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material. The goal is to evaluate the importance of different factors and to suggest a well-balanced post cure mode thatsupports the application of the material. Polymer matrix composites are post cured at elevated temperature to increase the amount of cross linking to achievebetter chemical and heat resistance and mechanical properties. Every material has an individual post cure process thatdepends from the raw materials. Post curing variables include temperature, duration of cure, the time between initialcuring 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 andphysical 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 timeand temperature. Glass transition temperature, residual exotherm, softening in ethanol, surface hardness, flexuralstrength and flexural modulus were determined. It is shown that the material should be cured at 60 °C – 80 °C. Withhigher 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, unsaturatedpolyesters, glass transition temperature. 1. INTRODUCTION\*Thermosetting resins can be reinforced withcontinuous or short fibres or particles to form a compositematerial. Particulate reinforcement has many favourableproperties. The addition of particles to the matrix materialincreases the stiffness, reduces the shrinkage and thermalexpansion, lowers the cost and modifies the rheologicalproperties [1]. Current study investigates particulate composites thatare used in building and construction industry. Moreprecisely the material is used for fabricating laboratory andculinary bench tops, vanity tops and sanitary ware likewashbasins, shower trays and bathtubs. There are a variety of resins and fillers available forsuch application. The most common filler materials forproducing non-gel coated particulate composite productsare alumina trihydrate (ATH), quartz, resin chips andrecycled thermoplastics [2, 3]. To obtain pure whiteproducts ATH is the choice of filler material. Aluminatrihydrate is a non-toxic, non-corrosive, non-cancerogenic, odourless, flame retardant filler material. It is a mineralderived from bauxite. ATH has specific gravity of2. 42 g/cm3 and Mohs’ hardness index of 2. 5 – 3. 5 [4]. Common resin systems used for producing particulatecomposites with this kind of application are acrylic, unsaturated polyester and unsaturated polyester modifiedwith acrylic. Unsaturated polyester resin modified withacrylic is the best compromise between cost and properties.∗ Corresponding author. Tel.: +372-56-227537; fax: +372-6203196. E-mail address: aare. aruniit@ttu. ee (A. Aruniit)Unsaturated polyester resin is widely used in a varietyof applications. It has natural resistance to householdchemicals and stains. Because of low viscosities that allowhigh filler content and easy casting it is the most commonresin in manufacturing of engineered stone products [5]. Casting applications contribute around 20 % to the overallunsaturated polyester resin usage [6]. Polyester is formed by the reaction of difunctional acidand difunctional alcohol (glycol). Properties of polyesterscan be varied by using different diacids and/or glycolsdepending from the application. For polyester resins meantfor casting sanitary ware neopentyl glycol (NPG) andisophthalic acid (ISO) are a good choice. Neopentyl glycolprovides good corrosion and weather resistance. Isophthalic acid based resins have high heat and chemicalresistance [5, 6]. Styrene is used as comonomer for unsaturatedpolyester resins. The mixture will copolymerize manytimes faster compared to homopolymerization of polyester. Styrene also makes the polyester resin an easily handledliquid [6]. The curing of this kind of polyester resin is initiated byadding cobalt carboxylates that promote the polymerisationof monomers. During curing the resin goes throughchemical reactions that finally cause the gelation andvitrification of the casting dispersion. Curing is anirreversible reaction where chemical covalent cross-linksare formed that are thermally and mechanically stable. Thecuring process plays a major role in achieving the finalmechanical properties and chemical resistance of thematerial. Complete cure is rarely achieved at roomtemperature. Not completed cure reduces the performance257of the material. Moreover, residual styrene that remains inthe material causes problems when the material is incontact with food and by evaporating and causing thematerial to smell. The solution to these problems is postcuring of the material at elevated temperature. This isnecessary to obtain extensive cross-linking of the system[6, 7]. There are several parameters that define the post-cureprocess. Two biggest variables are temperature and time, but also the time between initial curing and post curing andtemperature profile gradient play a role. In literature it isstated that the post cure temperature is the most importantfactor that influences the extent of cross linking [5, 8, 9]. The goal of the study is to determine a post cure modethat brings out the desired properties of the material thatsuit best to this kind of products and to investigate theparameters that influence the post curing process. 