RECENT DEVELOPMENTS IN SYNTHETIC MARBLE PROCESSING

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Received: April 3, 2012

Abstract. Cultured or synthetic marble is a cheaper alternative for real marble. It is a composite of resins like acrylate, polyester and fillers. Fillers can be silica, calcium carbonate etc. Fillers and resin are mixed, followed by curing and molding to yield marble. Various techniques like slip casting, isostatic pressing, dry casting are also used to cast marble. The real marble look is simulated using pigments, chips etc. Onyx is another compound similar to marble but with more transparency containing aluminium trihydroxide, glass frits as fillers. A detailed description of the works carried out on the various processing techniques, fillers, polymers used and the resulting properties such as mechanical behaviour, appearance such as color and pattern is presented here.

1. INTRODUCTION

Cultured marble or synthetic marble also known as ‘engineered composite’, is formed by mixing high strength resin, marble dust and catalyst. Natural marble is generally heterogeneous with impurities and fractures. They are available in remote areas and require extensive handling in shaping and finishing. This increase the price for these stones. To overcome these difficulties, synthetic marble is produced artificially. The desirable properties in an artificial marble are high mechanical strength, excellent weather resistance, flexural strength, improved surface hardness, heat resistance, stain resistance and an excellent processability. Cultured marble offers a number of advantages over natural marble. These include lesser cost and incredible design flexibility compared to stone. They have uniformity in colour and no random variations occur as in natural stone. Natural marble is limited to flat surfaces while cultured marble can easily be formed to one piece bath tub, shower stall etc. Despite the several advantages offered by artificial marble, it also inherits certain disadvantages. For instance, the marble surface can be scratched and care should be taken to avoid placing objects on it that might cause scratches. Minor scratches or cigarette scorch marks may be removed by using 600 grit wet or dry sandpaper followed by rubbing and buffing with standard auto body rubbing compound. However, it is highly recommended that minor dents or nicks be repaired by trained persons familiar with the proper techniques. The resin material in the synthetic marble is not impervious to burns and might melt, scar, or the glossy marble surface might get damaged. Excessive tightening of plumbing fixtures could result in cracking of marble. However, the safety of marble sinks can be increased by controlling a number of parameters like defoaming time, resin ratio, hardener amount, oven time, oven temperature and amount of transparent glue (Wang et al., 2009).

2. CHEMICAL COMPOSITION

The raw materials required for making cultured marble are filler, resin, gel coat, solid or liquid pigment and catalyst. Filler acts as an aggregate and must
be present up to 85% to 95% by weight (Steven and Larry 2002). Fillers used can be like aluminium hydroxide, calcium carbonate and silica. The resin acts like a glue and thereby strengthening the marble. Resin content in synthetic marble is generally about 12 to 15%. Based on the resin type, artificial marbles can be acrylic or polyester or polycarbonate type. Artificial marbles are prepared by mixing fillers, pigment and a curing agent with a syrup of a monomer/polymer, e.g., methyl methacrylate, polymethyl methacrylate, polyester etc. This is followed by molding the mixture in a mold or a continuous steel belt, and curing the molded mixture. A study on the complex and multiple interactions between filler and polymers revealed that intrinsic properties of the stone substrate, like composition, porosity, and crystalline characteristics, play a relevant role together with the factors related to the polymeric system (Poli et al. 2004). Pigment is added to get the desired color. Pre-determined designs can well be included in these and can be made to resemble the veining and color of natural marble. The color and pattern occurs throughout its thickness. Decorative additives are distinguished from stone fillers primarily by the amount present in the composition. Quantities of decorative material used depend on fashion, design. It generally do not exceed 5% by weight, and preferably, should not exceed 2% by weight (Steven and Larry 2002). These artificial marbles require gel coats since castings made without gel coats are susceptible to stress cracking and have a tendency to stain. Many of these materials retain the properties of the plastic matrix and are subjected to some hot water whitening due to fissure at the filler/resin bond, and/or under-cured or incompletely cured resin (containing residual monomer). There are many other minor constituents involved in marble production - additives like initiators, activators, adhesion promoters, fluidizing agents, viscosity control agents, curing agents, antioxidants, catalyst etc. The coupling agent is a small molecule that aids in the dispersion of a solid particulate material into a liquid medium. They are of the following types: silanes, titanates, and zirconates. Initiators produce free radicals which are required for polymerization. E.g. Peroxides such as, peroxycarbonates, peroxysters, and dialkyl peroxides. Azo type initiators that also thermally decompose may be used (Steven and Larry 2002).

Artificial marble formation involves recrystallization during curing under high temperature and pressure. Evolution of grain size in synthetic marbles was traced from compaction of unconsolidated powder, through primary recrystallization and normal grain growth, to a size stabilized by second phases (Olgaard and Evans 1988). Reagent grade CaCO₃ was used in the experiment. It was mixed with 0, 1, and 5 volume % mica and heat-treated under pressure with added water. Negligible recrystallization occurred within one hour at 500 °C and 500 MPa confining pressure. Primary recrystallization occurred at 500–550 °C, causing increases of grain size of factors of 2–5. Resulting samples had uniform grain size, gently curved grain boundaries and near-equilibrium triple junctions; they were used subsequently for normal grain growth studies. Normal grain growth occurred above 550 °C, till 800 °C. It was observed that minor amounts of pores or mica particles inhibited normal grain growth and lead to a stabilized grain size, which depended on the size of the second phases and the inverse of their volume fraction being raised to a power between 0.3 and 1. Once stabilized grain size was reached, normal growths continued only if second phases were mobile or coarsen, or if new driving forces were introduced that could cause unpinning of boundaries.

