

RESEARCH ARTICLE



# The effects of low-profile additives on shrinkage and mechanical properties of cultured marble materials

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## ABSTRACT

Cultured marble is a blend of unsaturated polyester and calcium carbonate that is combined with pigments and additives to produce a wide range of colours and realistic, natural-looking patterns. This study aims to investigate process conditions (catalyst, temperature, cured time, etc ...) of cultured marble at high temperatures. The optimized process conditions are obtained by thermal analysis from DSC with a temperature of 110°C and curing time of 20 min, respectively. The optimum catalyst for process conditions in a bulk moulding compound (BMC) machine is 2 phr of benzoyl peroxide (BPO). The styrene amount in UP resin is determined at 37.40% by the Gas chromatography-mass spectroscopy – headspace (GCMS-HS) technique. Anhydride maleic (MA) is found to improve outstanding mechanical properties in terms of flexural properties, the strength of impact, and the resistance of volume shrinkage of UP resin in cultured marble material.

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volume shrinkage

## Introduction

Natural stone is a non-renewable resource used both in buildings and interior decorations. It is mainly exploited from mountains, which causes some serious environmental issues such as flooding or mountains collapsing. The main drawback of natural stone is the heavyweight of the natural stone resulting in time-consuming when using it in the building. Moreover, climate and environmental changes affect the texture of the rock and cause cracking, mildew, and dandruff on the surface. In addition, natural stone has high permeability, insufficient elasticity and its stains are hard to clean. Therefore, many studies to find a suitable artificial stone with outstanding properties to replace traditional natural stone have been conducted for years [1–4]. Artificial stones could be manufactured to look like granite and they are often used to create bathtubs, walls, countertops, and floors. Moreover, artificial stones can be easily produced in a relatively short time, compared to the process of natural stone exploitation from natural quarries. Artificial stones provide many benefits, not only for buildings and constructions but also their most eco-friendly materials. There are three types of

artificial stone: cultured marble, cultured onyx, and cultured granite. In general, the cultured marbles are a mixture of thermosetting resins such as unsaturated polyester, epoxy acrylate, urethaneacrylate, with inorganic fillers and colour pigments. There are also some required additives to enhance durability, shrinkage and mechanical properties. Cultured marble materials are flexible to form into complex shapes and intricate design elements since the resin-based artificial stones are easily gone through the procedure of moulding, solidifying, knockout, drying and polishing [5]. The density of cultured marble is lighter than that of natural stones. Additionally, a clear gel coat resin on the cultured marble to protect the coloured surface and provide visual depth which makes the cultured marble glossy, dust and dirt resistance, waterproof, and easy cleaning. However, this gel coat layer is easily scratched, which could change the colour and aesthetics. Recently, many researchers combined the inorganic minerals with polymer resins to produce novel, artificial, ornamental stone for civil construction [2,6–10]. Fabricating artificial marble from dolomite marble waste and evaluating the

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effects of microstructure on the physical properties of artificial marble has been recently reported [11]. The influence of different components on the physical and mechanical properties of cultured marble was carried out in many previous studies [4,12–14]. The effect of elevated temperature curing on the compression strength of composite with unsaturated polyester and quartz filler was reported [15]. The changes of thermal degradation and fire behaviour of unsaturated polyester with metallic oxide filler were investigated [16]. In addition, the effect of nano-clay or bentonite on the performance of unsaturated polyester was also studied in the previous literature [17,18]. One of the biggest problems of artificial stones is volumetric shrinkage behaviour. Laboratory determination of volumetric shrinkage behaviour of the artificial marble during the curing process has been described [19]. Low-profile additives (LPA) could strengthen the toughness and shrinkage resistance. To increase the shrinkage resistance of polyester concrete, a variety of PLAs including liquid rubber [20,21], poly (vinyl acetate), polystyrene, poly (methyl methacrylate) [22], and synthetic low-shrinkage resin [23] have been used. The production of cultured marble has been extensively performed at room temperature and this process can be done without the required energy. However, for sophisticated-shaped products prepared by process manufacturing including bulk moulding compound (BMC) or sheet moulding compound (SMC), the main difficulties and drawbacks to these methods are the rapidly hardened materials in cylinder at high temperature.

In this paper, we study the parameters such as catalyst, additives, and styrene concentration for producing cultured marble at high temperature as well as for improving mechanical properties.

## Materials and experiment

### Materials

Commercial unsaturated polyester (UP) (code P5-954B) was supplied by DSM Resins Company., Ltd. Benzoyl Peroxide (BPO), a free radical initiator, was supplied by Peroxide Company. Both additives including Anhydride maleic (AM) and Methyl methacrylate (MMA) were purchased from Merck. Acrylonitrile butadiene styrene (ABS) was purchased from Zibo Linzi Yixiang Chemical Co., Ltd. The styrene was contributed by Merck and Calcium carbonate ( $\text{CaCO}_3$ ) was supplied by VNT7 Joint Stock Company.

### Determining styrene content in unsaturated polyester

There are three methods to analyse free styrene in unsaturated polyester: the first is to remove the styrene

from the UP resin in an air-circulating oven at  $110^\circ\text{C}$  for 2 h (DIN 16945) [24], the second is to precipitate and re-precipitate in petroleum or benzene [25], and the final method is to precipitate the resin in pentane, then analyse the supernatant liquid through gas chromatography [25]. In this paper, we used a new method using standard addition combined with the Gas chromatography-mass spectrometry – headspace (GCMS-HS) technique, to determine the amount of styrene in unsaturated polyester. According to the method of standard addition, pure styrene was added to unsaturated polyester in different amounts, and then samples were analysed by GC/MS – QP 2010 Shimadzu. Standard addition plot was drawn based on the different amounts of additions. This intercept of line reveals the amount of the styrene in sample.

### Determining the particle size of calcium carbonate

Calcium carbonate ( $\text{CaCO}_3$ ) is one of the main components of cultured marble materials. The dispersion of  $\text{CaCO}_3$  in UP as well as the final properties of cultured marble principally depend on the particle size of  $\text{CaCO}_3$ . In this study, distribution particle size of  $\text{CaCO}_3$  is determined using Particle Size Analysis S3500 after dispersing  $\text{CaCO}_3$  in distilled water.