2. EXPERIMENTAL2. 1. Sample preparationThe properties of composite plastics depend a lot onthe manufacturing process. In order to get adequate resultsthe material samples were prepared in the productionfacility. For the fabrication of specimens an unsaturatedpolyester casting resin based on isophthalic acid andneopentyl glycol was used. The resin is developed toproduce non-gel coated products and contains methylmethacrylate. It is pre-accelerated, medium reactive, lowviscosity resin. The styrene content in the resin is 36 %. For curing a peroxide mixture based on methyl ethylketone peroxide was added with ratio of 1/100 wt%. Theperoxide is intended for room temperature cure of UPresins and it has low peak exotherm (suitable for thickparts) and good final cure (low residual styrene content). 60 wt% of ATH with medium particle size was used asfiller material.(500 × 1, 000 × 10) mm slabs were casted. The slabswere casted with a closed mould with a special vacuumassisted casting machine. A closed mould guarantees equalthickness and flatness of the slab. That is necessary to gettest specimens like specified in testing standards. Vacuumchamber of the machine removes air from the castingdispersion and helps to achieve non-porous material. Theproportion of filler and other components is controlled bythe machine. Preliminary cure of the composite was done at roomtemperature (23 °C }2 °C) for 12 h. That was followed bypost cure. There are several different oven types that areused for post curing composite plastics – infrared oven, microwave oven and conventional thermal oven. Aconventional thermal oven was used in current study toimitate accurately the production process. From allmaterials 5 specimens were cut for all tests. The testspecimens were cut from the slabs with water jet. 2. 2. Cure characteristicsAs the cure characteristics are resin specific and dependon various variables these are usually obtained heuristically. Nevertheless, there are some numerical methodsto simulate the curing process of composites, but these arenot widely used [10]. From literature one can find thefollowing 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 materialbegins to degrade and discolour [11];• 24 h cure at room temperature (RT) followed by postcure 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 transitiontemperature (TG) or slightly above it (TG of currentresin is 108 °C); [5];• 80 °C for 4 h to achieve optimum stain resistanceproperties [13];• 50 °C for 5 h – 15 h or 90 °C for 2 h (resinmanufacturers suggestion). It was decided that the tests would be made as shownin Table 1. Table 1. Post cure modes2. 3. Thermal analysisDifferential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amountof heat required to increase the temperature of a sampleand reference is measured as a function of temperature ortime. The technique provides qualitative and quantitativeinformation about physical and chemical changes thatinvolve endothermic or exothermic processes or changes inheat capacity. It is a common tool in the research of postcuring mode [9, 14 – 17]. The calorimetric measurementswere conducted with a PerkinElmer Instruments DSC-7differential scanning calorimeter. All samples were curedin a nitrogen atmosphere. The weight of the samples was3 mg. Heating was performed from 20 °C to 200 °C withheating rate of 10 °C/min. The glass transition event isobserved as an endothermic stepwise increase in the heatflow. Glass transition temperature represents the region inwhich the resin transforms from a hard glassy solid to aviscous liquid. With a further increase in the sampletemperature, the resin eventually undergoes curing and thisis observed as an exothermic peak. At the completion ofcross linking the DSC heat flow returns to a quasilinearresponse [18]. The area under the exothermic peak can be integratedto give the heat of the cure ΔHcure (J/g). The heat of curemaybe used to determine the percentage of cure. It is theheat of cure of a post cured sample (ΔHc) compared to theuncured sample (ΔHuc) (Eq. 1) [16 – 18]. Percentage cure (%) ×1002582. 