Artificial marble can be classified as acrylic or unsaturated polyester artificial marble depending upon the base resin it contains. Organic base resin leads to low weather resistance (Goh et al. 1996). On the contrary, inorganic artificial marbles have more colour resistance and durability. Fillers are generally calcium carbonate, dolomite or aluminium tetrahydrate (ATH). Theses components are all mixed and filled in a mould and followed by a curing process. Conventionally hand lay up moulding and spray molding had been used (Amekawa 2001). Otherwise compression moulding can also be done using sheet moulding compound (SMC) or bulk moulding compound (BMC) (Hayashi and Kameda 2002). Unsaturated Polyester is a major component of these SMC and BMC. Researches are going on to provide SMC or BMC with high productivity, excellent handling property, molding processability and storage stability (Koyanagi et al. 2001). In one particular work by (Shinji et al. 1999), a SMC or BMC had been developed by kneading an acrylic monomer or acrylic syrup, an inorganic filler and a polymer powder containing a remaining emulsifier in an amount from 0.01 to 0.95 wt.%, and if desired, an inorganic filler-containing resin particle, at a kneading temperature from 20 to 70 °C for 20 minutes or less (Shinji et al. 2001).
2.1. Acrylic marble

Acrylic resins offer greater transparency. The acrylic monomer can be methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, acrylic acid derivatives or a mixture thereof. Acrylic artificial marbles show good workability like wood and superior weather resistance. They are lightweight and nonporous. In addition, acrylic artificial marbles have an elegant color tone, high strength and excellent weather resistance like natural marbles (Sung et al. 2009). But there are certain disadvantages too. The acrylic syrup has a lower boiling point. So the curing temperature must be sufficiently low to prevent boiling off of the resin. This increases the curing time. Hence productivity decreases (Koyanagi et al. 2001). Yet, methacrylic resin as the matrix resin has attracted attention because of its good transparency and mechanical strength. Methacrylic resin is now used as the matrix resin more frequently than unsaturated polyester resin or epoxy resin (Uchida et al. 1992). The stresses built up by the mismatch in thermal expansion coefficients between the polymer and stone filler are related to temperature. When a composite is heated, the acrylic polymer is able to relieve these stresses more easily than unsaturated polyester. It is considered that the acrylic polymer possesses a mechanical response with an improved strain to failure. The improved temperature performance with respect to crack initiation is delayed as the polymer is slightly tougher (as characterized by the work to break results) and the stresses that are built up can be absorbed more readily (Steven and Larry 2002). Hayashi and Kameda (1992) used methacrylate resin for their work. Various fillers like magnesium hydroxide, magnesium carbonate and aluminium oxide were incorporated with the resins. Fillers comprised 30 to 90% based on weight. The curable component formulated by them was a combination of a multifunctional allylcarbonylate monomer or its precondensate.

2.2. Unsaturated polyester marbles

The unsaturated polyester resin can be obtained by conventional polycondensation reaction between an unsaturated dicarboxylic acid such as maleic acid, maleic anhydride, fumaric acid, etc., and a polyol component such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butane-diol, 1,6-hexane-diol, neopentyl glycol, 1,4-cyclohexane-diol, glycerine, pentaerythritol, etc. (Rha et al. 2006). In unsaturated polyesters, cross-linking occurs between growing styrene homopolymer and the unsaturation sites in the polyester. Unsaturation sites occur where maleic anhydride is copolymerized with the polyester. The degree of cross linking can be controlled by regulating the concentration of maleic anhydride (Steven and Larry 2002). These have poor weather resistance and heat resistance and difficult thermoforming over acrylic artificial marbles (Sung et al. 2009). Unsaturated polyester based marbles have lesser transparency. Hence the visibility of the internal patterns and designs is very less (Hayashi and Kameda 2002). Also unsaturated polyester resin of the above composition poses a problem of lesser durability and lesser resistance to hot water. Hence polyester resin is inferior to polyacrylic resin. Ikezoe and Motomiya (1994) worked on unsaturated polyester consisting essentially of an acid component and an alcohol component that offered superior impact resistance and thermal shock resistance; moreover has superior hot water resistance and chemical resistance. The alcohol component contained at least a glycol (30 mole % or more) selected from a group consisting of 2-methylpropane-1, 3-diol, 3-methylpentane-1,5-diol, 3-methyl-2-pentene-1,5-diol, 2-isopropylidene-1,3-propanediol, 2-isopropyl-1,3-propanediol, and 2-methylene-1,3-propanediol. As cure accelerators, metallic salts of organic acids were used, in particular cobalt salts, for example, metallic soaps such as cobalt naphthenate and cobalt octoate, and amines such as acetylamidone, p-diketones, quaternary ammonium salts such as dimethylbenzyl-ammonium chloride, dimethylaniline, N-ethyl-metoluidine, triethanolamine, and the like. Independent polymers or copolymers consisting of monomers such as styrene, vinyl chloride, vinyl acetate, and the like were in the process. Copolymers consisted of at least one vinyl monomer and at least one monomer selected from a group comprising lauryl methacrylate, isovinyl methacrylate, acrylamide, methacrylamide, hydroxylalkylacrylate or methacrylate, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, and cetylstearyl methacrylate, and in addition, cellulose acetate butyrate, cellulose acetate propionate, polyethylene, polypropylene, saturated polyester and the like.

