

Effect Of Talc On The Physical, Microstructural And Mechanical Properties Of Reaction Sintered Zirconia Toughened Mullite Composites

H.Aydın* , G.Tokataş

Department of Metallurgy and Material Engineering, Kütahya Dumlupınar University, 43100 Kütahya, TURKEY

*Corresponding author H.Aydın;

ABSTRACT: In this study the effect of talc $Mg_3Si_4O_{12}H_2$ additive on the physical, microstructural and mechanical properties of zirconia toughened mullite (ZTM) is discussed. The talc additive in ZTM not only stabilizes the tetragonal zirconia phase but also acts as a sintering aid for the formation of cross-linked mullite grains. Specimens such as pellets and rectangular bars were manufactured for ZTM with various amounts of talc additions (4 and 7 wt.%). The manufactured samples were sintered at 1450, 1500 and 1550°C temperatures for 5 hrs. The physical properties of sintered samples such as bulk density, theoretical density, percentage of linear shrinkage were examined. X-ray diffraction patterns confirm the constituent phases present in the samples were mullite and zirconia. The microstructure of all the composites is composed of irregularly shaped mullite grains, and round-shaped zirconia grains which are distributed homogeneously. The samples were subjected to mechanical tests like modulus of elasticity, flexural strength. It was observed that the addition of talc was improved the elastic modulus, flexural strength of the ZTM.

KEYWORDS: Zirconia toughened mullite composites, Talc, Properties, Reaction sintering.

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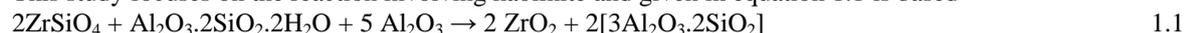
I. INTRODUCTION

Over the past years a number of different studies have been conducted on zirconia toughened mullite (ZTM) composites selecting different synthesis methods and using different kinds of raw materials by various researchers due to their excellent thermomechanical properties [1-8].

ZTM is one of the basic ceramic matrix composites traditionally used for refractories and glass industry because of its high temperature mechanical properties as well as good wear and thermal shock resistance. Improving physical and mechanical properties with zirconia additives in the mullite matrix is a well accepted phenomena [9-10]. Many other additives are used to manufacture zirconia toughened mullite ceramics: these are mainly magnesia, calcia, titania, yttria, ceria, dysprosia, colemanite, ulexite etc [1,2, 7-11]. Various manufacturing methods for preparing mullite-zirconia composites have been reported [12] including: (a) sintering of mixed mullite and ZrO_2 starting powders, (b) reaction sintering of silica, alumina and zirconia, and (c) reaction sintering of alumina and zircon. In this study, unlike the literature kaolinite was added to the mixture of zircon and alumina.

Among these manufacturing methods, the reaction sintering is the most common one because of its advantages to use cheap traditional raw materials and low manufacturing cost [13].

This study focuses on the reaction involving kaolinite and given in equation 1.1 is based



Due to the high purity of the precursors, complete decomposition of $ZrSiO_4$ into ZrO_2 and SiO_2 , owing to its high purity, is assumed; similar to the disintegration of kaolinite which yields 1 mol of Al_2O_3 and 2 moles of SiO_2 . Correspondingly, Al_2O_3 used in the reaction is also considered to be highly pure, in regards to synthesize 2 moles of mullite.

Owing to the impurity content of the precursors (besides the molar ratio), the weight ratio of Al_2O_3/SiO_2 is kept approximately as 2.5. The amount of talc, which consists of natural sources, is precisely controlled due to the limits of MgO content that plays a significant role in partially stabilizing the zirconia.

The goal of the present investigation is to characterize the reaction sintered zirconia toughened mullite composites, prepared from zircon, kaolinite and alumina in presence of talc additive. The effects of talc content and sintering temperature on the phase evolution, microstructure and mechanical properties of the investigated bodies are thoroughly studied. Another goal of the study is to make a contribution to scientific literature concerning studies on sintering of mullite-zirconia composites at lower temperatures by taking advantage of talc ($Mg_3Si_4O_{12}H_2$). Apparently, if zircon's dissociation occurs at lower temperature and reaction of alumina with silica is fast, mullite-zirconia synthesis gets pulled to low temperature. There is a case study in which the MgO addition lowers the zircon decomposition temperature and hence the mullite-zirconia synthesis temperature [14].

