Recycling Studies of Marble Processing Waste: Composites Based on Commercial Epoxy Resin

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ABSTRACT: Marble waste was obtained from marble processing plant wastewater with precipitation using different coagulants, such as sepiolite, zeolite, and pumice in dosages of 0.5–8 g/500 mL and mixed in 20 wt % with commercial epoxy resin. The effects of marble, coagulant type and dosage on the physicomechanical and thermal properties were investigated. The incorporation of marble processing waste particles increases the 10% decomposition temperature of pure epoxy by 5–50°C. Surface hardness, tensile strength, percentage elongation, and stress at maximum load of the composites were higher than those of pure resin, too. The composites reinforced with marble processing waste-pumice showed about 10% increase in elastic modulus, whereas the composite reinforced with marble processing waste-sepiolite or zeolite showed about 76.67–143.33% increase in elastic modulus over the pure epoxy matrix. Scanning electron microscopy (SEM) was used for characterization of surface and cross sections of the composites to verify the results. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 24–30, 2012

Key words: waste; composites; mechanical properties; thermal properties

INTRODUCTION

The demand for advanced materials with better properties to meet new requirements or to replace existing materials is continuously increasing. Among them, epoxy resins are one of the most important classes of thermosetting polymers. Epoxy resins are widely used for many applications from microelectronics to space vessels in modern technology. Research efforts on epoxy resins have been focused on improving their thermal and mechanical stability, raising glass transition temperatures, increasing dimensional stability, lowering the dielectric constant, and enhancing flame retardance. An approach aiming to simultaneously achieve these objectives is reasonably attractive for epoxy resins used in modern electronic and electrical products, sealants, paints, coatings, and adhesives.[1–5] Due to their increasing engineering applications, epoxy resin and epoxy based composites have been extensively studied in recent years. However, these composites have some disadvantages related to the matrix dominated properties which often limit their wide application and create the need to develop new types of composite materials. In the plastics industry, the addition of filler materials to a polymer is a common practice. This improves not only stiffness, toughness, hardness, heat distortion temperature, and mold shrinkage but also reduces the processing cost significantly. In fact, more than 50% of all polymers produced are in one way or another filled with inorganic fillers to achieve the desired properties.[6–10] Formation of organic–inorganic nanocomposites has shown the ability to provide such a simultaneous improvement in several properties. To improve toughness and thermal resistance, the addition of filler particles of micro- or nano-size is becoming a common practice, because it not only improves the mechanical properties of the resulting polymer but also significantly reduces the processing cost.[11–16] This improvement depends strongly on the particle content, particle shape and size, surface characteristics, and degree of dispersion.[14–23]

Among the different curing paths, amine-cured epoxies are one of the most commonly used matrix materials in engineering applications of reinforced polymeric matrix composites, in part due to their excellent engineering performance and ease of processing before cure. Depending on the chemical structure of the curing agent, it is possible to vary the mechanical properties ranging from extreme flexibility to high strength and hardness, and the physical properties such as adhesive strength, chemical resistance, heat resistance, and electrical resistance.[24–27]

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Figure 1 Wastewater treatment of marble processing plant: (a) sedimentation pool, (b) marble waste.

Recently many researchers have investigated epoxy composites with silica, clay, carbon, or glass to improve the mechanical properties of the resin.[28–38] Lee et al.[39] recycled waste glass and stone fragments as raw materials for making artificial stone slabs using unsaturated polyester as binder. Calcite-polyacrylamide composite was used for the pore filling process by Demirdag.[40] Borsellino et al.[41] used marble powder to make a composite material with polyester and epoxy resin. Rheological, static flexural, and Izod impact tests of composites have been carried out. As seen from the literature, marble-epoxy resin composites were studied only to a limited extent, and some properties, such as thermal stability, surface hardness, tensile strength, and percentage elongation were not investigated.

Marble is a metamorphic rock composed mainly of calcite (a crystalline form of calcium carbonate, $CaCO_3$) and other minerals such as muscovite, sericite, and chlorite. One of the crucial problems of the marble industry is the particles, which are generally less than 150 microns, generated during the cutting stage. Cutting and polishing are wet processes whose resultant wastewater is generally treated by flocculation.[42] The amount of marble dust waste produced in Turkey reaches 2.7 tons/m^3 (Fig. 1) and is used as a filler or additive for industrial applications, including paint, glass, paper, cement, and concrete production. It can be used to make a new class of waste/polymer composites. Therefore the aim of this study was to evaluate the effect of the different contents of marble processing waste filler on the physicomechanical properties and thermal stability of epoxy resin.