The moulds of unsaturated polyester (UPR), cracks easily under stress due to shrinkage when it is being cured. Also when immersed in hot water they show some color changes (Goh et al. 1996). Low shrink agents like lower alkyl esters of acrylic acid or methacrylic acids such as methyl methacrylate, ethyl methacrylate, butyl...
methacrylate, methyl acrylate, ethyl acrylate, and the like are often used to minimize such effects (Ikezoe and Motomiya 1994).

2.3. Epoxy resin

Marble can also be produced by mixing dolomite and epoxy. In one of the works (Hussin et al. 2006) 70% dolomite and 30% epoxy had been used. Diamine was used as a hardener. Dolomite was ground into different range of mesh size 4 mm, 2.36 mm, 1.18 mm, 600 µm, 300 µm, 150 µm, 75 µm. The mixture was poured on mould and cured for about 6 hrs at room temperature. The produced marble was named as 'kukum artificial marble'. Various mechanical tests like three points bending, modulus of rupture (MOR) and Charpy impact test were performed to compare it with the other available stones of market. The dolomite marble had lesser density than the ceramic tiles and provided several advantages like flexible style and design, solid structure with heat, fire and moisture resistance, good strength and long-lasting, easy to assemble and easy machining to the desired shape. Starzec and his co-workers (2006) had done a study on how temperature cycling initiates changes in the porosity of fresh and impregnated marbles. The results indicated that intergranular decohesion was more pronounced in calcitic marble than dolomitic marble. This proved that the dolomitic marble is less prone to weathering.

2.4. Inorganic artificial marbles

Park et al. (2010) formulated an inorganic marble. Inorganic artificial marble contains inorganic matrix consisting of an inorganic powder and an activator. The inorganic powder comprised an alkali metal hydroxide powder, alkaline earth metal hydroxide powder, kaolin, brucite or a combination thereof. An inorganic polymer such as poly(sialate), poly(sialate-siloxo), poly(sialate-disiloxo), or a combination thereof can be used as the polymer base. Instead of using an organic resin all throughout the marble, chips were used. In a study by Dutta Puri (2007), marble of desired shape was produced by mixing powdered marble, magnesium oxide with solution of magnesium chloride, and pigment in appropriate proportion. The fluid was poured on mould and solidified for 6 to 8 hours. The produced marble could be used as sanitary ware and for ornamental purposes. The product did not require any further treatment like curing, healing etc.

2.5. Onyx

Onyx is a form of chalcedony, part of the quartz group. Onyx has a smooth, waxy luster. Cultured Onyx has a semi transparent look like that of natural onyx. Aluminium trihydrate (ATH) is used as the filler instead of limestone. ATH has a specific gravity of 2.4 (Wiener 2000). Cultured onyx differs from cultured marble in their high degree of translucency. The refractive index of ATH, the filler, matches well with the resin. This, together with the little opacity (due to the pigments added) gives the stone-like veining, typical to onyx. Other hollow, light weight fillers are generally not used since they have multiple surfaces for reflection and refraction. This causes increased opacity. Air spaces also increase opacity due to increased differential refractive index (Ross and Stevens 1984). Aluminium trihydrate gives a three dimensional pattern to it. Onyx can be found in a wide range of colors, often layered. Cultured onyx products are made with a low color, clear, unsaturated ortho polyester resin and a peroxide-containing catalyst such as commercially available methyl ethyl ketone peroxide (MEKP) product. Conventional cultured onyx has a weight of approximately 6.5 lbs. for a 1’ square, 3/4’ thick sample. In contrast, a sample of cultured marble, 1’ square×3/4’ thick, typically weighs approximately 8 lbs. The primary difference between the weight of conventional cultured onyx and conventional cultured marble is due to the low specific gravity of the ATH compared to the specific gravity of calcium carbonate, and the higher percent of resin typically used in a cultured onyx product (Wiener 2000).

Onyx can also be produced by blending polyester resins filled with silica, glass frit in a special manner so as to inter-distribute like polyester phases. This is then cured to produce onyx. But there are several disadvantages like non-polishable, dull surface, excessive weight. This can be minimized by providing gel coats. But these also over the years allow water seepage and the gel coat separates off from the base. US Patent 4544584 (Ross and Stevens 1985) provides for a process to produce onyx and marble with appropriate surface properties. The structure comprised a locally discontinuous phase and a continuous phase. The discontinuous phase comprised a synthetic organic resin portion hardened to the predetermined hardness. The continuous phase comprised a synthetic organic resin portion (less than about 50 U.S. mesh in mean average particle size diameter) separately hardened to the predetermined hardness with the discontinuous phase intimately distributed therein.
The resulting structure surface was simulative of onyx and uniformly polishable with undifferentiated phase. The resin particles (diameter less than about 80 U.S. mesh) of the discontinuous phase are hardened to a pre-determined degree before combining. The discontinuous resin portion particle chips typically comprise from about 5% to 55% of the weight of the product, and may be artificially colored. The second resin portion constituted from 25% to 50% of the structure by weight. The combined resin is cured by heating or by catalysis. The best feature of the invention was that by virtue of the like hardness of the two resin portion phases it was possible to polish the surface of the structure to a uniform gloss, without use of an over layer of gelling resin, i.e. in gel coat free relation. In one highly useful form of the invention, water receptacles, such as pullmans, lavatories, water closets and other receptacle apparatus, the shaped product includes a passage within the product, for water or other fluid or for receiving bolts, screws and other fastening hardware, or for defining a wall aperture for water flow or insertion of fixtures.