### DSC thermal analysis

The thermal studies were made using a Differential Scanning Calorimeter (DSC) from TA DSC Q200. A definite milligram of the samples was precisely weighed and put into aluminium with a cover. The samples were isothermally heated at different temperature ranges according to ASTM-D7029-09 [26] to obtain  $\Delta H_{\text{iso}}$ , the isothermal heat released from cured samples [27]. This method was also used to optimize catalysts amount, process conditions, and contents of  $\text{CaCO}_3$  for cultured marble production.

### Effect of low-profile additives on volume shrinkage of UP

The effect of low-profile additives (with amount of 5 phr compared to UP) (phr is defined as one part per 100 parts, 5 phr means 5 g of additives is added to 100 g UP resin) such as anhydride maleic (AM), acrylonitrile butadiene styrene (ABS), and methyl methacrylate (MMA) on shrinkage property of UP resin was investigated. To obtain changed volumetric values of mixture of low-profile additive and UP before and after curing, the density method was conducted. The UP was poured into test tubes in the same volume ( $V_0 = 21 \text{ ml}$ ). These test tubes were scaled and the initial weight values were recorded ( $m_0$ ). Then, these test tubes were immersed in a heated tank at  $82.2^\circ\text{C}$

**Table 1.** Ingredients in cultured marble.

Components	Content (phr)
UP resin	100
BPO catalyst	2
CaCO <sub>3</sub> powder	200
Dispersing agent	3
Additives	5

in 20 min until the curing process completed. These cured samples were taken out of the test tubes, scaled again to define weight after curing ( $m'$ ), then soaked into a measuring cylinder containing distilled water. Based on the change in volume of distilled water, the volume of UP after curing ( $V'$ ) was recorded. The percentage of volume shrinkage (%V) was calculated as the following formulation [28].

$$\%V = \frac{V' - V_0}{V_0} \times 100\% = \frac{\left[\frac{1}{\rho'} - \frac{1}{\rho_0}\right]}{\frac{1}{\rho_0}} \times 100\%$$

where  $V'$  and  $V_0$  are volume of initial and cured samples;  $\rho'$  and  $\rho_0$  are density of initial and cured samples.

### Manufacture of cultured marble materials

Cultured marble is composed of many ingredients including BPO catalyst, UP resin, calcium carbonate powder, dispersing agent, and three different low-profile additives as listed in Table 1. All components of materials were mixed with a mechanical mixer Dewalt (US) at 300 rev min<sup>-1</sup> for 30 min at room temperature. Then, the mixture was filled into an aluminium mould with a dimension of 120 × 90 × 3 mm). The mould was pressed at a temperature of 110°C, under a pressure of 1700 kgf for 20 min. Finally, the mould was slowly cooled down at room temperature and stored in the press for 24 h to avoid warping. All steps of cultured marble manufacture are summarized in Figure 1.

In this study, when the content of CaCO<sub>3</sub> powder was high (>100 phr), it leads to a very high viscosity

which was difficult in processing as well as decreasing miscibility between CaCO<sub>3</sub> and UP resin. The mixture became too lumpy and thick to be processed. However, in this study we aim to produce the cultured marble with a high CaCO<sub>3</sub> content of 200 phr. Therefore, a dispersion agent (Tamol-N) at 3 phr was added to the mixture during the process.

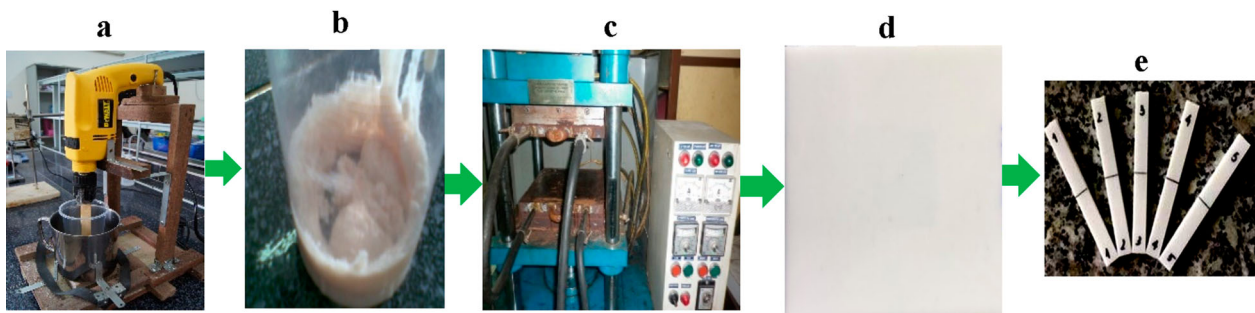
### Mechanical properties tests

The flexural properties' tests of cultured marble were performed with the 3-point flexural measurement using an AG-Xplus Series Precision Universal Tester (Shimadzu Inc., Japan). The specimens were prepared according to ASTM D790 standard. The specimens were measured until completely broken and the results were an average of a set of 5 values. An impact strength test was performed with the Charpy method in accordance with ISO 179 standard, using a Zwick/Roell device (Germany). The test specimens were prepared with standard dimensions of 80 × 10 × 4 mm<sup>3</sup> and the impact strength result was an average of a set of 5 values. The hardness of materials was performed using a Vickers Testing machine (Germany) in accordance with ASTM C1327-08 standard; the hardness result was an average of a set of 5 values.

## Results and discussion

### Effect of the styrene concentration

Styrene plays a vital role in unsaturated polyester curing. If the styrene concentration is too low, cured UP will be too brittle and the viscosity of uncured UP will be so low that it causes many disadvantages for producing. If the styrene concentration is too high, homo-polystyrene will compete with the curing between styrene and unsaturated polyester which decreases mechanical properties of cured UP. The effects of styrene on the curing kinetics of unsaturated polyester have been reported in many literatures [29–32]. During the curing process, both styrene and UP involve in two simultaneous reactions including



**Figure 1.** The steps for cultured marble manufacturing, (a) mechanical mixer Dewalt (US) for preliminary mixing of all components, (b) mixture, (c) hydraulic presses for cultured marble forming; (d) an example of cultured marble after fabrication, and (e) specimens for impact testing.

