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Introduction of reversible crosslinker into artificial marbles toward chemical recyclability

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ABSTRACT

Organic/inorganic composites containing thermally breakable crosslinker were prepared for exploring the possibility in fabrication of recyclable artificial marble composed of acrylic resin and aluminum hydroxide. The breakable crosslinker was fabricated using Diels–Alder reaction from furfuryl methacrylate and bismaleimide. De-crosslinking reaction was also triggered by retro-Diels–Alder reaction. The basic properties of artificial marbles fabricated by breakable crosslinker, i.e chemical, thermal, mechanical and coloring properties, are compared to that of conventional one, which is based on unbreakable crosslinker.

Introduction

In recent, materials for construction industry have attracted great attention because of increasing requirements in properties for housing technology, and thus broad range of researches have been conducted to develop gentrified and highly qualified building materials [1–3]. Among them, a natural marble has been used in area such as the construction and kitchen industry because it shows high strength and unique characteristic patterns [4]. However, the natural marble has weaker resistance to scratch and heavier weight than other materials, and the raw material was rare and expensive as well [5]. Therefore, artificial marbles, which are basically inorganic–organic composite including polymers and inorganic fillers, replace the natural marbles. Nowadays, the artificial marbles have used in large area such as out walls and inner walls of building, sink-tops of furniture because they have several superior properties to natural one in terms of their weight, processibility and cost [6–8]. The artificial marble was roughly categorized into acrylic resin, unsaturated polyester resin, polyurethane resin, epoxy resin and phenol resin according to the polymeric matrix [9,10] aluminum hydrate and silicate powders were generally used as the inorganic filler. In addition, several additives such as coupling agents for improving an affinity between the organics and the inorganic materials, crosslinking agents for enhanced mechanical strength and de-foaming agent for improving the strength of marbles through removing bubbles in marbles. Among them, the artificial marbles based on polymethylmethacrylate (PMMA) and aluminum hydroxide which are invented by Dufont co. since 1968 is the most common and widely used in industry due to their low cost and easy processibility [11].

On the other hand, as increasing supply amount of artificial marbles in recent years, the inevitable concerns for industrial waste of artificial marbles also increases. In addition, a great amount of industrial wastes are normally generated during the processing and manufacturing the artificial marbles such as cutting, grinding and polishing. Therefore, recycling these marble waste has been of particular interest in recent year [12,13]. The artificial marbles such as PMMA resin are basically thermoset polymer composite, and thus their recycling pathway is generally depended on pyrolysis to obtain several organic molecules which is inefficient and time consuming [14–17]. In the case of PMMA resin, crosslinking-agent containing di-vinyl group is introduced to improve chemical and mechanical properties of thermoplastic

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polymers. Typically, ethyleneglycol dimethacrylate (EGDMA) was used as cross-linker for polymer resins. [11] Cross-linked PMMA is basically thermoset polymer, and thus it is intrinsically impossible to recycle these resins as a resource. Therefore, development of novel type of cross-linker containing di-vinyl groups with chemically breakable moiety is strongly required to reuse the marble waste as a resource material.

In this study, we tried to introduce thermally breakable crosslinker (TBC) into PMMA composite in order to develop chemically recyclable artificial marbles. A Diels–Alder reaction was used for synthesis of breakable crosslinker [19–22], which is based on reaction of dienes and dienophile such as cyclopentadiene–cyclopentadiene and furan–maleimide [23–26]. The successful fabrication of cross-linked PMMA with reusable properties can be confirmed by solvation test in high temperature [18,27–29]. Several key properties of artificial marbles prepared by TBC are compared to those of conventional acrylic based artificial marble.

Experimental

Materials

Furfuryl methacrylate (FM, Tokyo Chemical Industry Co. Ltd), 1,1′-(Methylenedi-4,1-phenylene)-bismaleimide (BM, Sigma Aldrich), and Chloroform (Samchun chemical) were used for synthesis of reversible crosslinker based-on Diels–Alder reaction. EGDMA (Miwon Commercial Co.) was adopted as irreversible crosslinker, which is commonly used in acrylic-based artificial marble. PMMA (Arkema Inc.), aluminum hydroxide (ATH, Chalco), 3-(trimethoxysilyl)propyl methacrylate (γ-MPS, Sigma Aldrich) and Benzoyl peroxide (BPO, Sigma Aldrich) were used for fabrication of acrylic-based artificial marbles.

Synthesis of TBC for recyclable artificial marble and preparation of model polymer with TBC

The TBC was synthesized by Diels–Alder coupling reaction between FM and BM. FM (5.0×10^{-4} mol) and BM (2.5×10^{-4} mol) were mixed in 1 ml of chloroform. Then, mixed solutions were stirred for 1 h and dried in room temperature. Before polymerization procedure, PMMA syrup was prepared by mixing PMMA and MMA with a ratio of 3:1. PMMA syrup (8 g), MMA (2 g), and BPO (0.1 g) were mixed in vial. After then, the polymerization of the mixture was achieved in oven at 60 °C for 2 h.