2.6. Processes to manufacture artificial marble

Conventionally the molding compositions comprising resin and filler have been mixed in a batch wise manner to produce a molding mixture. Commercially available bread dough mixers have been employed for the batch wise mixing. US Patent 4269798 (Frank 1981) provided for the following process of marble production. After placing uncatalyzed resin in the mixing container, catalyst is added and mixed with the resin. Thereafter, the filler is placed into the mixing container of the dough mixer. The resin and filler are then mixed until the resin is evenly dispersed throughout the filler. Normally, when using a dough mixer, several minutes are required to evenly disperse the resin throughout the filler. A measured amount of pigment is added to the mixture after dispersing the resins and is partially distributed or streaked through the mixture, leaving distinct portions of the mixture free of pigment. Thereafter, the mixing container is removed to a location where the molding mixture is poured into a mold and allowed to cure. Normally the resin is catalyzed so that it will begin to cross-link shortly after it is poured into the mold. Consequently, a new batch of resin cannot be mixed in the container used for a previous batch as the residue of the molding mixture in the container will have cross-linked and thus solidified. For further use, the container as well as the mixing tool should be cleaned properly with solvent. The batch wise processes are not labor-efficient because of the long time required for the resin to be thoroughly mixed throughout the filler. Cleaning time is also required after each batch is poured into a mold. Moreover, since a substantial amount of time is required to disperse the resin throughout the filler (when prior art mixing methods are used), the resin/filler mixture may begin to cross-link prior to the time it is thoroughly mixed and placed in a mold.

Over the years, many different processes were developed to manufacture artificial marble and onyx. Griggs (1951), devised a method of strain hardening at room temperature. The deformed material was then heated to a point of annealing recrystallization. Recrystallization due to shear strain was found to provide a highly preferable orientation. A pressure of 5 kilobars was used for the purpose. These requirements made the process economically impractical. Rostoker (1969) demonstrated that marble could even be produced at lower pressures but in that case, temperature requirement enhances. He prescribed grinding of calcium carbonate to a size of lesser than 350 mesh, followed by pressing the particles to make marble. The pressing was done in a carbon dioxide environment and at temperatures of 775 to 1000 °C, 1000 to 3000 psi pressure for 10 to 120 minutes. To sustain such high temperatures, expensive equipments of molybdenum or nickel alloy was required. But at such operating conditions, the materials proved to be reactive. Hence a protective coat was needed for the dies. In another process by (Rostoker and Bush (1965), calcium carbonate particles together with a proportionate amount of alkali carbonate were pressed. Alkalis like lithium, calcium, sodium carbonate were used in the process. Mixing the additives could lower the operation temperature from 775 – 1000 °C to 500-600 °C.

There are several techniques other than the hot pressing to form a green body. The different techniques available are: dry pressing, isostatic pressing or slip casting. A green body formed by any of these processes, was then sintered. A green body refers to a ceramic compound, usually clay or powder, before it has been fired or sintered, respectively. For this sintering process, the particles must be compactable. The particles in intimate contact must get fused together or sintered. The high temperature and pressure requirement can be reduced by using CO, atmosphere or alkali additives. The drawback of these two processes was that they were not economical and hence could not be adopted at commercial level. Rostoker and Bush (1965) found that instead of alkali, fluoride fluxes...
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(2%) could be used. Fluoride fluxes could be used in other forming and sintering processes like slip cast technique. Fluoride flux (zinc fluoride 79% and lithium fluoride 21%) meet the specific requirements of sintering i.e. sintering to occur below calcinations temperature.

There are several advantages of Slip casting techniques (Rostoker and Bush 1965). They are the least expensive and metal anchors and other fastening devices can be fastened directly to the body. Also the produced marble is sufficiently porous and may be impregnated with silicones to make it impervious. Slip cast can be organic or aqueous type. In organic type casting the above fluoride flux works best. But due to handling and manufacturing difficulties often the aqueous slip is preferred. If aqueous slip is used, zinc fluoride (water soluble) should be replaced by other ions like aluminium fluoride-calcium fluoride mixture.

Another process for marble production is the Roberts process (Roberts John and William 1983). In this, the mould is stored in a heated room at a constant temperature for e.g. 30 °C. A bulk container of stainless steel with aluminium or stainless steel blades or aluminium cutter is used to mix resin, filler, and pigment. The blades are driven by an electric motor. The mix is then pressurised to approximately 20 lbs/sq.foot and stored. In the spray area, the gelcoat is applied on the mould. The releasing gel helps separation of the mould from the product after curing. Application of the colored pattern of pre-determined design on the gelcoated surface is done using silk screen. Feeder lines of PVC etc are used to transfer the mix in the bulk container to the mixing head area. The catalyst is added to the mix and deposited onto the mould. The mould is then shifted back to the heated room. The product is cured for twenty minutes, separated from the mould and stored in the heated room.