EXPERIMENTAL

Materials

Marble processing waste used in this experimental research was obtained from the wastewater of Kombassan Marble Plant of Konya City, Anatolia Region of Turkey, kindly supplied by the Mining Engineering Department of Selcuk University (Fig. 1). The chemical compositions of the marble and coagulants are given in Table I. The thermosetting matrix used in this study was a commercially available bisphenol A-type epoxy resin (DER 321, Dow Chemical Co.) modified with aromatic diluent and cured at high temperature with 30 wt % Polypox Hardener 043. The curing agent was a cycloaliphatic polyamine. The epoxy content of ER was 23.12%, as determined by acid titration.[43]

TABLE I
Chemical Composition (wt %) of the Marble (Kombassan Marble Plant) and Coagulants

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	SO_3	Na_2O	CaO	TiO_2	MnO
Marble	0.67	0.13	0.070	0.007	0.67	–	0.028	54.57	–	0.005
Zeolite	70.9	12,4	1,21	4.46	0.83	–	0.28	2.54	0.089	<0,01
Sepiolite	60.42	1.83	–	0.14	20.65	0.07	–	1.82	–	–
Pumice	60.50	17.15	3.38	4.54	2.09	0.16	4.30	4.68	0.41	–

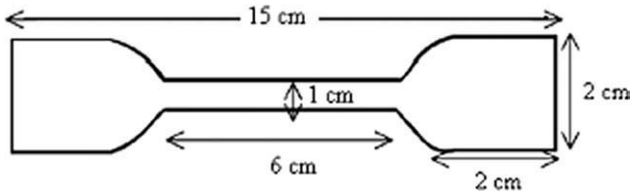

Figure 2 Dumb-bell shape of MPS specimens.

Separation of marble processing waste

Sepiolite, zeolite, and pumice were added in various dosages to marble processing wastewater, mixed, and then left to settle. The resulting precipitate was filtered and dried.[44]

Forming of composites

The marble processing waste in 20 wt % and epoxy resin matrix were mixed with mechanical stirring for 30 min. Afterwards, 30 wt % Polypox Hardener 043 was added and the mixture was degassed for 60 min at 40°C and then transferred into the mold. Composite specimens were prepared in stainless-steel molds according to ASTM D 638 standard. The curing procedure was realized in an oven within 24 h while increasing the temperature from 60 to 120°C. The dumbbell shape of the specimens with proper dimensions is shown in Figure 2.

Characterization of composites

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) was performed to investigate the interface between the filler and the polymeric matrix with a Philips XL30 SFEG instrument.

Mechanical testing

A Shore Durometer TH 210 tester is used for measuring hardness. The resistances to stretch properties were determined by Stretch and Pressing Equipment TST-Mares/TS-mxe.

Thermal analysis

The thermal analysis experiments were performed with a Seteram thermogravimetric analyzer. Samples were heated under a nitrogen atmosphere from 50 to 600°C at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Characterization

Morphological investigation of epoxy/marble processing waste composites

The morphology of the cured epoxy/marble processing waste resins was determined by means of SEM. The pure epoxy matrix is transparent but the addition of marble processing waste made the composite opaque. Figures 3 and 4 show typical SEM images of the neat epoxy and composites, as an example. SEM has the advantage of giving a broad overview of the microscale dispersion of the marble in these materials. For pure epoxy, the fracture surface was smooth, typical of a glassy material (Fig. 3). In contrast, the specimens containing marble processing waste showed a considerable fracture surface roughness. The SEM images show a combination of coarse features with debonding between the matrix and marble at different locations. It can be seen that marble particles in these composites exist in the form of aggregates.