II. EXPERIMENTAL

Starting powders were zircon with $D_{0.5} = 1.62 \mu m$ ($ZrSiO_4$, Johnsen Matthey, Sereltas, Istanbul, kaolinite with $D_{0.5} = 10.20 \mu m$ ($Al_2Si_2O_5(OH)_4$, Kutahya Porselen, Kutahya), commercial calcined alumina with $D_{0.5} = 92 \mu m$ (Al_2O_3 , BDH Limited Poole, Germany) and talc with $D_{0.5} = 15.20 \mu m$ ($Mg_3Si_4O_{12}H_2$, Kutahya Porselen, Kutahya). Three batches, M1-M3, were calculated according to Table 1. The starting powders were mixed in a ball mill for 6 h in zirconia pot using zirconia ball as grinding media in methyl alcohol medium at the speed of 300 rpm/min. Resulting mixtures were initially 24 h naturally dried followed by 24 h drying at $100^\circ C$ in drying oven. Dried mixtures obtained were crushed to break the lumps and passed through 500 μm sieve to get the desired powder mixtures. Afterwards, prepared mixtures were uniformly mixed with 5 wt.% PVA solution as binder and shaped into bars (size 75 mm \times 5 mm \times 55 mm) for flexural strength and elastic modulus measurements and pellets (size d 10 mm) for density, phase and microstructure analyses by uniaxially pressing at 2 tons. The formed specimens were sintered at 1450-1550 $^\circ C$ for 5 hr. at a heating rate of 5 $^\circ C \text{ min}^{-1}$. Bulk density of specimens were determined by the Archimedes method. It was measured by calculating the linear shrinkage of the samples as a percentage of the original length of the sample, L_0 (in mm), from the equation:

$$\text{Percentage of Linear Shrinkage} = \left(1 - \frac{L_D}{L_0}\right) 100$$

Where L_D is the length of the sintered sample (in mm).

Table 1: Investigated batches compositions.

	Compositions, wt. %			
	Zircon	Alumina	Kaolinite	Talc
M1	30	45	25	-
M2	23.80	45	27.21	4
M3	40	43	10	7

Phases of sintered specimens were defined by X-ray diffraction (XRD, Rigaku, MiniFlex) at $10-45^\circ$ and a scanning speed of $2^\circ (2\theta)$ per minute. The microstructure of the specimens and energy dispersive X-ray (EDX) analyses were carried out by means of scanning electron microscope (SEM, FEI Nova NanoSEM 650).

The flexural strength (σ , MPa) and elastic modulus (E, GPa) of composites at room temperature were evaluated by three-point bending method (with a span of 40 mm and cross-head speed of 0.5 mm/min) using universal testing machine (model No. Instron 5581). For each specimen, at least 5 bending tests were applied, and mean values were taken as strength and elastic modulus (experiments were repeated for non-logical findings).

III. RESULTS AND DISCUSSION

1.1. Phase compositions

Figure 1-3 represented the XRD patterns of the sintered specimens. Diffractograms of as sintered composites are shown in Figures 1 and 3 presenting at $10-40^\circ$ of 2θ . According to figure 1, mullite as the main phase, t-ZrO₂ and m-ZrO₂ phase of zirconia and some corundum and zircon phases were detected. Zircon, corundum, mullite and m-ZrO₂ phases which indicated a low dissociation of zircon were observed in XRD patterns belonging to M1 batch sintered at $1450^\circ C$. Results show that zircon was partially decomposed and alumina played a significant role in mullite formation. Zircon dissociation usually starts at a temperature of $1670^\circ C$, but the presence of impurities in the starting powders could be at the origin of the lower temperature of dissociation [15-16]. At temperatures of 1500 and $1550^\circ C$, corundum phase disappeared, yet zircon remained partially unreacted.