Another method (Sato and Amano 1995) of manufacturing the artificial marble sheet was defined in US Patent 5403631. The general method for resin molded article involves a resin concrete layer having plasticity to be first formed on a carrier film. The concrete layer does not contain glass fiber. Next a SMC layer is formed on a second carrier film. The resin concrete layer and the SMC layer are then brought into an intimate contact to each other. Carrier films are removed from the artificial marble sheet and press molding is applied under heating such that the resin concrete layer was located on the side of the surface of the product. For the production of artificial marble in the form of a resin molded article, the SMC (sheet molding compound) is formed by impregnating a glass fiber or the like with a resin composition having an inorganic filler or other bulking agent incorporated therein and wrapping both the surfaces with a film. BMC (bulk molding compound) similarly prepared in the form of a bulk can also be compression-molded to form marble (Uchida et al. 1992).

2.7. Enhancing mechanical and surface properties

Dresen and his co worker (1993) carried out a study on brittle and semi-brittle deformation of synthetic marbles composed of two phases. It was conducted on samples formed by isostatic pressing of fine calcite crystals containing 5-20% rigid inclusions. Conditions like room temperature, constant strain rate and pressure of 5-300 MPa were maintained during the test. Resulting microstructures were examined by using optical and electron microscopy. Rigid inclusions caused an increase in the range of pressure over which the brittle-ductile transition occurs. In the brittle field, two-phase aggregates were generally 50 MPa weaker than the pure material. At 5 MPa confining pressure, pure material failed catastrophically along a single fault and aggregates with 20% inclusions showed stable cataclastic flow. In the semi-brittle field, strength of the two materials converged at higher pressure. The strengthening effect of the inclusions was due to interactions between dispersed particles and crystals defects. In one study (Eleonora 1998), the influence of the concentration, color, refractive index, density, particle size and shape, and microstructure of filler on the color, translucency, texture, density, elasticity, plasticity, reversibility, water sensitivity, and working properties of their composites had been studied. A total of 187 samples were tested for density, water absorption, color, and stress-strain at break. Results of the tests show that fillers, when used in high concentration, will significantly influence the visual and mechanical properties of composites. The properties of glass microballoons (Microspheres and Eccospheres), marble dust, and Globe-o-sil fillers were found to be preferable to those of calcium carbonate, mica, and Cab-o-sil fillers. The most promising results were obtained using the hollow, glass sphere fillers (Microspheres, Eccospheres) in a Sikadur epoxy resin-to-filler w/v concentration range of 1-30%. As early as 1973, some manufacturers of cultured marble began using microspheres to reduce the density of their sinks and panels. The need for lightweight filler gained momentum as larger vanities and cultured marble
bathtubs increased in popularity. This trend enhanced the value of microspheres since they not only reduce the weight of the cultured marble component, but also improve its resistance to hydrothermal shock (www.potterseurope.com). The lustre of artificial marble is also improved by adding glass beads and glass flakes. But the process changes the color of the marble (Masato et al. 2000). The advantages of glass microspheres are: improved resistance to hydrothermal shock, weight reduction in the range of 20 to 35%, greater ease of finishing (drilling, sawing and sanding), less tool wear, reduced packaging and shipping costs, increased production through faster mould turn-around, impact resistance, pigmentation value (whiter colour) and reduced catalyst consumption. Glass beads also improve mircrovisor’s hardness, barcol hardness and heat resistance but pencil hardness of the resin fails to improve.