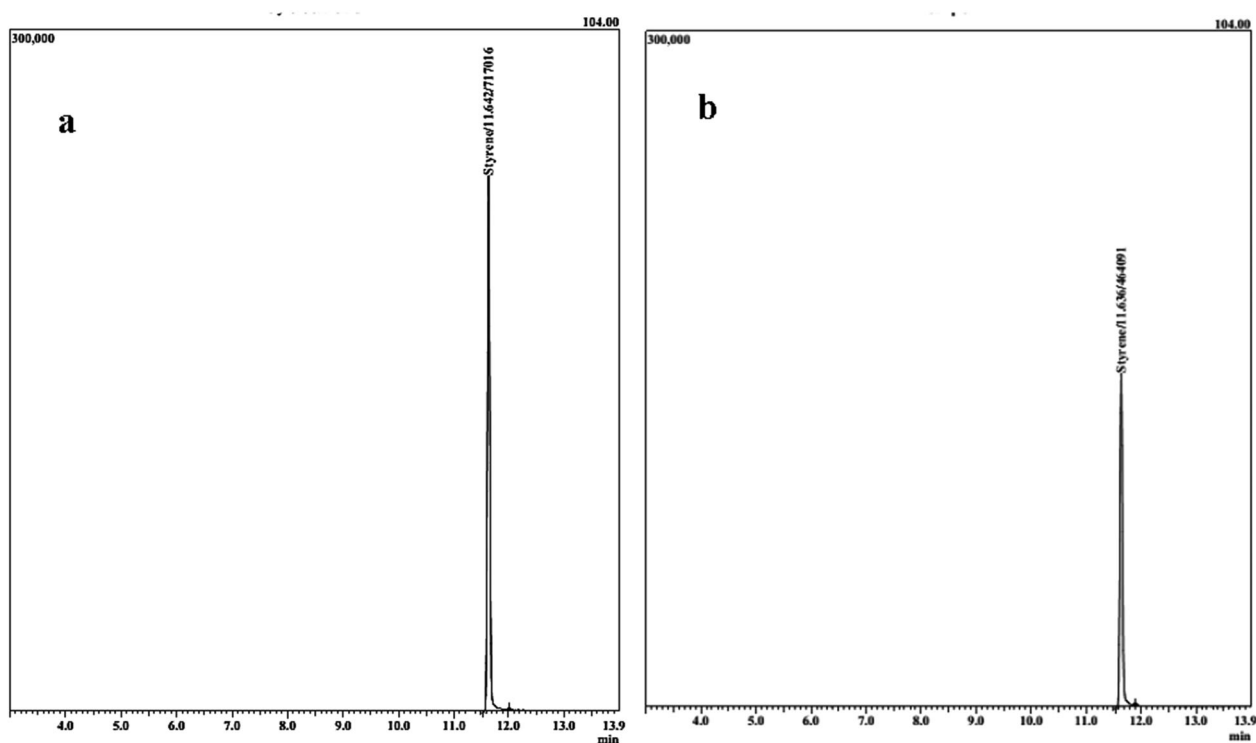
inter-molecular and intra-molecular crosslinking [27,29]. High amount of styrene could enhance the intramicrogel crosslinking reaction while low amount of styrene could diminish the intermicrogel crosslinking reaction [27,29]. Therefore, it is important to determine styrene concentration in UP to assure the balance between inter- and intra-reactions [27]. Figures 2(a,b) show the peak of styrene after 1 ml (correspond to 13,600 ppm) of pure styrene was alternatively added into an unsaturated polyester compound (with an unknown amount styrene) for two times. The integrations of these two peaks were 464,091 and 717,016, respectively. According to the method of standard addition, pure styrene was added into UP compound many times, and the GCMS of styrene with an increased integration peak was obtained. A standard addition plot was drawn with the  $x$ -axis corresponding to the amount of styrene in the test sample and the  $y$ -axis corresponding to the integrated peak after adding styrene. The result of the amount of styrene in the UP compound was 37.4% after extrapolating this standard addition plot.

After determining styrene in UP, a variety of styrene amounts were added into UP to change the styrene concentration at different ratios. Increasing the amount of styrene leads to decrease the viscosity of UP, which rises concerned question such as how much styrene amount is good for viscosity control for curing process. The curing of UP resin was conducted with a variety of different styrene amounts to find the best value for the curing process. Figure

3 shows that if the amount of styrene is too high, the styrene will not be thoroughly soluble in UP. A styrene phase separation appeared in the test tube when the styrene amount increased from 45 to 60% wt. Thus, the suitable styrene amount for processing varied from 36 to 40%. To control the amount of styrene, we incorporated a viscosity instrument and changed styrene in those samples. The different styrene amounts resulting in different viscosity indexes are recorded. This is a simple method to define the amount of styrene. Therefore, in this paper, the styrene amount is kept constantly at about 37.0% wt throughout the whole experiment (Table 2).