4. Indirect assessment of curePolymer softening in ethanol solution was used as anindirect evaluation of the degree of cross-linking. Firstlythe specimens were stored in air at 37 °C for 24 h and theBarcol hardness was measured. After that the specimenswere placed into 80 % ethanol-water solution at 37 °C for24 h and the Barcol hardness was determined again. Themeasurements were done promptly after the treatment. 2. 5. Indentation hardnessThe indentation hardness of the material was measuredwith GYZJ 934-1 Barcol impressor according to ASTM D2583-99. Barcol hardness can be used as a basic determinationof how cured a material is, or as an indication of thewear resistance of a surface. 2. 6. Flexural propertiesThe flexural properties of the material were determinedby 3 point bending test (Fig. 1) as specified in ISO178 " Plastics – Determination of flexural properties". Thedimensions of the test specimens were (50×300×10) mm. A test speed of 4 mm/min was used. The support span was250 mm. The tests were conducted with Instron 5866. Fig. 1. 3-point bending test3. RESULTS AND DISCUSSION3. 1. Thermal analysisGlass transition temperature (TG) is a thermodynamicand thermo mechanical characteristic. TG is acharacteristic, which indicates the softening point atelevated temperatures, effectiveness of curing agents andpercentage of cure. The TG depends on different factors, including composition of the resin molecule, cross-linkdensity, curing agent, cure time and temperature. The curetime 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 resinsduring curing. A general rule is that the TG achievedduring a post cure will increase with increasing post curetemperature but will not exceed the cure temperature itself. When TG reaches the cure temperature the curing reactionstops [14, 19, 20]. As can be seen from Fig. 2 the TG increases rapidlybetween temperatures 40 °C till 80 °C. The trend linesuggests that the increase in TG slows down at 80 °C, although the TG achieved with post curing at 90 °C ishigher. As the TG reflects the mobility of polymer chains itcan provide an estimate of the crosslink density. So thedecrease in TG increase suggests that the polymer reachesits maximum crosslink density. The post cure temperatureof the material under observation should be above 80 °C toreach high TG and thus high cross linking. The time of post cure seems to play a role in the TGvalue at lower temperatures. The TG achieved with postcuring the material for 12 hours at 60 °C is 13 °C higherthan post curing it for 6 hours at the same temperature. Nevertheless, independent of the time the TG of thesample post cured at 60 °C for 12 h does not reach the TGthat is achieved at higher temperatures. At highertemperature the system receives more energy and the TG ishigher. This verifies the assumption that temperature playsmore important role in post curing than time. The same hasbeen observed by Lipovsky and Groenendaal [5, 21]. Fig. 2. Test materials TG dependence on post cure temperatureThe physical significance of TG is that at temperaturesabove TG the values of physical and mechanical propertieslike tensile strength reduces and the coefficient of thermalexpansion increases [19 – 22]. From practical view point itmeans that the TG has to be considerably higher than thematerials service temperature because reduction inmaterials physical and mechanical properties start belowthe glass transition temperature. Heat deflectiontemperature is a method that is used for assessing thepractical temperature where a polymer deforms under aspecified load. The HDT is determined by the testprocedure outlined in ASTM D648 and ISO 75. It has beenproved by several authors that there exists a goodcorrelation between the TG and HDT [5, 9, 23]. The HDTfor sanitary ware would have to be around 70 °C becausethe maximum temperature of tap hot water is in the rangeof 60 °C – 65 °C. In kitchen environment the temperaturesare up to 100 °C or even more, especially around heatemitting sources like cooker and kettle. Based on resinmanufacturers tests the HDT of the UP resin is 20 °C –25 °C lower than the TG. This means that the compositehas to be cured at least at 60 °C to achieve the necessary259HDT for bathroom environment and at 90 °C for kitchenenvironment. It has been observed that also the stainresistance of the material is related to the TG. Materialswith low TG will pick up dirt more easily compared toones with higher TG (too tacky). It is related to the lowercross linking and thus lower chemical resistance. The DSC graphs have a further value besidesdetermining the TG. Since the DSC is measuring the heatflow then any heat flow from unreacted material of thesample is recorded on the graph. It is expressed as Jouls ofenergy left in a gram of material (J/g). Less residual energymeans that the material is closer to fully cured state [24]. The DSC results are depicted in Figure 3 and are expressedas percentage of cure. Fig. 3. Percentage of cure achieved with different post curemodes based on DSC graphsThe samples that were cured at room temperature or at40 °C reach around 90 % of cure. The percentage of cureimproves as the temperature rises. For a more than 99 %cure the system needs post curing temperatures above80 °C. This correlates with the obtained TG results. 