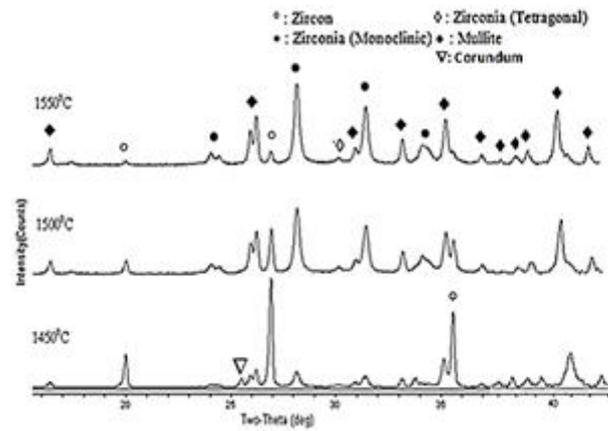


Fig.1:XRD patterns for additive-free mixture (M1) sintered at a temperature of 1450, 1500 and 1550°C.

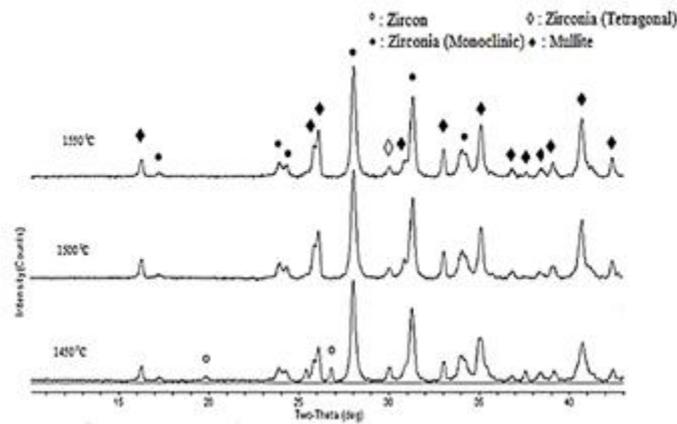


Fig.2:XRD patterns for M2 sintered at a temperature of 1450, 1500 and 1550°C.

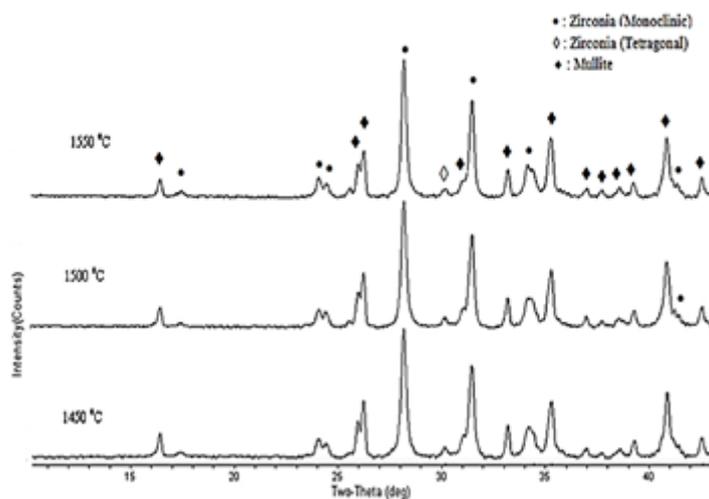


Fig.3:XRD patterns for M3 sintered at a temperature of 1450, 1500 and 1550°C.

When kaolinite is calcined at elevated temperatures, dehydroxylation occurs which collapses the crystal structure to produce amorphous metakaolinite ($\text{Al}_2\text{Si}_2\text{O}_7$). The thermal transformation of metakaolinite above 1000 °C first produces aluminasilicate phase which transforms into mullite. Above 1150 °C, amorphous silica (cristobalite, SiO_2) is formed [17]. Similarly, zircon decomposes into zirconia and silica. Released silica again reacts with alumina to form stoichiometric mullite [11].

Sintering of M2 and M3 at 1450-1550 °C resulted in an ocularly dissociation of zircon to zirconia and amorphous silica which reacted with alumina to form mullite. The zircon dissociation was enhanced considerably with the 4-7 wt.% talc additions. Besides, the increase of sintering temperature was more effective in the dissociation of zircon when the talc was added. XRD pattern of M3 at 1550 °C, zircon phase did not appear (Fig.3). Although MgO in talc addition was expected to stabilization zirconia in the tetragonal form [8, 15], most of the zirconia reflections indicated the monoclinic zirconia. Required amount of talc was not sufficient to provide the suitable amount for the stabilization.