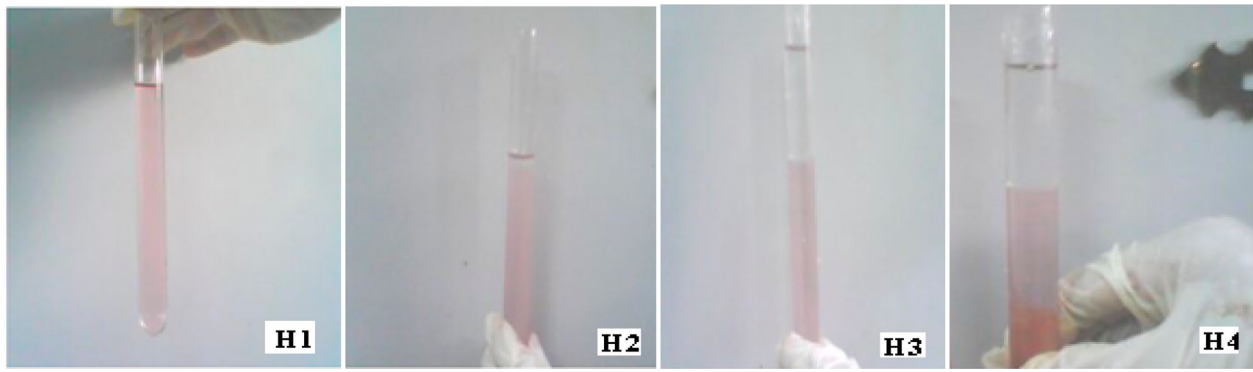
### Effect of catalyst amount on high temperature curing condition

Figure 4 and Table 3 show the heat released from the isothermally curing process with 1, 2, 3 phr BPO at 82.2°C. At 2 phr BPO, the released heat ( $\Delta H$ ) is 176.2 J/g while those are 136.1 and 151.0 J/g at 1 and 3 phr, respectively. This can be explained with two cross-linking mechanisms including inter-molecular and intra-molecular reactions that affected network formation [27]. BPO with 2 phr would balance the inter-molecular and intra-molecular reactions during the curing process resulting in the highest values of  $\Delta H$  and conversion rate. The mechanism of creating microgel particles in crosslink network is affected by using various catalyst concentrations. When the BPO concentration is 3 phr, the reaction rate between



**Figure 2.** GCMS-HS of pure styrene (1a) and GCMS-HS of styrene in unsaturated polyester sample after adding 1 ml of pure styrene (1b).





**Figure 3.** Incompatibility of styrene in UP.

microgel particles is high, but the reaction rate inside the microgel particles is slow. Therefore, in this concentration, many microgel particles could be formed and overlaid, preventing the diffusion of styrene monomer into the microgel particles. When the catalyst concentration is 2 phr, the reaction rate of microgel particles is moderate so that the styrene monomer could easily diffuse into the microgel particles then perform the crosslink reaction inside microgel particles. When the catalyst concentration is 1 phr, both the reaction rate between microgel particles and the reaction rate inside microgel particles are slow which lead to the lowest conversion rate. The styrene monomer can diffuse into the microgel particles and react with the  $-C=C$  bonds inside the microgel particles, resulting in the crosslink network structure [27]. In summary, the optimal catalyst content for UP curing is 2 phr.

### Investigation of processing conditions by DSC

The condition for cultured marble processing was optimized by DSC, the UP resin containing 2 phr BPO which was isothermally heated at 82.2°C, 110°C and 150°C for 50 min with a heating rate at 5°C/min to obtain the  $\Delta H_{iso}$ , respectively (Figure 5). On the other hand, samples were heated from 25°C to 210°C with the same heating rate to obtain the  $\Delta H_{total}$ ; the conversion rate was calculated as formulation follows:

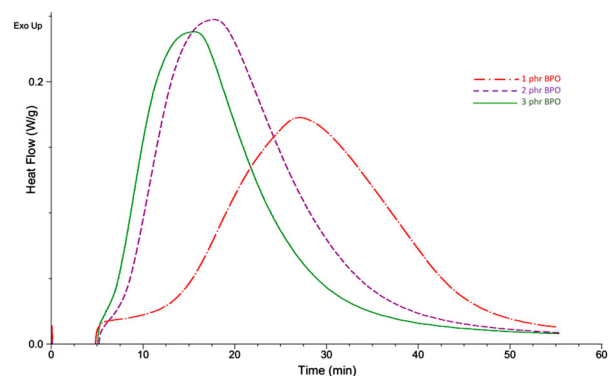
$$\text{Conversion, } \alpha = \frac{\Delta H_{iso}}{\Delta H_{total}}$$

The thermal properties and conversion rate of the samples at different temperatures are shown in

**Table 2.** Styrene concentration and its compatibility with UP resin.

Styrene amount (wt-%)		Obvious phenomenon
UP	Styrene	
62.60	37.40	Compatible (H1)
55	45	Incompatible after 90 min (H2)
50	50	Incompatible after 30 min (H3)
40	60	Incompatible (H4)

Figure 5 and Table 4. Increasing temperature leads to increasing both the mobility of UP polymer chains and the diffusion of styrene monomers, which accelerate the reactions inside and outside microgel particles. In fact, the reaction between vinylene groups from the UP chain and styrene vinyl monomers depend on the temperatures. At low temperature, the mobility of  $-C=C$  bonds of UP is low, which favours homopolymerization of styrene. However, at high temperature, the high rate of orientation of vinyl groups of UP could speed up copolymerization between vinyl groups of UP chains and vinyl styrene monomers. Moreover, the styrene and UP curing process depend on both inter- and intra- molecular reactions [27]. Some studies indicated that the competition between the two crosslinking reactions would depend on the reaction temperature [29–32] and the high temperature reaction could accelerate to ‘microgel particles’ forming [27,29]. However, we realized that curing process at temperature higher than 110°C could cause some problems including styrene loss and internal stress. In detail, when curing the cultured marble material at 150°C, crack material is observed on the final product due to internal stress. The crosslink reaction rate at 110°C is as same as that at 150°C, while the conversion rate of 110°C (86.04%) is lower than that of 150°C (90.49%). However, the final product cured at 110°C gave better property than that cured at 150°C. We suppose that at 110°C, both inter- and intra-



**Figure 4.** DSC profiles at 82.2°C by 1, 2, 3 phr BPO.

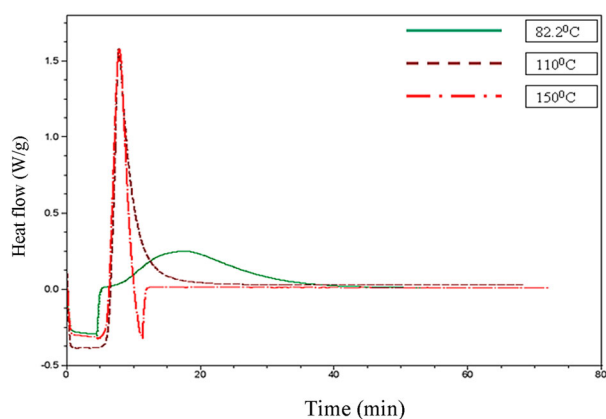
**Table 3.**  $\Delta H$  isothermally and conversion rate from DSC initiated by 1, 2, 3 phr BPO.