3. 2. Indirect assessment of curePolymers properties are largely related to its crosslinkdensity. Highly cross-linked material tends to be harder, stiffer, more heat and fracture resistant. To assess the state of cure of the composite (crosslinkdensity) the glass transition temperature and residualexotherm were determined with DSC. In addition to that aswelling test was conducted. Ethanol has softening effecton polymers. It is assumed that a more linear polymersoftens more than a cross-linked polymer. It is explainedby the interaction between solvent and polymer. A suitablesolvent that is able to constitute secondary bonds withpolymers chains replaces interchain secondary bonds anddissolves linear and branched polymers. However, thesecondary bond cannot overcome primary valence crosslinks, so cross-linked polymers do not dissolve. Nevertheless, the cross linked polymers may swell andbecome soft depending from the cross link density. Theswelling and softening effect gets smaller as the cross-linkdensity increases [11, 25]. Figure 4 presents how much percentage a sample lostin indentation hardness when samples that were stored inair in 37 °C for 24 h were compared to samples that wereplaced into 80 % ethanol-water solution at 37 °C for 24 h. The samples that were post cured in elevated temperatureslost less than 20 % in indentation hardness. Samples thatwere not post cured or were treated at lower temperatureslost up to 36 % of their hardness. Post curing at 90 °C gavethe highest hardness number after swelling test. When thehardness numbers of samples that were stored in air at37 °C for 24 h were compared to hardness values of regularsamples than a similar loss in hardness was observed. Theloss is much smaller but the pattern is the same. Fig. 4. The cross-link density increases with increased post curetemperature (smaller loss of hardness in swelling test)If the cross link density is evaluated based on this testthan it can be seen that post curing at higher temperaturegives higher cross link density, although the difference getssmaller as the temperature rises. The time of post curingplays a role at lower temperatures. Similar trends can beobserved from the DSC graphs that present the TG andresidual exotherm. 3. 3. Indentation hardnessThe Barcol hardness values of differently post curedsamples are presented in Fig. 5. The composite wasmanufactured with a vacuum assisted casting machine thatproduces air void free casting dispersion. That shouldassure a homogeneous material. When the hardness testwas conducted this assumption was verified by measuringthe hardness on both sides of the test specimen. Nodiscrepancy was found. The hardness values show that theincrease of post curing temperature increases the hardnessof the surface. A bigger step can be observed when thehardness of at room temperature and at 40 °C post curedsamples are compared to the ones treated at 60 °C. Thenext step is much smaller. The hardness value increasesonly 1. 5 % when the temperature is raised from 60 °C to80 °C. At 90 °C for 2 h post cured material shows even aminor loss in hardness when compared to the sample postcured at 80 °C for 12 h. The application of the material demands great scratchand wear resistance so the indentation hardness of thematerial is of great importance to the manufacturer. Therecommended Barcol reading by the ICPA is between 45and 65. A lower number might indicate an under curedmaterial and higher number too brittle material [2]. The260surface hardness also depends on the resin and fillermaterials, from the concentration of filler material andother factors. The Barcol values obtained are in the upperrange of the suggested numbers. This indicates that there isnot a necessity to post cure the material above 60 °Cbecause of the surface hardness. Fig. 5. Necessary Barcol hardness can be achieved with postcuring at 60 °C3. 