The fracture surface images of composites were different because of various coagulants in marble processing waste which affected the morphology of composites. As seen from Figure 4(a), marble processing waste aggregates with sepiolite are randomly dispersed in the epoxy matrix, but are well connected with each other, which results in enhanced mechanical properties as shown in "Physico-mechanical properties" section. The best results for the tensile test were obtained for these composites. Marble with pumice was well connected with the epoxy matrix, but created a layered structure in the composite [Fig. 4(b)]. Therefore, these composites showed elongation values close to composites containing sepiolite, but higher tensile strength. The spaces in the composite fracture surface SEM image depending on the structure of zeolite affected the elongation percentage of the composite [Fig. 4(c)]. The lowest elongation was seen for composites containing marble processing waste with zeolite.

Physicomechanical properties

Mechanical analysis was performed to study how different morphologies influence the mobility of the epoxy. To investigate physicomechanical properties, such as tensile strength, elongation at break, and hardness of the composites, mechanical testing was performed. The results are summarized in Table II.

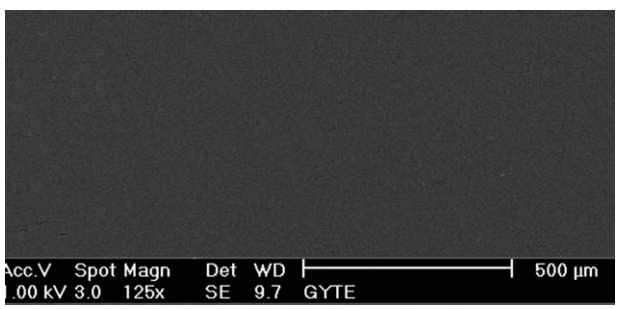

Figure 3 Surface SEM image of neat epoxy sample.