In another study (Veronica et al. 2008), an unsaturated polyester resin (UPR) thin coating containing styrene monomer was used to consolidate Marrón emporador marble pieces. Different amount of nanosilica (0.5-3 wt.%) was added to improve several properties of marbles especially mechanical properties. Addition of nanosilica to UPR-resins caused a noticeable increase in impact resistance of coated marble pieces. Studies have shown that improvement in UPR properties is directly proportional to the nanosilica loading. This is due to a network created between the nanosilica and the UPR matrix which conferred stiffness and toughness to the cured polymer. The rheological properties of the UPR solution like viscosity, imparting pseudoplasticity and thixotropy were also enhanced by adding nanosilica (more than 2 wt.%). Goh et al. (1996), developed vinyl ester (VER) which had both improved surface properties like pigmentability, transparency, lesser loss of glossiness, color change and improved mechanical properties like boiling water resistance etc. The vinyl ester resin was formed by reacting epoxy resins with methacrylic acid under special conditions. Vinyl ester had never been used before because they tend to change color. Hence special care was taken during the experiment to produce the desired ester. Several tests were performed on the obtained resin to evaluate its performance like yellowness index, hot water resistance test, and color change in hot water. An artificial marble was formed with the developed resin (100 parts by weight), ATH (200 parts by weight) and initiator (2 parts by weight). The higher transmittance by the new resin gave it more transparency like that of ATH. Also the linear expansion coefficient of the formulated marble was much lesser than that using the traditional VER. Hence deformation due to temperature was much lesser. Clouding also occurred after a much later time compared to traditional VER. A prototype bath tub was made out of the above marble of about 1.2 m in length and could be moulded within 30 minutes without any cracks. Thus productivity was greatly enhanced. It had excellent translucency and pigmentability. The bath tub was tested for hot water resistance (24 cycles). Each cycle included supplying hot water at 90 °C for 8 hrs followed by cooling down to ambient temperature. Changes were observed with naked eye. There were no cracks or blisters and very little color changes and loss in glossiness were found. Koyanagi et al. (2001) formulated a new resin comprising an unsaturated monomer having atleast two double bonds, copolymerized with another unsaturated polymer 0.01 to 5% by weight of a radical polymerization initiator, 0.1 to 20% by weight of a resin having a methyl methacrylate unit 50 to 85% by weight of an inorganic filler and 1 to 20% by weight of a cross-linked resin particle. The resin had excellent handling property and easy moldability. Patent 5164425 (Uchida et al. 1992) disclosed a composition for artificial marble having a deep appearance characteristic of marble and having a high strength and high abrasion resistance. It comprised (a) 10 to 60% by weight of an allyl-terminated oligomer, (b) 40 to 86% by weight of an inorganic filler and (c) 0 to 30% by weight of a reactive monomer. Accelerated weathering studies are conducted to evaluate the in-service performance of marble (Crump 1996). In one study progressive loss of cohesion along grain boundaries was found to occur in widely used White Macael marble due to thermal changes along with humidity (Luque et al. 2010). US Patent 4871596 (Kamiya et al. 1989) offered a process to produce artificial marble with a good stability in dimensions and suitable to apply to a composite panel or a decorative laminate panel. The marble did not show tearing even after long time use. For the production of marble, an unmodified melamine resin or an alcohol-etherified melamine resin was used. In the etherified resin, formaldehyde-to-melamine molar ratio was in between 1.2 to 3.0. This resin together with a modifier (alcohol, glycol, acrylic monomer, acrylic oligomer and vinyl acetate monomer) was impregnated into a porous substrate. Artificial marble was produced by laminating many of such pre-impregnated sheets. The melamine resin composition might be incorporated with a variety of fillers to impart desired characteristic properties. Examples of
the fillers included silicon dioxide to improve whiteness, aluminium hydroxide to improve clearness, and aluminium dioxide to improve wear resistance. The porous substrate was paper made of .alpha.-cellulose fiber or linter fiber. The cellulose fiber might be incorporated with 1 to 50 wt.%, preferably 5 to 30 wt.%, of glass fiber, carbon fiber, polyester fiber, nylon fiber, or the like as reinforcing fiber. The dimensional change was found to be smaller than 0.5% in both the lateral and longitudinal directions. Inclusion of p-toluenesulfonamide, lactam, benzoguanamine resin, or methyl glucoside in the melamine resin caused an improvement of crack resistance and fabricability for bending. The reinforcing fiber improved the crack resistance and warpage resistance of the molded product. Reinforcing fiber in excess of 50 wt.% greatly reduced the strength of the substrate because of poor.

2.8. Developing color and patterns in artificial marble

Works have been done to mimic the surface appearance of marble. In one particular work (Ohtsuka and Oishi 1996), granular surface appearance like that of marble was obtained by mixing and dispersing 0.001-10 parts by weight of a thermosetting resin with 100 parts by weight of a thermoplastic resin. Thermosetting epoxy resins, thermosetting phenolic resins, etc., could be used for the purpose. It overcame the problem faced in conventional processes like poor surface appearance, while using polycarbonate resins (a thermoplastic resin). Artificial marble or granite having many qualities (Traverso and Renzi 1994) like excellent aesthetic properties, patterns and tonalities can also be prepared from a composition containing a polymerizable poly (allyl carbonate) of a polyl in a limited quantity and mineral filler(carbonate type in the case of marble , and silicate or silica type in the case of granite). The filler is in the form of particles of which at least 40% to 100% by weight have a particle size greater than 0.5 mm. Works have also been done to simulate the fissured look of natural travertine marble into the artificial marble. (Mentzer and Nancy 1989) simulated the travertine marble. Slurry of magnesium or calcium carbonate in water was prepared and screened through a screen having a specified thickness and mesh openings onto a casting surface to deposit carbonate on casting. Castings of glass, fiber glass-reinforced polyester, polycarbonate or acrylic polymer were used. The deposits were dried and framed as per the desired configuration and height of the simulated marble article. Two components: (i) a reaction solution of alumina, phosphoric acid and water and (ii) a mixture of magnesium oxide and calcium silicate were made. The two components were mixed at a specific temperature and for a period necessary to provide a viscosity of the mix between 350,000 and 600,000 poises. When the mix solidified carbonate deposits generated carbon dioxide to produce a substantially solid article having a fissured surface, resembling travertine marble.