It is well known that ZrO_2 phase transformation is related to a presence of SiO_2 . At low temperature such as 1400°C, ZrO_2 and amorphous SiO_2 is formed due to zircondissociation. ZrO_2 particles is immersed in the amorphous SiO_2 matrix, which stabilizes ZrO_2 as t- ZrO_2 phase. At higher temperature, the amorphous SiO_2 is consumed to form mullite and losing the ability to stabilize ZrO_2 ; thus, the ZrO_2 in the samples obtained at higher temperature mainly exist in m- ZrO_2 phase [20].

1.2. Densification behaviour

Increasing the sintering temperature have shown a positive effect on the densification behaviour for all composites, as expected. It can be seen that densification rate of the specimens containing talc additive is higher than that of the specimen without additive. The results approve that increasing the sintering temperature leads to an increase of the bulk and teorical density (Table 2). At 1550°C, bulk density reached 3.31 g/cm^3 . However, all the composites were not pore free. Hence, by the presence of large pores and formation of a small amount of highly viscous liquid phase, which lead to sealing of some pores as closed pores, which inhibited them to merger [18].

The theoretical densities of the composite materials can be calculated from the sum of the product of the density of each phase and the volume fraction.

The mathematical expression of the described method is as follows.

$$\rho_{\text{Comp.}} = f_A \rho_A + f_B \rho_B + f_C \rho_C$$

In this study, it can be considered that the theoretical density will vary between 3.52 and 3.54 g/cm^3 when both monoclinic and tetragonal phases of zirconia are present in most monoclinic mullite-zirconia

composites synthesized. It can be seen that densification rate of the samples containing talc additive is higher than that of the sample without additive. All specimens with talc additive have achieved optimum bulk and theoretical density at 1550 °C, whereas specimens without additive haven't attained the same level of densification at 1550 °C.

Table 2: Percentage of linear shrinkage, bulk density in g/cm³ and theoretical density values

		M1	M2	M3
1450°C	Linear Shrinkage	% 2	% 9	%
	Bulk Density	2.14	3.06	3.16
	Theoretical Density	61	87	90
1500°C	Linear Shrinkage	% 4	%	%
	Bulk Density	2.21	3.10	3.24
	Theoretical Density	63	88	92
1550°C	Linear Shrinkage	% 9	%	%
	Bulk Density	2.96	3.19	3.31
	Theoretical Density	84	91	94

1.3. Mechanical properties

Room temperature flexural strength (σ) and elastic modulus (E) of M1-M3 specimens are presented in Table 3 and Table 4, respectively. The values for the samples with talc additive were higher than those for the sample without the additive. Sample M1 (without additive) have shown flexural strength of 166 MPa and elastic modulus of 92 GPa at 1550 °C. With addition of talc, slight improvement in flexural strength and elastic modulus is provided. Specimens with 4 wt.% talc exhibited 171 MPa of flexural strength and elastic modulus of 112 GPa. The mechanical properties of samples were gradually enhanced when the amount of talc added was increased (7 wt. %). It is mentioned that uniform microstructure and dense structure can improve the mechanical properties of the composite in terms of flexural strength and elastic modulus [19].

Table 3: Flexural strength (σ) of M1-M3 sintered at 1450-1550 °C, 5 h.

Temperature (°C)	Strength (σ -MPa)		
	M1	M2	M3
1450	63±8.5	97±15.33	102±8.3
1500	108±13.36	148±15.47	156±10.25
1550	166±12.21	171±15.78	176±8.16

Table 4: Elastic modulus (E) of M1-M3 sintered at 1450-1550 °C, 5 h.

Temperature (°C)	Elastic Modulus (E-GPa)		
	M1	M2	M3
1450	34±8.25	57±12.86	62±10.45
1500	72±8.68	98±19.19	103±12.59
1550	92±9.59	112±16.52	117±11.99