Fabrication of marbles including TBC

For fabrication of artificial marble, PMMA syrup (240 g), MMA (60 g) and γ-MPS (3 g) were mixed in a 500 ml three-neck round bottom reactor connected with vacuum pump, mechanical stirrer, and a silicone rubber septum in each neck to remove bubbles. Then, aluminium hydroxide (530 g), BPO (3 g) and the breakable crosslinker synthesized using FM (0.016 mol) and BM (0.0075 mol) in 3 ml of chloroform were added carefully into the reactor and stirred vigorously for 30 min in vacuum state. The resulted solution was poured into a mold covered with PVA film. Polymerization of the MMA in the solution was carried out at 60 °C for 2 h.

Characterization

FT-IR spectra were obtained by attenuated total reflection (ATR) method with ZnSe prism (Thermo Scientific). The breaking reaction of crosslinker by retro Diels–Alder was confirmed by differential scanning calorimetry (DSC, Metteler Toledo) in the temperature range from 25 °C to 250 °C with a heating rate of 10.0 °C/min. The solubility of artificial marbles with breakable crosslinker was confirmed by solvation test using DMF at room temperature and 160 °C, respectively. The mechanical properties of marbles were measured by flexural test machine and Rockwell hardness tester. Flexural properties were measured by 3-point flexural strength using a universal test machine (UTM, series IX automated materials testing system, Instron Corp). The samples were prepared with dimensions of 20 cm × 1.5 cm × 10 mm (thickness). The Rockwell hardness was measured using B scale 100 kg by TH300 Rockwell type hardness tester (Time Group Inc.). Thermal decomposition behaviors of the marbles were measured by thermos-gravimetric analysis (TGA, Metteler Toledo) at a heating rate of 10 °C/min under nitrogen atmosphere. Chrominance of artificial marble were measured using a chroma meter (CR-410, Konica Minolta) by 3 times for each sample.

Result and discussion

Preparation of thermally breakable crosslinked PMMA

Overall strategy for preparation of reusable artificial marble with TBC synthesized using FM and BM (TBC-FM–BM) is schematically illustrated in Fig. 1. The acrylate-based artificial marble was basically consists of PMMA, aluminum hydroxide, several coupling agents, and crosslinker for increasing their physical and chemical properties. Among them, the crosslinker such as EGDMA, and the coupling agents containing double bond such as γ-MPS results in thermoset polymeric composite after processing. As mentioned previously, in order to fabricate the chemically reusable artificial marbles, the de-crosslinking reaction must be carried out in the matrix. Therefore, in this study, we attempted to replace the un-breakable crosslinker such as EGDMA to TBC-FM–BM as shown in Fig. 1. In addition, when the furan and the maleimide was decoupled by retro Diels–Alder reaction in high temperature, the de-crosslinking reaction was occurred which makes it possible to reduce the final product into resource materials.

Fig. 2 shows the FT-IR spectra of the FM, BM and the TBC-FM–BM synthesized, respectively. FTIR spectrum of FM shows characteristic bands at 1020 cm^{-1} which is due to furan moiety, at 1714 cm^{-1} from C=O stretching and at 1160 cm^{-1} from C–O–C of furan moiety. The characteristic bands for maleimide moiety in the BM molecules were confirmed by peaks at 1702 cm^{-1} from C=O stretching, 3037 cm^{-1} from =C–H stretching, 1509 cm^{-1} for aromatic C=C bonds, and 1374 cm^{-1} which is due to aromatic C–N stretching of maleimide ring. In the case of synthesized TBC-FM–BM, new intense peak was presented at 1664 cm^{-1}, which is due to $>$C=C$<$ formation occurred during crosslinking reaction between FM and BM as shown in Fig. 1. In addition, the decreasing of the peaks at 1160 cm^{-1} and 1020 cm^{-1} of FM indicates that the furan moiety has used for Diels–Alder reaction after synthesis, implying successful preparation of TBC [27].

Fig. 3 shows the DSC thermogram of synthesized crosslinker, in order to prove retro Diels–Alder reaction in temperature range of 25–250 °C. In general, retro-Diels–Alder reaction of furan and maleimide take place at above 150 °C [27]. The endothermal reaction related to retro Diels–Alder reaction was observed at 158 °C as shown in Fig. 3, implying successful preparation of TBC. This result also indicates that de-crosslinking reaction of synthesized crosslinker was possible at above 160 °C, and therefore, the thermoset PMMA with this thermally breakable polymer can be transferred to Thermo-plastic under this condition.

Before testing retro Diels–Alder reaction, successful fabrication of crosslinked PMMA using this TBC should be checked out. Fig. 4a shows crosslinked PMMA synthesized by introduction of TBC-FM–BM. In addition, Fig. 4b and c shows the photography of crosslinked