Later chips were developed to form patterns and designs. Transparent chips give the ability to provide the artificial marble with different patterns. The chips are conventionally made of the same material as that of the artificial marble. The chips can also be of a thermoplastic resin, such as polyvinyl chloride (PVC) or polystyrene (PS), or a thermosetting resin, such as epoxy resin or unsaturated polyester. Conventional chips are single-colour chips in fine powder form or having a size of 2.5 mesh or less. The patterns obtained by mixing these with resin fail to resemble natural ones. This happens due to the colour difference between the chips and the resin used for artificial marble. Also chips in conventional artificial marble, have excessively low transparency regardless of the material of the chips. So the final product has a limited transparent effect (Kim and Choi 2007). The specific density of the chip should match that of the artificial marble. Hence inorganic filler is used. If this is not present in chips, they float and do not come in contact with the rear end on the steel. Problem in surface physical properties occur due to the difference in distribution between the upper and the lower face. To prevent chip separation the specific density of the chips should be equal to that of the base material. But to maintain transparency like natural material, filler should not be added. Transparency gives a marvellous three dimensional feel to the material. (Kim and Choi 2007) came up with a solution for this. They developed a novel quartz chip with transparent look and same specific density as that of the marble. Quartz chips were prepared by crushing a flat plate made of a mixture of the transparent chips and a composite for the artificial marble, which contained inorganic filler. Thus the specific gravity of the quartz chips, and the artificial marble was made uniform. The artificial marble was then prepared by applying the quartz chips to a raw material composite for the artificial marble. Marbles resembling more to the natural stone can be made using multicolour chips (Sung et al. 2009). For this different colored slurries
need to be prepared using different pigments. These are then mixed partially in batch mixer, cured and crushed to produce multicolour chips. Optimum size of chips is between 0.1 mm and 10 mm. Beyond 10 mm, cracks can develop between the chips and a base. Also the chips can get caught in an impeller of a batch mixer. Chip size larger than 10 mm may also adversely affect the flowability of raw materials. The reason for the limited size is because the multicolour chips are commonly made into a flat plate having a thickness of about 14 mm. Although relatively smaller chips are advantageous in use over relatively larger chips, larger chips are better in terms of manifestation of designs in the final product. So the multicolour chips are crushed to various sizes and mixed before molding to prepare an artificial marble. US Patent 3670060 (Cuffaro et al. 1972) provided a method to produce artificial marble with good light-fastness and high resistance to weathering and can be easily machined and polished. It claimed to reproduce the colors, the patterns and lustre of valuable natural marbles perfectly. The procedure according to the invention consisted essentially of the following operations: intimate mixing of ground stones with thermosetting resins, pigments, a catalyst for the resins and a dispersant for the pigments; pouring of the mixture into forms; heating of the mixture under pressure to the complete hardening of the resin, removal of the products so obtained from their forms, and, if needed, their finishing. Single mixture was formed with 82-85% of powdered natural stones, preferably limestone, 15-11% resins using paratoluene sulphonic acid, oxalic acid, phthalic anhydride, preferably zinc sulphate as a catalyst 0.20-1.66% of pigments with dispersants. Many single mixtures of the above composition with different pigments were used. These color components were mixed together partially so that separate streaks, bandings or veins could be visualized. The layers and shapes of the color components in the mixture were modified and altered by pouring the mixture once or repeatedly into other containers. Pressure in the range of 140-180 kg/cm² was used, with a starting temperature of 10-30 °C and a hardening temperature of 145-160 °C. Oh et al. (2007) were successful to produce an artificial marble using chips made of a low specific gravity material via a lamination or crunch technique. This gave it a natural stone-like texture. They also developed a process for preparing the artificial marble. In one process, a high specific gravity layer containing high specific gravity inorganic filler was laminated on a low specific gravity layer made of a low specific gravity material to form a flat board. The flat board was then crushed to produce chips. In another process, low specific gravity regions made of a low specific gravity material was coated with a high specific gravity slurry containing a high specific gravity inorganic filler, to produce crunch chips. Thus, a low specific gravity material, which could not be used conventionally, was used to produce artificial marble. Rha et al. (2006) developed transparent chips. Colors or metals like Au, Ag, Al, Ni, etc. are deposited. The amount of these transparent surface treated marble chips varied between 0.1 to 150 parts by weight, per 100 parts by weight of acrylic resin for aesthetic appeal. The composition was cured in a conveyor belt or under hot blast. The cured material was then sanded to a certain depth to remove the top coat as well to provide a smooth surface. This gave a three dimensional look as if gems studded in the marble since the colors were visible from the top transparent face. Few processes have been tried for decorating cultured marble. Earlier objects like metal, wood, glass etc were laid and moulded together with the marble. But the surface had to be treated further. Gaps had to be stoned with cement and then polished or enamelled. This proved to be quite time consuming. Seifert et al. (1985) proposed a new technique in 1983 to include floral designs etc as integral part of the cultured marble and not as an added fabric. Hand-made designs were made using acrylic paint over the gelcoat. This was followed by pouring of the marble mix and its hardening. Such process prevented any distortion of the designs during the curing process. Some other works like US Patent 9899125 (Lin 2003) discusses on forming of patterns on marble using polymers. In general there are three methods for producing patterned marble. Either by hand digging or by computer controlled tools designs are sculpted into the marble and then filled with the decorative material. In the last process, the marble is split into pieces. These pieces are then fitted together to form the pattern. The above-mentioned methods all can produce patterned marble/granite/solid surface material. However, there are several disadvantages existing such as production methods, product cost, product quality etc. These methods are time consuming, labour intensive and often very expensive. Manual fitting produces uneven, rough surface, improper fitting. Also computer controlled tools fails to produce certain angles, and complex designs. Hand tooling is not suited for small patterns and lot of residue is produced which cannot be used. This patent disclosed a procedure to produce patterned marble. First a mould with a pattern was formed. Two
materials - basic material and pattern material were formed. The component of the basic material of the artificial marble/granite/solid surface material was composed of one kind of resin like acrylic resin, epoxy resin, or unsaturated polyester (10 to 90%), at least one kind of filler material (10 to 90%) and an accelerating reagent mixed in different proportions. The filler materials were natural marble powder, agate powder, aluminum hydroxide powder and calcium carbonate powder. The pattern material also contained the same components but in different proportions. However, some additives (1 to 30%) such as colorful plastic grains, marble pebbles, granite pebbles were selectively added into the pattern material to make the pattern material vivid.