BPO (phr)	$\Delta_{iso}$ (J/g)	Conversion (%)
1	136.1	67.04
2	176.2	71.28
3	151.0	54.77

crosslink reactions are balance as well as the styrene loss during the curing process is slow down, which resulted in decreasing internal stress.

### Effect of low-profile additives on volume shrinkage of UP

Low-profile additives (LPAs) are thermoplastic polymers that are blended with UP resins to adjust shrinkage, increase mechanical properties, and improve surface gloss of the materials. The content of LPAs should be used at a low amount to prevent the increment of viscosity, which leads to reduce the heat resistance of the product. In previous studies, thermoplastics additives could reduce shrinkage properties of thermosetting [33–36]. Moreover, there is a significant difference in curing process at low and high temperatures. In fact, the vaporization rate of styrene solvent at high curing temperature is higher than that of styrene in low curing temperature. Therefore, we investigated these low-profile additives on the shrinkage property at high cured temperature. In this study,  $\text{CaCO}_3$  amount is empty in all experiments because the  $\text{CaCO}_3$  itself played a role as a un-shrinkage substance. The  $\text{CaCO}_3$  powder amount (200 phr) is much higher than the amount of additives (under 10 phr). Thus, if these additives (MMA, ABS, and AM) were added into the mixture of  $\text{CaCO}_3$  and UP, it would be difficult to clearly recognize the changes in shrinkage. According to Figure 6, the volume shrinkage of UP resin during the curing process was observed at 12%, this is the same value reported in the previous study [37,38]. Thus, all three additives play important role in the anti-shrinkage of UP resin after curing. In detail,

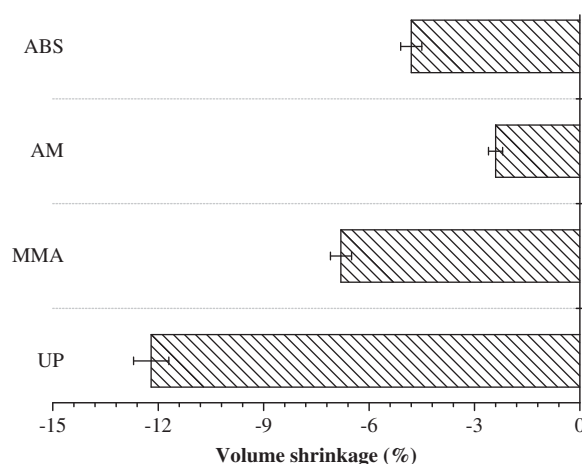
**Figure 5.** DSC curves of UP resin with 2 phr BPO at 82.2°C, 110°C and 150°C.**Table 4.** The  $\Delta H_{iso}$  (J/g),  $\Delta H_{total}$  (J/g), and conversion rate (%) of UP and 2 phr BPO at different temperatures.

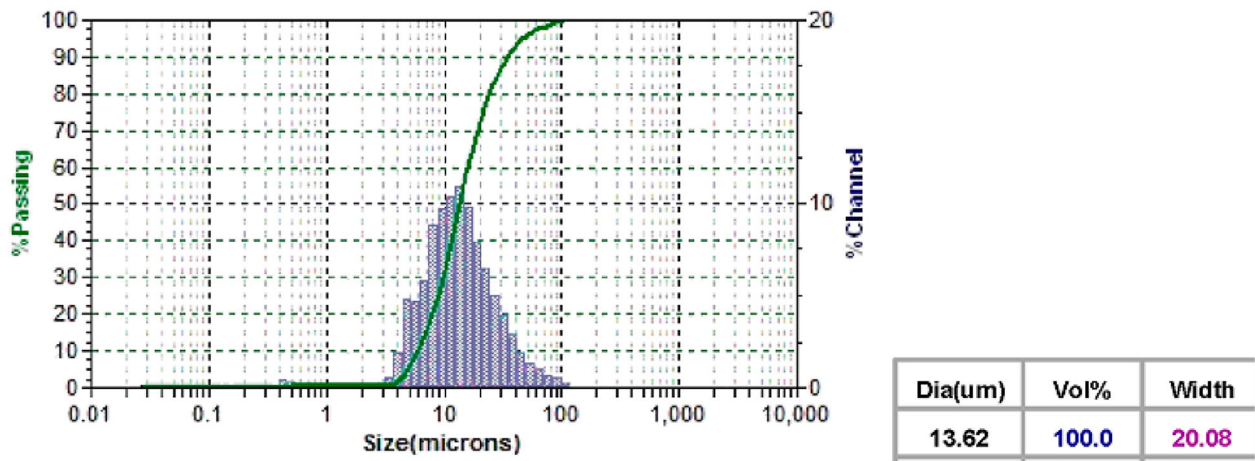
Temperature (°C)	$\Delta_{iso}$ (J/g)	$\Delta_{total}$ (J/g)	Conversion (%)
82.2	176.2	247.2	71.27
110	212.7	247.2	86.04
150	223.7	247.2	90.49

AM is the best additive in decreasing shrinkage property with a 2.44% of volume shrinkage compared to 6.76% of MMA and 4.82% of ABS. The achievement of shrinkage of LPAs in UP resin could be explained due to the segmental structures of three additives are well dispersed in the microvoids of UP resin during the curing. Moreover, with the presence of double bonds, AM acts as a coupling agent to form the cross-linking network structures with UP chains, thereby reducing the volume expansion of the resin after curing. In addition, the compatibility of AM with UP could accelerate the well dispersion of AM in UP matrix, which increase the crosslink reactions between them.