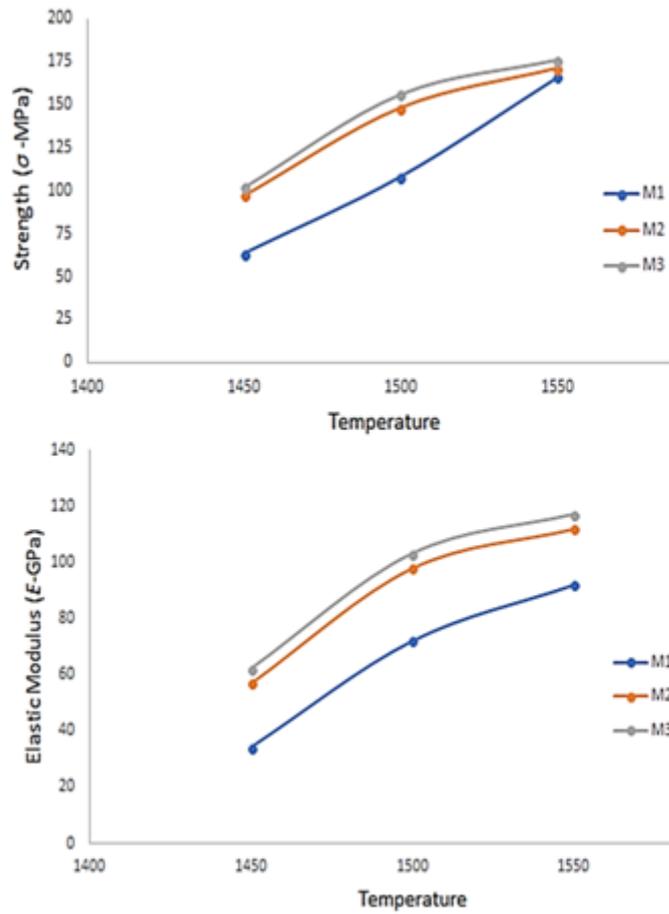


Fig.4: Flexural strength (σ) and Elastic modulus (E) of M1-M3 sintered at 1450-1550 $^{\circ}\text{C}$, 5 h.

1.4. Microstructure characterization

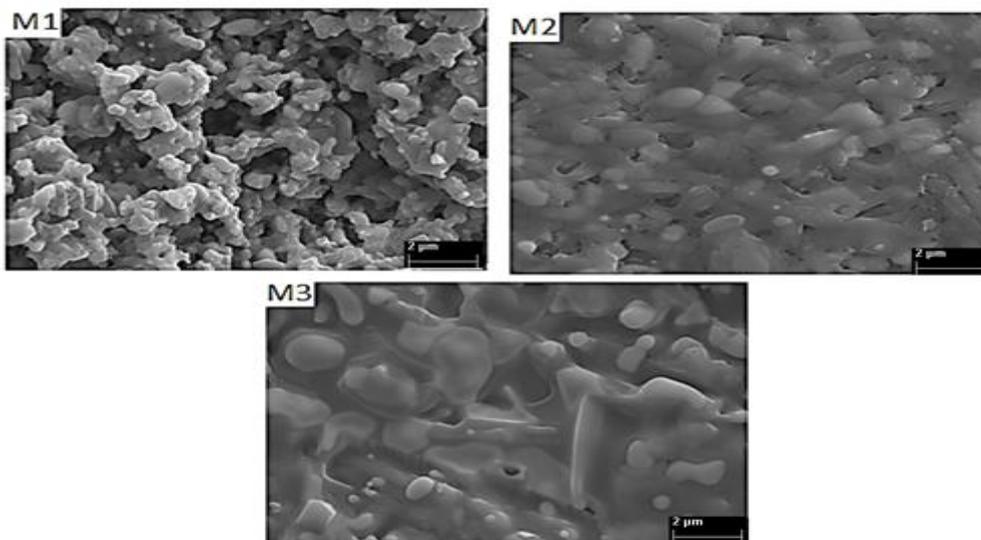


Fig. 5: SEM micrographs of samples sintered at 1550 $^{\circ}\text{C}$ for 5 h.

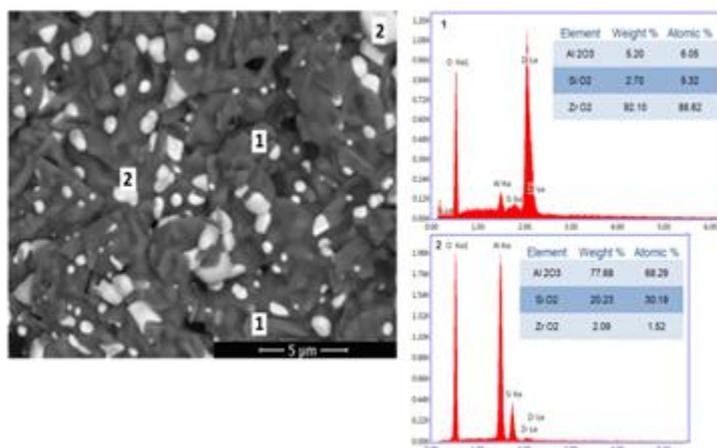


Fig. 6: SEM photomicrograph and corresponding EDX spectra of the sample M3 sintered at 1550 °C: (1) mullite grain and (2) zirconia grain