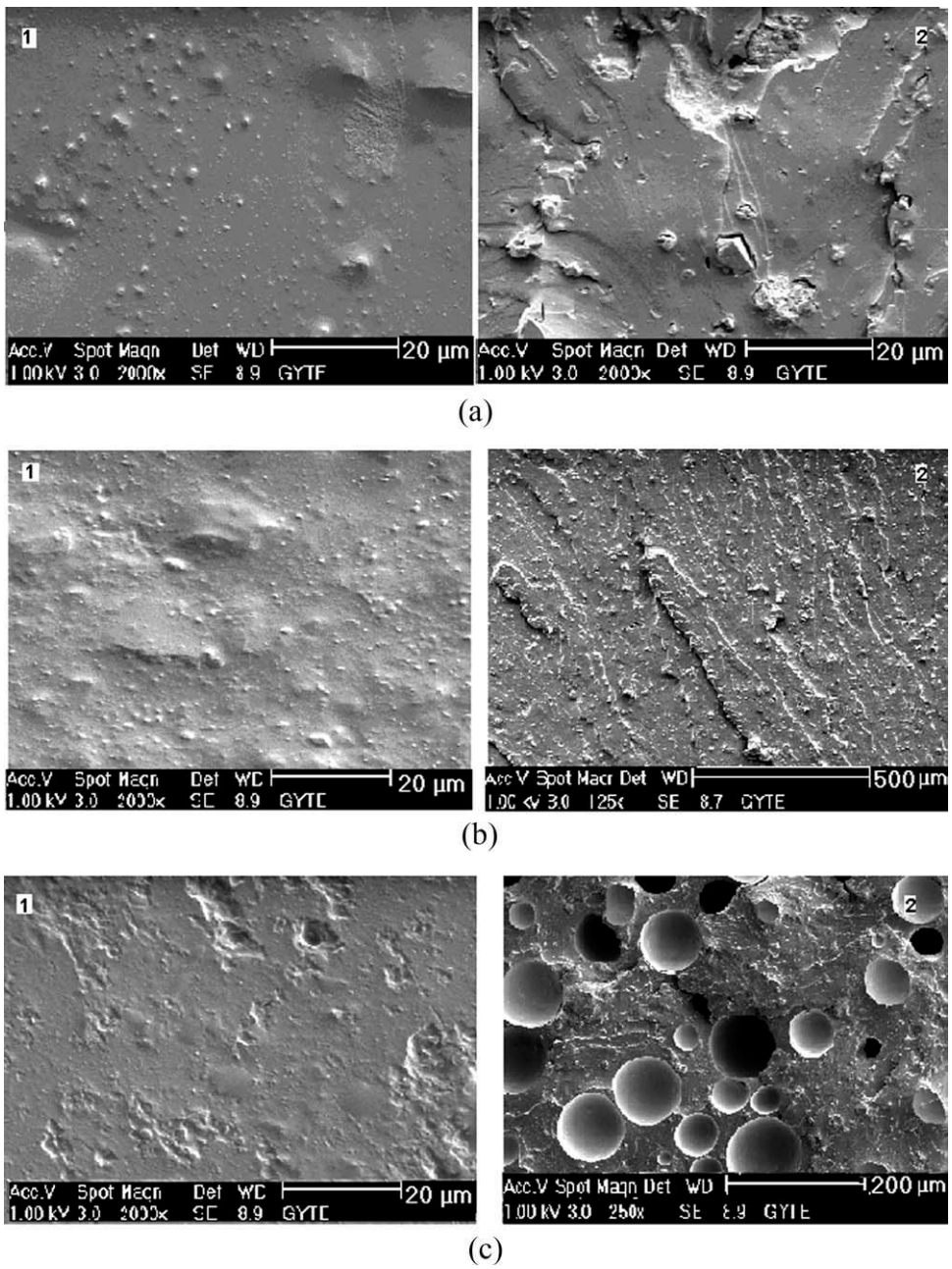

Figure 4 SEM images of epoxy/marble waste samples (1-upper surface; 2-fracture surface) with: (a) sepiolite dosage 2 g/500 mL; (b) pumice dosage 4 g/500 mL; and (c) zeolite dosage 8 g/500 mL.

The tensile stress–strain curves of neat epoxy and epoxy/marble waste composite systems are shown in Figure 5. It was determined that the physicomechanical properties of composites changed depending on the content of filler, i.e., coagulant type. The tensile test results obtained for pure epoxy resin were as follows: elongation percentage at break was 0.372% and tensile strength was $2.18N/mm^2$. It can be seen that all composites show higher elastic (Young) modulus and strength than the pure epoxy matrix. The composites reinforced with marble processing waste-pumice showed about 10% increase in elastic modulus, whereas the composite reinforced with marble processing waste-sepiolite or zeolite showed about 76.67–143.33% increase in elastic modulus compared with the pure epoxy matrix. The improvement in strength and modulus can be attributed to the high strength and high aspect ratio of marble particles as well as to the uniform distribution and good interfacial adhesion between the particles and the epoxy matrix. They also showed a higher elongation percentage than the pure epoxy. Elongation at break of composites increases with an increase in the filler of coagulant dosage up to 2 g/500 mL in all cases. The rigid filler usually decreases the elongation of the matrix, but it is

TABLE II
Effect of Sepiolite, Pumice, and Zeolitr Dosage on Physico-Mechanical Properties of ER/Marble Waste Composites

Coagulant dosage, g/500 Ml	Elongation at max. load, %	Tensile strength, N/mm^2	e-modulus	Hardness, Shore D
–	0.372	2.18	10	58
For sepiolite				
0.5	0.582	5.83	18.571	60
2	0.959	5.43	18.929	63.5
4	0.630	5.75	17.857	57
8	0.589	5.52	17.667	58
For pumice				
0.5	0.917	1.63	5.517	56
2	0.684	2.94	8.276	61
4	0.637	3.01	11.379	57.5
For zeolite				
0.5	0.794	6.47	18.276	60
2	0.568	6.99	24.333	61
6	0.657	6.99	22.069	67.5
8	0.532	7.49	21.786	67

reported in the literature[45–49] that rigid fillers can be increase the elongation at break. Tien and Wei[45] reported that the elongation at break of the nanocomposites with montmorillonite were 27–69% higher than that of pure polymer matrix. Interfacial interaction between clay and polyurethane contributed to the dangling chain formation in the matrix and caused a plasticizing effect in polymer. Chen et al.[46] studied the mechanical properties of organoclay/polymer composites. The tensile strength and elongation of composites were found higher than that of pure polymer. The effects of Al_2O_3 nanoparticles on thermal, dynamic mechanical and tensile properties of epoxy/Al_2O_3 nanocomposites were investigated by Chen et al.[47] It was observed that both tensile modulus and elongation at break of epoxy based nanocomposites were increased as the Al_2O_3 contents were increased. The tensile strength and elongation at break of carbon nanotube/epoxy composites were