### Particle size distribution of $\text{CaCO}_3$

Theoretically, the storage module increased when increasing the amount of fine aggregate in the same particle size. At the definite amount of filler, the increase of storage module was inversely proportional to the size of filling material [39]. The composite with finely dispersed fillers increase the strength and density, while decreasing the water absorption [40]. In addition, polymer concrete with 30% UP and 70% filling material in different sizes have been successfully synthesized [41,42]. In fact, the filling material (in various sizes) increased the amount of filling material to the highest value (from 150 to 300 phr compared to UP). However, production in BMC machines requires homogeneous powder fillers. Therefore, we decided to use calcium carbonate powder in the same size. The result of calcium carbonate powder size is shown in

**Figure 6.** The effect of low-profile additive on shrinkage property of UP after curing.



**Figure 7.** Particle size analysis of  $\text{CaCO}_3$ .

**Figure 7.** The diameter of calcium carbonate powder is  $13.63 \mu\text{m}$ , and the dispersion of calcium carbonate powder is quite homogeneous. In our experiment, we realize that the amount of  $\text{CaCO}_3$  should not be higher than 200 phr. Owing to the small size and its being homogeneous, the  $\text{CaCO}_3$  has an upward trend to precipitate when concentration of powder filler is higher than 200 phr which resulted in increasing viscosity of mixtures.

#### **Effects of $\text{CaCO}_3$ contents on cross-linking and mechanical properties of cultured marble**

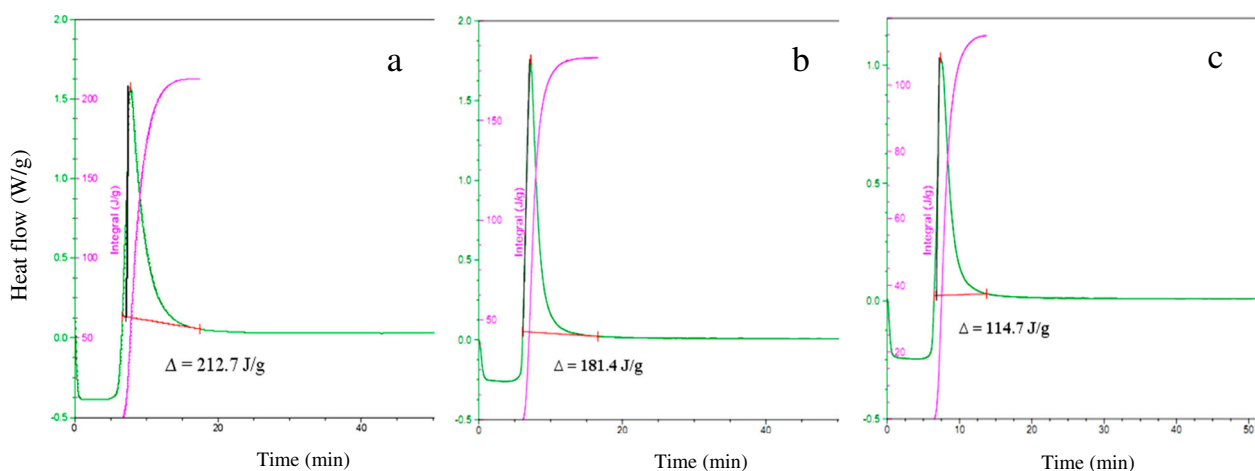
The cross-linking rate of cultured marble containing different  $\text{CaCO}_3$  contents was investigated using the DSC method with an isothermal heating at  $110^\circ\text{C}$  and  $5^\circ\text{C min}$  for 50 min to obtain the reaction heat value ( $\Delta H_{\text{iso}}$ ). The  $\Delta H_{\text{iso}}$  value of each sample during curing process was identified through the DSC curve (Figure 8). Indeed,  $\Delta H_{\text{iso}}$  obtained decreases with the addition of  $\text{CaCO}_3$  contents, it could be observed at about  $212.7 \text{ J g}^{-1}$  for a sample without  $\text{CaCO}_3$ ;  $181.4 \text{ J g}^{-1}$  for a sample with 50 phr  $\text{CaCO}_3$  and

$114.7 \text{ J g}^{-1}$  for a sample with 100 phr  $\text{CaCO}_3$ . The presence of  $\text{CaCO}_3$  reduces the cross-linking rate inside the microgel particles, leading to a decrease in conversion rate during the curing process.

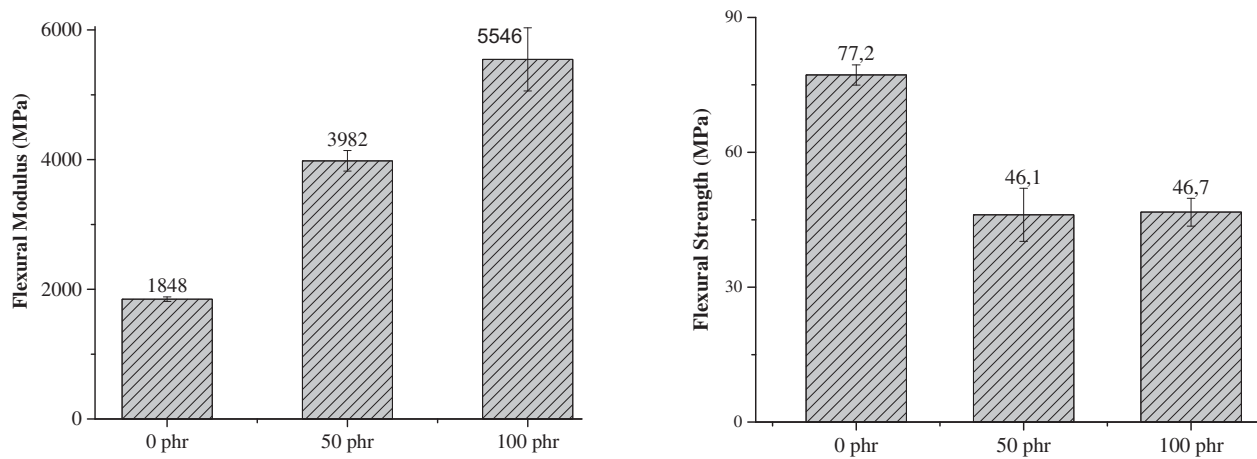
The influence of  $\text{CaCO}_3$  contents on flexural strength of cultured marble materials was also investigated in Figure 9. When increasing the content of  $\text{CaCO}_3$ , the flexural modulus increased but the flexural strength decreased. Similarly, when increasing the  $\text{CaCO}_3$  content up to 200 phr (Figure 10), the flexural module increases but the flexural strength decreases, the material becomes harder but more fragile. At a high content,  $\text{CaCO}_3$  plays the role as inorganic fillers, increasing hardness but becoming more brittle and fragile.