Fig. 5 shows the SE-SEM microstructure of a sintered surface of M1, M2 and M3 samples. As seen in Fig. 4, apparent grain growth of mullite and zirconia contributed decrease in porosity for specimens sintered at 1550 °C. In contrast, micrographs of M2 and M3 samples, which the zirconia grains demonstrated a large growth compared to M1, represent the effect of talc addition. Via reaction sintering process inter-particle pores could be eliminated by atomic diffusion which arised from capillary forces [17]. SEM photomicrograph and corresponding EDX spectra of the sample M3 sintered at 1550 °C has been shown in Fig. 6. As mentioned condition can be explained by our current research results, which shows that mullite-zirconia ceramics initiated effective densification at 1550 °C.

IV. CONCLUSIONS

Mullite-zirconia composites from zircon, kaolinite, alumina can be synthesized by the reaction sintering process in the temperature range of 1450-1550 °C with talc as an additive.

It is well known, zircon usually dissociates at a temperature higher than 1650 °C [21]. Thermal dissociation of zircon was found during the processing (1550 °C for 5 h) for M1 sample. The presence of mullite-zirconia grains promoted this decomposition process. Talc addition reduces the decomposition temperature of zircon thereby enables mullite-zirconia composite synthesis at much lower temperatures, compared to the batches without talc (M1).

XRD patterns confirm the reaction between kaolinite, alumina, zircon to form the mullite-zirconia composite at 1500 °C after 5 h of soaking (Fig. 2 and Fig. 3). The zircon phase is not detected in the mixture of M3 sintered below 1500 °C, while the mixture of M1 zircon peaks appear at high sintering temperature (e.g. 1550 °C). Kaolinite converts into mullite and amorphous silica [19] on heating. Similarly, zircon flour decomposes into zirconia and silica after heat treatment and yields the source of zirconia. Released silica again reacts with calcined alumina to form stoichiometric mullite. XRD patterns of the samples sintered at 1550 °C have been illustrated in Fig. 3. In all samples sintered at 1550 °C, three major phases are identified: mullite, tetragonal zirconia (t-ZrO₂) and monoclinic zirconia (m-ZrO₂). The reason for the dominance of m-ZrO₂ phase in XRD analysis is either due to the large size of the t-ZrO₂ particles and/or dissolving of impurities such as MgO, B₂O₃, CaO and Al₂O₃ in mullite structure rather than the zirconia structure.

In presence of talc (Mg₃Si₄O₁₂H₂) additive, crystallinity of the specimens has been improved further [22]. Talc exhibited a positive role on the formation of mullite and zirconia. The sintering temperature has a significant role on the formation of mullite in mullite-zirconia composite. According to XRD results of all the samples, evident increase in mullite formation was observed with the increase in sintering temperature from 1450 to 1550 °C. Especially, at a sintering temperature of 1550 °C for M2 and M3 samples, the zircon dissociation was almost complete, and therefore, with an increase in the sintering temperature from 1450 to 1550 °C, the proportion of zirconia phase (t-ZrO₂ and m-ZrO₂) significantly increased.

Linear shrinkage for M1 batch (without additive) ranged from 2 to 9 %, which increased to 12 % with talc additive (M2 and M3). The density of the composites varied between 2.17 and 3.31 g cm⁻³. Presence of talc as sintering aid and sintering temperature increased the rate of densification and yielded dense composites.

As showed with the mineralogical analysis the microstructure of M2 and M3 samples shows a mullite-zirconia composite (two phase). The microstructure of all composites is composed of irregularly shaped mullite grains, and round-shaped zirconia grains which are distributed homogenously. Composites with 4 wt. % and 7 wt. % talc have shown flexural strength of 171 MPa and 176 MPa at room temperature, respectively. Similarly, composites with 4 wt. % and 7 wt. % talc performed an elastic modulus of 112 GPa and 117 GPa at room temperature, respectively.

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