemical resistance [5, 6]. Styrene is used as comonomer for unsaturated polyester resins. The mixture will copolymerize many times faster compared to homopolymerization of polyester. Styrene also makes the polyester resin an easily handled liquid [6]. The curing of this kind of polyester resin is initiated by adding cobalt carboxylates that promote the polymerisation of monomers. During curing the resin goes through chemical reactions that finally cause the gelation and vitrification of the casting dispersion. Curing is an irreversible reaction where chemical covalent cross-links are formed that are thermally and mechanically stable. The curing process plays a major role in achieving the final mechanical properties and chemical resistance of the material. Complete cure is rarely achieved at room temperature. Not completed cure reduces the performance of the material. Moreover, residual styrene that remains in the material causes problems when the material is in contact with food and by evaporating and causing the material to smell. The solution to these problems is postcuring of the material at elevated temperature. This is necessary to obtain extensive cross-linking of the system [6, 7]. There are several parameters that define the post-cure process. Two biggest variables are temperature and time, but also the time between initial curing and post curing and temperature profile gradient play a role. In literature it is stated that the post cure temperature is the most important factor that influences the extent of cross linking [5, 8, 9]. The goal of the study is to determine a post cure mode that brings out the desired properties of the material that suit

best to this kind of products and to investigate the parameters that influence the post curing process.

2. EXPERIMENTAL

2.1. Sample preparation

The properties of composite plastics depend a lot on the manufacturing process. In order to get adequate results the material samples were prepared in the production facility. For the fabrication of specimens an unsaturated polyester casting resin based on isophthalic acid and neopentyl glycol was used. The resin is developed to produce non-gel coated products and contains methyl methacrylate. It is pre-accelerated, medium reactive, low viscosity resin. The styrene content in the resin is 36 %. For curing a peroxide mixture based on methyl ethyl ketone peroxide was added with ratio of 1/100 wt%. The peroxide is intended for room temperature cure of UP resins and it has low peak exotherm (suitable for thick parts) and good final cure (low residual styrene content). 60 wt% of ATH with medium particle size was used as filler material. (500 × 1,000 × 10) mm slabs were casted. The slabs were casted with a closed mould with a special vacuum assisted casting machine. A closed mould guarantees equal thickness and flatness of the slab. That is necessary to get test specimens like specified in testing standards. Vacuum chamber of the machine removes air from the casting dispersion and helps to achieve non-porous material. The proportion of filler and other components is controlled by the machine. Preliminary cure of the composite was done at room temperature (23 °C ± 2 °C) for 12 h. That was followed by post cure. There are several different oven types that are used for post curing composite plastics – infrared oven, microwave oven and conventional thermal oven. A conventional thermal oven was used in current study to imitate accurately the production process. From all materials 5 specimens

were cut for all tests. The test specimens were cut from the slabs with water jet. 2. 2. Cure characteristics As the cure characteristics are resin specific and depend on various variables these are usually obtained heuristically.

Nevertheless, there are some numerical methods to simulate the curing process of composites, but these are not widely used [10]. From literature one can find the following suggestions to the post curing cycle of neopentylglycol and isophthalic acid based polyester resin: • 80 °C – 90 °C, 4 h – 6 h, not over 107 °C – the material begins to degrade and discolour [11]; • 24 h cure at room temperature (RT) followed by post cure at 60 °C for 8 h [12]; • 24 h cure at RT followed by post cure at 80 °C for 4 h [12]; • After demoulding 120 °C for 1 h [12]; • Post cure temperature should be at glass transition temperature (TG) or slightly above it (TG of current resin is 108 °C); [5]; • 80 °C for 4 h to achieve optimum stain resistance properties [13]; • 50 °C for 5 h – 15 h or 90 °C for 2 h (resin manufacturers suggestion). It was decided that the tests would be made as shown in Table 1. Table 1. Post cure modes