The patterned artificial marble was formed by multicasting basic and pattern material. This process offered several advantages. Processing time could be controlled by the concentration of the accelerating agent. Raw materials were cheap and not wasted. The mould allowed each single piece to be of same size, pattern with fine trimmed edges. Also no redundant material was left to cause environmental problem.

2.9. Gel coat

The gel coat selection determines the look of the composite product over the years. The performance of a gel coat should be considered at two levels: (Crump 1996).

- At the time of manufacture of the composite (application performance)
- During the usage of the composite (in-use performance)

The different application performances may include good sag resistance, no porosity, must cure well, should sand/buff well etc. In-service performance refers to properties like good weather resistance, water resistance, crack resistance etc. (Crump 1996). The basic generic types of gel coats are:

1. Orthophthalic based systems. These are the oldest base polyesters used in industry. Their benefits are
   - excellent handling characteristics
   - very low in cost.

   But these have 'lousy' thermo-shock properties. A thermal shock value of <100 is 'normal' for this type of gel coat system.

   Orthophthalic NPG based polyester gel coats have better properties than the straight Ortho/PG/DEG types of gel coats. They tend to be a bit tougher and less brittle and have better water resistance than the non-NPG type systems. The Orthophthalic/NPG gel coats can be expected to have better thermal shock properties than the conventional non-NPG Orthophthalic-based gel coat systems. In general they will provide thermal shock properties in the range of 550 to 650 cycles when used with a good quality matrix system. The Orthophthalic/NPG gel coats are probably the most common types of cultured marble gel coat in use today.

Isophthalic/Propylene Glycol systems are, and have been for many years, the workhorse of good marine gel coats and some cultured marble gel coats. They demonstrate good toughness, fair to good water resistance and good thermal shock properties. They are somewhat higher in cost than the Orthophthalic/PG systems and are slightly higher in cost than the Ortho/NPG gel coat systems. Handling properties tend to indicate that these products are a bit less easy to use than the Orthophthalic systems or the Orthophthalic/NPG systems. A typical clear cultured marble gel coat prepared from an Isophthalic-Propylene Glycol type of system will typically provide thermal shock values in the 700 to 800 cycle range.

NPG/Isophthalic Systems. Currently the best polyester ‘backbone’ for both clear and pigmented gel coat systems that are used in the cultured marble industry is based on NPG/Isophthalic polyesters. While a little more sensitive, handling wise, than are the Orthos and some Isophthalic systems, the little extra effort is well worth it when properties such as chemical resistance, abrasion resistance, and water resistance are considered. Thermal shock values of 2500-8000 cycle range are often obtained with these systems. This type of resin is the basis for ‘G’series clear cultured marble gel coats.’ (HK Research Corporation Product).

A study had been carried out by Tommaso Poli et al. (2004) about the surface treatment of stone materials which helps in protecting those materials from the attack of environmental pollutants. Natural and synthetic waxes, acrylic and siloxane resins, perfluoropolyethers, fluorinated polyolefin and fluoroelastomers are some of the most used commercial products employed as protective coatings for stone materials. These products are applied not only to prevent the attack of the environmental pollutants but also the penetration of water, with the connected risks of freezing and thawing cycles and the crystallization of salt solutions, in order to slow the stone degradation processes. The easiest way is, through the deposition method, on the stone surface, and possibly deeper beyond the surface, of a coating layer able to modify the interaction of the stone with...
water, turning the partial hydrophilic character of the stone surface into a high hydrophobic interface. This modification should be achieved by affecting only the thermodynamic superficial potentials, but leaving unaltered, as long as possible, the superficial aspect, morphology, open porosity and roughness. The coating materials do not react with the stone material in order to respect its natural chemistry. Stability and resistance to the photoxidative and thermal ageing of the different polymeric classes are other crucial problems: Sometimes a long term chemical integrity does not correspond to a similar protection efficacy. After applying a polymer to a stone surface, physical rearrangements could occur to the protective layer, reducing the shielding efficacy but leaving the chemical structure unaltered.

3. CONCLUSION

The light weight, beautiful cheaper cultured marble has become a competitive alternative for natural marble. Conventionally, resins like acrylate, polyester etc. are mixed with fillers, pigments and applied on molds followed by curing to yield artificial marble. Besides this conventional process, many other processes exist like strain hardening at room temperature, isostatic pressing, slip casting, Robert’s process. The mechanical and aesthetic properties of artificial marble depend on the resin and filler composition together with other decorative substances like pigments, chips etc. Many works have been done to simulate the look of natural marble as closely as possible. Transparent chips have been used to give a transparent surface so that the inner veining is visible. Cultured marble can be easily made into one piece shower stall or bath tubs. Despite these several advantages, it also has some drawbacks like lower hydro thermal shock resistance and proneness of surfaces to easily get scratched. Yet its grand look and cheaper price makes it very attractive.

REFERENCES

Recent developments in synthetic marble processing

[31] PQ Hollow Spheres, South Yorkshire, U.K. Website: www.potterseurope.com