4. Flexural propertiesThe flexural strength is considered to be ademonstrative parameter for brittle materials like ceramicsand particulate composites. The tensile strength tests ofbrittle materials are difficult to conduct and the resultshave a large deviation. From Figure 6 one can see that theflexural strength of the material changes a bit differentlythan TG or cross link density. Fig. 6. Flexural strength rise comes to a halt at 60 °CThe flexural strength raises from 40 MPa to 52 MPawhen the material is post cured at 60 °C for 6 h. Postcuring at higher temperature than 60 °C does not give anyremarkable rise in the flexural strength of the material. There is a drop in the flexural strength when the material ispost cured for 12 h at 60 °C, but it does not seem to haveany correlation with the temperature nor time and shouldbe treated as aberrancy. From the manufacturer’s point ofview higher flexural strength is better because the productdoes not require elasticity on the contrary the products areexpected to be rigid. The other flexural property that was measured wasflexural modulus. The modulus of the material increasesremarkably after post curing it at 40 °C, from 3300 MPa to7700 MPa. After that the rise is not as rapid and there isonly 6. 5 % rise in flexural strength when the post curetemperature is raised from 60 °C to 80 °C. The increase offlexural modulus shows that the stiffness of the compositeincreases. That trend was confirmed by the deflectionvalues that were obtained during the testing. Stiffness isgenerally a good property when considering the applicationof the material. On the other hand the material gets morebrittle as the flexural modulus increases. Brittleness is notthe material property a manufacturer of bench tops orwashbasins is looking for because it makes the productsprone to cracks and breakage by falling objects. Fig. 7. Materials stiffness increases with higher post curetemperatureIt is clear that post curing influences the stiffness andbrittleness of the material but it is also largely related to thefiller material. Particulate fillers increase the flexuralmodulus of the composite, while flexural strength remainsthe same or decreases [26]. The stiffness and impactstrength are dependent on the particle size. Smaller particlesize provides higher stiffness [27]. In this case it might benecessary to increase the particle size or decrease the fillerwt% to decrease the stiffness. A correlation exists between the content of unpolymerisedmaterial and the mechanical and physical properties ofthe material. Unpolymerised material is residual styreneand phlegmatizers. The unpolymerised material hasnegative effect on hardness, flexural strength, flexuralmodulus and chemical resistance. In the first days and upto a month the styrene will build very quickly. After thatthe polymerization reaction will slow down or come to astandstill that is caused by the increasing rigidity of thepolyester network [5, 19]. The reaction continues when thenetwork is flexibilised again. An optimal cure can only beachieved at elevated temperature. As test data shows highcross link density of ISO/NPG based UP resin isachievable at temperatures above 60 °C. The curing is lesstime dependent as the temperature rises. The rise oftemperature increases the heat resistance and chemicalresistance of the material but has unfavourable effect on261the flexural modulus and small positive effect on thehardness and flexural strength. Temperature of 60 °C and acure time of 12 h seem to be optimum balance betweencross link density and mechanical properties. Moreover, higher temperatures demands powerful post curingequipment. Nevertheless, the statement that the materialneeds post curing at 80 °C for 4 h to achieve optimum stainresistance has to be looked into. 4. CONCLUSIONSThe research was carried out to study the effect ofdifferent post curing modes to mechanical and physicalproperties of particle reinforced composite. Experimentalpart included fabrication of material specimens, heattreatment, DSC analysis, ethanol swelling test and testingof mechanical properties. The test data acquired from DSC analysis and ethanolswelling test showed that increased post curingtemperature increases the heat resistance and cross linkdensity. The mechanical tests showed an ascending trendof the mechanical properties with increased post curetemperature. From the experimental data one can concludethat the manipulation of post cure temperature influencesmany variables. Aspects like brittleness and impactstrength need to be considered. The test results obtained betoken a prospect for thetested material to be used commercially as a material forlaboratory, culinary, marine or agricultural products. Acknowledgments