2. 3. Thermal analysis Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature or time. The technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. It is a common tool in the research of postcuring mode [9, 14 – 17]. The calorimetric measurements were conducted with a PerkinElmer Instruments DSC-7 differential scanning calorimeter. All samples were cured in a nitrogen atmosphere. The weight of the samples was 3 mg. Heating was performed

from 20 °C to 200 °C with heating rate of 10 °C/min. The glass transition event is observed as an endothermic stepwise increase in the heatflow. Glass transition temperature represents the region in which the resin transforms from a hard glassy solid to a viscous liquid. With a further increase in the sample temperature, the resin eventually undergoes curing and this is observed as an exothermic peak. At the completion of cross linking the DSC heat flow returns to a quasilinear response [18]. The area under the exothermic peak can be integrated to give the heat of the cure ΔH_{cure} (J/g). The heat of cure may be used to determine the percentage of cure. It is the heat of cure of a post cured sample (ΔH_c) compared to the uncured sample (ΔH_{uc}) (Eq. 1) [16 - 18]. Percentage cure (%) $\times 100 = \frac{\Delta H_c - \Delta H_{uc}}{\Delta H_{uc}} \times 100$. 4. Indirect assessment of cure Polymer softening in ethanol solution was used as an indirect evaluation of the degree of cross-linking. Firstly the specimens were stored in air at 37 °C for 24 h and the Barcol hardness was measured. After that the specimens were placed into 80 % ethanol-water solution at 37 °C for 24 h and the Barcol hardness was determined again. The measurements were done promptly after the treatment. 2. 5. Indentation hardness The indentation hardness of the material was measured with GYZJ 934-1 Barcol impressor according to ASTM D2583-99. Barcol hardness can be used as a basic determination of how cured a material is, or as an indication of the wear resistance of a surface. 2. 6. Flexural properties The flexural properties of the material were determined by 3 point bending test (Fig. 1) as specified in ISO178 "Plastics - Determination of flexural properties". The dimensions of the test specimens were (50×300×10) mm. A test speed of 4 mm/min was used. The support span was 250 mm. The tests were

conducted with Instron 5866. Fig. 1. 3-point bending test³. RESULTS AND DISCUSSION³. 1. Thermal analysis Glass transition temperature (TG) is a thermodynamic and thermo mechanical characteristic. TG is a characteristic, which indicates the softening point at elevated temperatures, effectiveness of curing agents and percentage of cure. The TG depends on different factors, including composition of the resin molecule, cross-link density, curing agent, cure time and temperature. The cure time and temperature have a considerable effect on the TG. Therefore, TG can be a measure of the cure of a material. The TG increases progressively in thermosetting resins during curing. A general rule is that the TG achieved during a post cure will increase with increasing post cure temperature but will not exceed the cure temperature itself. When TG reaches the cure temperature the curing reaction stops [14, 19, 20]. As can be seen from Fig. 2 the TG increases rapidly between temperatures 40 °C till 80 °C. The trend line suggests that the increase in TG slows down at 80 °C, although the TG achieved with post curing at 90 °C is higher. As the TG reflects the mobility of polymer chains it can provide an estimate of the crosslink density. So the decrease in TG increase suggests that the polymer reaches its maximum crosslink density. The post cure temperature of the material under observation should be above 80 °C to reach high TG and thus high cross linking. The time of post cure seems to play a role in the TG value at lower temperatures. The TG achieved with post curing the material for 12 hours at 60 °C is 13 °C higher than post curing it for 6 hours at the same temperature. Nevertheless, independent of the time the TG of the sample post cured at 60 °C for 12 h does not reach the TG that is achieved at higher temperatures. At high temperature the system