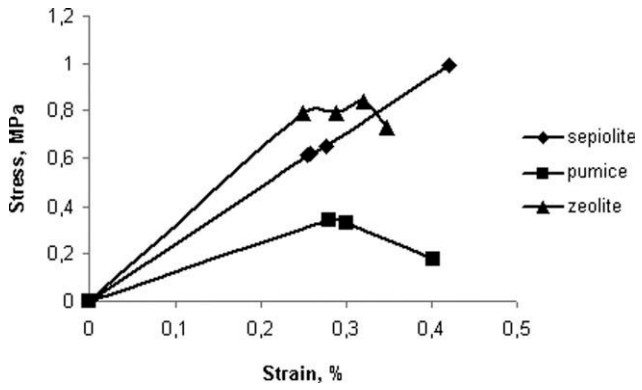

Figure 5 Tensile behavior of epoxy/marble processing waste systems with sepiolite, pumice, and zeolite.

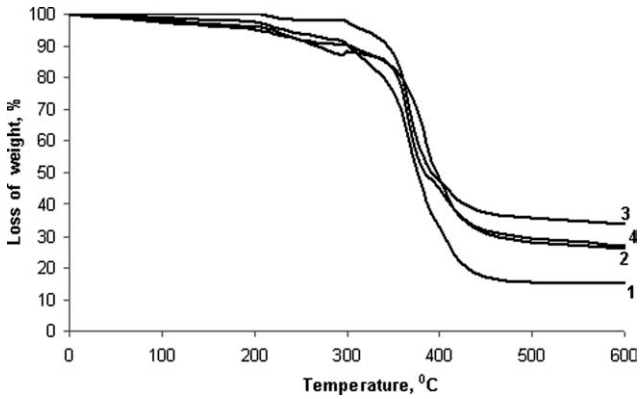

Figure 6 TGA curves of neat epoxy (1) and epoxy/marble waste samples with: (2) sepiolite dosage 2 g/500 mL; (3) pumice dosage 4 g/500 mL; (4) zeolite dosage 8 g/500 mL.

improved by 0.9% and 7.7%, respectively, compared with neat epoxy.[48] Elongation % at break of carbon nanotube/epoxy composites were found higher than pure epoxy by Sun et al., too.[49]

From the tensile test results, as the coagulant dosage in marble processing waste increased, the tensile strengths of the composites usually increased. The hardness measurements showed similar results to the tensile tests, since there is a corelationship between the hardness and the tensile strength in terms of mechanical property. In marble processing waste composites with sepiolite, the tensile strength changed in the range 5.43–5.83N/mm^2. The highest elongation percentage obtained for composite was 0.959%, in which the marble processing waste used was precipitated with 2 g/500 mL sepiolite dosage. As the sepiolite dosage is further increased, there is a decrease in the composite's elongation percentage. In marble processing waste composites with pumice, the best results obtained for elongation and tensile strength were 0.917% and 3.01N/mm^2, respectively. The appropriate pumice dosages were 0.5 g/500 mL and 4 g/500 mL. Among all coagulant types, the highest tensile strength data were found to be 6.47–7.49N/mm^2 for marble processing waste composites with zeolite. The hardness of these composites was higher than others, too. The appropriate zeolite dosage was determined as 8 g/500 mL.

As seen from Figure 5, the curve for the epoxy/marble composite with pumice shows yielding followed by much-broadened strain-hardening region as compared with the composites with sepiolite and zeolite counterpart indicating increased ductility. The composite with zeolite exhibits higher yield stress and a short strain-hardening region. The composite with sepiolite shows significant improvement in stress–strain properties as it exhibits much higher yield stress and ultimate stress with slight improvement in ductility in contrast to the other composites.