#### **Effects of LPAs on mechanical properties of cultured marble materials**

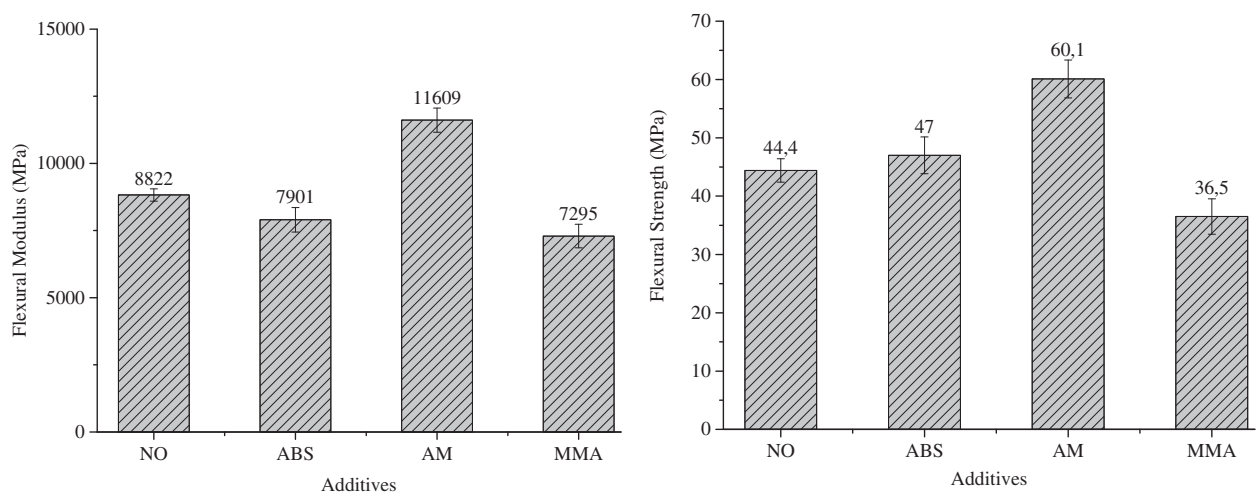
LPAs are thermoplastic polymers mixed with UP resins to adjust shrinkage and improve the mechanical properties of cultured marble materials. The LPAs are used at the same concentration of 5 phr compared to UP



**Figure 8.** DSC curves of UP resin containing 2% BPO and different  $\text{CaCO}_3$  contents at  $110^\circ\text{C}$ : (a) 0 phr  $\text{CaCO}_3$ ; (b) 50 phr  $\text{CaCO}_3$ ; and (c) 100 phr  $\text{CaCO}_3$ .



**Figure 9.** Influence of CaCO<sub>3</sub> on flexural properties of cultured marble materials.

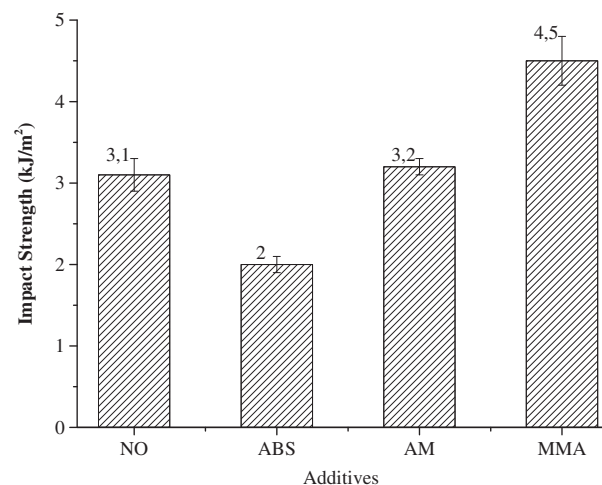


**Figure 10.** Flexural modulus and flexural strength of cultured marble with different low-profile additives at 5 phr. \* NO: Cultured marble sample with 200 phr CaCO<sub>3</sub> and without additives

resin. The effect of LPAs on flexural properties of cultured marble material is shown in Figure 10.