receives more energy and the TG is higher. This verifies the assumption that temperature plays a more important role in post curing than time. The same has been observed by Lipovsky and Groenendaal [5, 21]. Fig. 2. Test materials TG dependence on post cure temperature. The physical significance of TG is that at temperatures above TG the values of physical and mechanical properties like tensile strength reduces and the coefficient of thermal expansion increases [19 – 22]. From practical view point it means that the TG has to be considerably higher than the materials service temperature because reduction in materials physical and mechanical properties start below the glass transition temperature. Heat deflection temperature is a method that is used for assessing the practical temperature where a polymer deforms under a specified load. The HDT is determined by the test procedure outlined in ASTM D648 and ISO 75. It has been proved by several authors that there exists a good correlation between the TG and HDT [5, 9, 23]. The HDT for sanitary ware would have to be around 70 °C because the maximum temperature of tap hot water is in the range of 60 °C – 65 °C. In kitchen environment the temperatures are up to 100 °C or even more, especially around heat emitting sources like cooker and kettle. Based on resin manufacturers tests the HDT of the UP resin is 20 °C – 25 °C lower than the TG. This means that the composite has to be cured at least at 60 °C to achieve the necessary HDT for bathroom environment and at 90 °C for kitchen environment. It has been observed that also the stain resistance of the material is related to the TG. Materials with low TG will pick up dirt more easily compared to ones with higher TG (too tacky). It is related to the lower cross linking and thus lower chemical resistance. The DSC graphs have

a further value besides determining the TG. Since the DSC is measuring the heat flow then any heat flow from unreacted material of the sample is recorded on the graph. It is expressed as Joules of energy left in a gram of material (J/g). Less residual energy means that the material is closer to fully cured state [24]. The DSC results are depicted in Figure 3 and are expressed as percentage of cure. Fig. 3. Percentage of cure achieved with different post cure modes based on DSC graphs. The samples that were cured at room temperature or at 40 °C reach around 90 % of cure. The percentage of cure improves as the temperature rises. For a more than 99 % cure the system needs post curing temperatures above 80 °C. This correlates with the obtained TG results.

3. 2. Indirect assessment of cure

Polymers properties are largely related to its crosslink density. Highly cross-linked material tends to be harder, stiffer, more heat and fracture resistant. To assess the state of cure of the composite (crosslink density) the glass transition temperature and residual exotherm were determined with DSC. In addition to that a swelling test was conducted. Ethanol has softening effect on polymers. It is assumed that a more linear polymer softens more than a cross-linked polymer. It is explained by the interaction between solvent and polymer. A suitable solvent that is able to constitute secondary bonds with polymers chains replaces interchain secondary bonds and dissolves linear and branched polymers. However, these secondary bond cannot overcome primary valence crosslinks, so cross-linked polymers do not dissolve. Nevertheless, the cross linked polymers may swell and become soft depending from the cross link density. The swelling and softening effect gets smaller as the cross-link density increases [11, 25]. Figure 4 presents how much percentage a sample lost in

indentation hardness when samples that were stored in air in 37 °C for 24 h were compared to samples that were placed into 80 % ethanol-water solution at 37 °C for 24 h. The samples that were post cured in elevated temperatures lost less than 20 % in indentation hardness. Samples that were not post cured or were treated at lower temperatures lost up to 36 % of their hardness. Post curing at 90 °C gave the highest hardness number after swelling test. When the hardness numbers of samples that were stored in air at 37 °C for 24 h were compared to hardness values of regular samples, a similar loss in hardness was observed. The loss is much smaller but the pattern is the same. Fig. 4. The cross-link density increases with increased post cure temperature (smaller loss of hardness in swelling test). If the cross link density is evaluated based on this test, it can be seen that post curing at higher temperature gives higher cross link density, although the difference gets smaller as the temperature rises. The time of post curing plays a role at lower temperatures. Similar trends can be observed from the DSC graphs that present the TG and residual exotherm.

3. 3. Indentation hardness

The Barcol hardness values of differently post cured samples are presented in Fig. 5. The composite was manufactured with a vacuum assisted casting machine that produces air void free casting dispersion. That should assure a homogeneous material. When the hardness test was conducted, this assumption was verified by measuring the hardness on both sides of the test specimen. No discrepancy was found. The hardness values show that the increase of post curing temperature increases the hardness of the surface. A bigger step can be observed when the hardness of at room temperature and at 40 °C post cured samples are compared to the ones

treated at 60 °C. The next step is much smaller. The hardness value increases only 1.5 % when the temperature is raised from 60 °C to 80 °C. At 90 °C for 2 h post cured material shows even a minor loss in hardness when compared to the sample postcured at 80 °C for 12 h. The application of the material demands great scratch and wear resistance so the indentation hardness of the material is of great importance to the manufacturer.