TABLE III
IDT, SDT, and MDT Values for Pure Epoxy and its Composites

Sample	IDT (°C)	SDT (°C)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	MDT (°C)
Pure ER	150	335	220	295	375	450
ER/marble waste (with sepiolite)	125	325	210	310	395	425
ER/marble waste (with pumice)	230	325	325	345	398	415
ER/marble waste (with zeolite)	125	310	250	300	398	425

Thermal stability

The principal characteristics and products of thermal degradation of a commercial epoxy resin prepared by reaction of 2,2-bis(4′-hydroxy phenyl)propane (bisphenol-A) with 1-chloro-2,3-epoxy propane (epichlorhydrin) have been studied by Grassie et al.[50] The principal volatile products, acrolein, acetone, and allyl alcohol, are formed at 280°C, although cross-linking is detectable at 220°C. Decomposition of the cross-linked resin occurs above 340°C, when phenolic compounds appear. Erickson studied the thermal degradation of epoxy at 340°C. Evolution of phenol, 4-isopropylphenol, bisphenol A, and 4-*t*-butyl-*o*-cresol indicate that bond scission involving the bisphenol A moiety in the epoxy is a major decomposition mechanism.[51] Neiman et al. reported that H_2, CO, CH_4, C_2H_4, C_2H_6, and C_2H_8 were found among the gaseous products formed in the thermal degradation in the temperature range 300–450°C of the epoxy resin hardened by polyethylene polyamine (PEPA). Ethane, ethylene, propylene, and propane are possibly produced by decomposition of the PEPA radical.[52]

Figure 6 show TGA curves of the pure and marble processing waste filled epoxy resins. The thermograms obtained during TGA scans were analyzed to give the percentage weight loss as a function of temperature (Tables III and IV). The thermal degradation of pure epoxy resin occurs in two steps. The first was in the range of 150–280°C and may be due to decomposition of the end hydroxyl group of polyamine-cured epoxy resin and olefin formation. The second degradation stage was observed at 335°C and showed decomposition of the bisphenol-A group (Fig. 6). T_5, T_{10}, and T_{50} (the temperatures of 5%, 10%, and 50% weight loss, respectively) are the main criteria indicating the thermal stability of the composites. The higher the values are, the higher is the thermal stability. Initial (IDT), second (SDT), and maximum (MDT) degradation temperatures and degradation temperatures at 5, 10, and 50% weight loss of composites are given in Table III, which indicate that the thermal stability of the pure epoxy was enhanced by the incorporation of marble processing waste particles with various coagulants. Further, the incorporation of marble processing waste particles with sepiolite, pumice, and zeolite in pure epoxy matrix increases the 10% decomposition temperature of pure epoxy by 15, 50, and 5°C, respectively. The composites also show higher char content or reduced weight loss at 600°C. While pure epoxy shows a char content of 15%, the composites show about 27, 34, and 26% for epoxy/marble with sepiolite, pumice, and zeolite composites, respectively, (Table IV). As seen from Tables III and IV, the best thermal results were obtained for pumice coagulant. Therefore, the incorporation of the marble processing waste particles resulted in pronounced improvement in thermal stability. This can be attributed to the homogeneous distribution of marble processing waste particles in the composites. The improvement of thermal stability due to the addition of nanoparticles has also been reported for other composites.[53–55]

CONCLUSIONS

Marble processing waste, which was precipitated from wastewater with different coagulants, was used to prepare 20 wt % marble/epoxy composites. Morphological, tensile, and thermal properties of a bisphenol A-based epoxy resin modified with waste

TABLE IV
Effect of Coagulant Type on Thermal Properties of ER/Marble Waste Composites

	Loss of weight, %					Residual weight, %
Composite	200°C	300°C	350°C	400°C	450°C	600°C
Pure epoxy resin	4	8	25	67	83	15
ER/marble waste (with sepiolite)	5	12	17.5	55	68	27
ER/marble waste (with pumice)	0	2.5	12.5	52.5	62.5	34
ER/marble waste (with zeolite)	2.5	8.5	17	52	69	26

filler and cured using polyamine were determined experimentally. The morphology of the cured samples, as seen by SEM, shows that a complete separation of the marble processing waste particles was not attained. All composites show higher elastic (Young) modulus, elongation at break, and tensile strength compared with the pure epoxy matrix. The incorporation of the marble processing waste particles resulted in pronounced improvement in thermal stability, too. In the tensile test, the best results were seen with the marble processing waste in which sepiolite coagulant was used. Composites consisting of marble processing waste with pumice coagulant have higher thermal resistance.

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