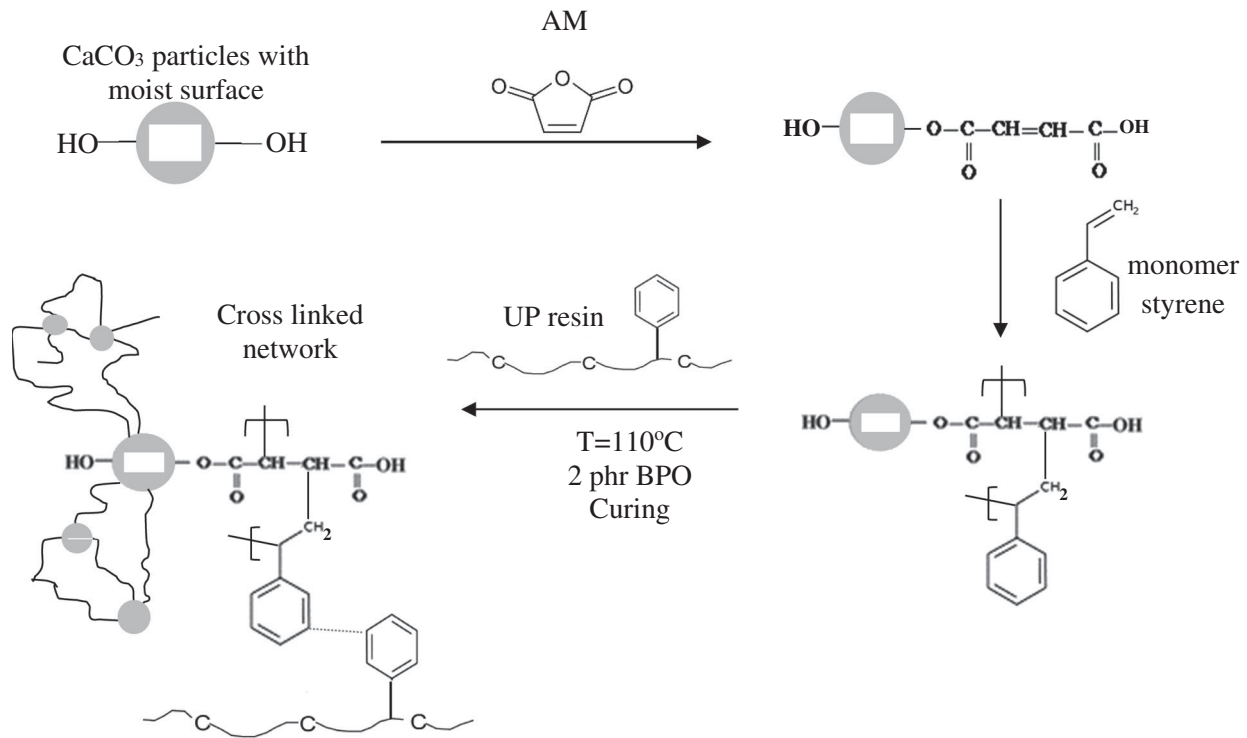
According to the diagram, the presence of MMA and ABS in the cultured marble caused the decrease of flexural modulus and flexural strength with an exception of the flexural strength of samples containing ABS, but not significantly. The reducing of the flexural modulus was observed when the LPAs were added into UP resin. This can be explained due to the fact that LPAs are thermoplastics, which have a lower modulus value than that of UP resin. The same results were found in literature [43–46]. However, only AM has shown the role in improving the flexural properties of this material. In detail, AM is the additive that has the highest flexural strength and flexural module values with the numbers being 60.09 and 11608 MPa, respectively. Results of flexural properties indicates that AM has the most positive effect; this is because AM can play a vital role as a linking substance or a coupling agent which takes part in the curing process. Moreover, AM has a higher compatibility with UP than MMA and ABS due to their similar benzen rings. This

makes a uniform dispersion and creates a homogeneous mixture when it was mixed with UP resin. During curing at high temperatures, AM molecules



**Figure 11.** Impact strength of cultured marble with different low-profile additives at 5 phr. \* NO: Cultured marble sample without additives.





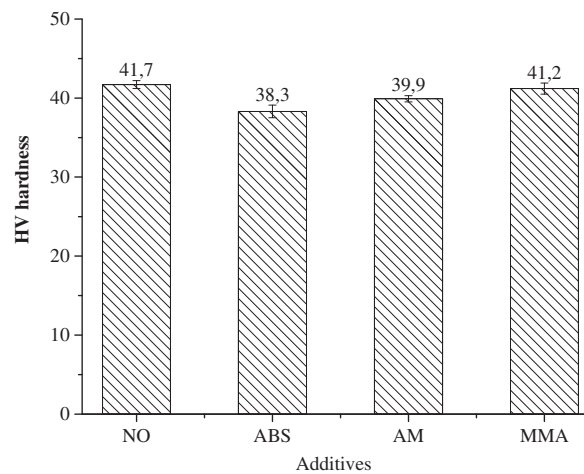
**Figure 12.** Effect of low-profile additive anhydride maleic on adhesion mechanisms between UP matrix and  $\text{CaCO}_3$  powder during curing process.

act as coupling agents, cross-linking the components together in the mixture, thereby contributing to the flexural strength of the cultured marble after curing. The results obtained in the flexural mechanical properties of cultured marble are also due to the high anti-shrinking effect of AM.

In addition, as shown from the Figure 11, the additives changed significantly, impacting the strength of cultured marble. While ABS decreases the strength of impact, at the lowest value of  $2.0 \text{ kJ m}^{-2}$ , MMA increases it at the highest value of  $4.49 \text{ kJ m}^{-2}$ .

AM also makes an increasing strength of impact value. According to a variety of mechanical property results, MMA and AM additives play the outstanding role that contribute to making a remarkable change in the strength of impact of cultured marble materials. Results of mechanical properties indicates that AM has the most positive effect on flexural and impact properties, because AM can play a vital role such as a linking substance that take part in the curing process, which enhanced their mechanical properties significantly.

In addition, the improvement of mechanical properties of cultured marble in presence of MA was explained by mechanisms as shown in Figure 12. Some functional groups such as anhydride and carboxyl in structure of AM react with hydroxyl groups of moist surface  $\text{CaCO}_3$  through esterification reaction. From there, coupling agents could be reacted with UP chains through the vinyl groups and benzene rings of styrene in UP resin during curing process at high temperature. Therefore, the low-profile additive AM acts as



**Figure 13.** HV Hardness of cultured marble with different low-profile additives at 5 phr. \* NO: Cultured marble sample without additives.

good chemical bridges to improve interfacial adhesion between UP matrix and  $\text{CaCO}_3$ , resulting in improving mechanical properties of cultured marble materials.

However, Figure 13 indicates that the HV hardness values of materials remained relatively stable regardless of used additives. It should be concluded that these additives have little influence on HV hardness of cultured marble.

## Conclusions

In summary, a cultured marble material was successfully prepared from unsaturated polyester and  $\text{CaCO}_3$

powder. All parameters for the production process as well as properties of product are studied and optimized such as catalyst, temperature, solvent, additives, CaCO<sub>3</sub> powder amount and mechanical properties. The utilization of unsaturated polyester and CaCO<sub>3</sub> powder to prepare a value product such as artificial stone would be a good option to replace natural stone. In addition, this study would be able to apply to manufacturing process including Bulk Moulding Compounds or Sheet Moulding Compounds to prepare complex shape products.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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