The recommended Barcol reading by the ICPA is between 45 and 65. A lower number might indicate an under cured material and higher number too brittle material [2]. The surface hardness also depends on the resin and

filler materials, from the concentration of filler material and other factors. The Barcol values obtained are in the upper range of the suggested numbers. This indicates that there is not a necessity to post cure the material above 60

°C because of the surface hardness. Fig. 5. Necessary Barcol hardness can be achieved with postcuring at 60 °C.

3. 4. Flexural properties The flexural strength is considered to be a demonstrative parameter for brittle materials like ceramics and particulate composites. The tensile strength tests of brittle materials are difficult to conduct and the results have a large deviation. From

Figure 6 one can see that the flexural strength of the material changes a bit differently than TG or cross link density. Fig. 6. Flexural strength rise comes to a halt at 60 °C. The flexural strength raises from 40 MPa to 52 MPa when

the material is post cured at 60 °C for 6 h. Postcuring at higher temperature than 60 °C does not give any remarkable rise in the flexural strength of the material. There is a drop in the flexural strength when the material is post

cured for 12 h at 60 °C, but it does not seem to have any correlation with the temperature nor time and should be treated as an aberrancy. From the

manufacturer's point of view higher flexural strength is better because the product does not require elasticity on the contrary the products are expected to be rigid. The other flexural property that was measured was flexural modulus. The modulus of the material increases remarkably after post curing it at 40 °C, from 3300 MPa to 7700 MPa. After that the rise is not as rapid and there is only 6.5 % rise in flexural strength when the post cure temperature is raised from 60 °C to 80 °C. The increase of flexural modulus shows that the stiffness of the composite increases. That trend was confirmed by the deflection values that were obtained during the testing. Stiffness is generally a good property when considering the application of the material. On the other hand the material gets more brittle as the flexural modulus increases. Brittleness is not the material property a manufacturer of bench tops or washbasins is looking for because it makes the products prone to cracks and breakage by falling objects. Fig. 7. Materials stiffness increases with higher post cure temperature it is clear that post curing influences the stiffness and brittleness of the material but it is also largely related to the filler material. Particulate fillers increase the flexural modulus of the composite, while flexural strength remains the same or decreases [26]. The stiffness and impact strength are dependent on the particle size. Smaller particle size provides higher stiffness [27]. In this case it might be necessary to increase the particle size or decrease the filler wt% to decrease the stiffness. A correlation exists between the content of unpolymerised material and the mechanical and physical properties of the material. Unpolymerised material is residual styrene and phlegmatizers. The unpolymerised material has a negative effect on hardness, flexural strength, flexural modulus and

chemical resistance. In the first days and upto a month the styrene will build very quickly. After that the polymerization reaction will slow down or come to a standstill that is caused by the increasing rigidity of the polyester network [5, 19]. The reaction continues when the network is flexibilised again. An optimal cure can only be achieved at elevated temperature. As test data shows high cross link density of ISO/NPG based UP resin is achievable at temperatures above 60 °C. The curing is less time dependent as the temperature rises. The rise of temperature increases the heat resistance and chemical resistance of the material but has unfavourable effect on the flexural modulus and small positive effect on the hardness and flexural strength. Temperature of 60 °C and a cure time of 12 h seem to be optimum balance between cross link density and mechanical properties. Moreover, higher temperatures demands powerful post curing equipment. Nevertheless, the statement that the material needs post curing at 80 °C for 4 h to achieve optimum stain resistance has to be looked into.

4. CONCLUSIONS

The research was carried out to study the effect of different post curing modes to mechanical and physical properties of particle reinforced composite. Experimental part included fabrication of material specimens, heat treatment, DSC analysis, ethanol swelling test and testing of mechanical properties. The test data acquired from DSC analysis and ethanol swelling test showed that increased post curing temperature increases the heat resistance and cross link density. The mechanical tests showed an ascending trend of the mechanical properties with increased post cure temperature. From the experimental data one can conclude that the manipulation of post cure temperature influences many variables. Aspects like brittleness and

impact strength need to be considered. The test results obtained betoken a prospect for the tested material to be used commercially as a material for laboratory, culinary, marine or agricultural products. Acknowledgments