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COMPOSITE FILMS BASED ON STYRENE-CO-BUTYL-ACRYLATE WITH COLEMANITE AND CALCIUM BENTONITE MINERAL FILLERS

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Composites are engineered materials made from two or more constituent materials, which remain separate and distinct on the macroscopic level within the finished structure and also with significantly different physical or chemical properties. In recent years, there has been a great interest in polymer/inorganic composites, which stems from their improved properties. Mineral fillers in composites are widely used in industrial applications such as adhesives and paints. They provide better mechanical properties and thermal resistance to the systems and also reduce manufacturing costs. In this study, a comparative evaluation of colemanite and calcium bentonite minerals used as a filler in an aqueous polymer emulsion (styrene-co-butyl acrylate copolymer) is performed. The effect of amount and type of mineral additives on the mechanical properties of composites is investigated. Meanwhile, a comparison between colemanite and calcium bentonite is made on the basis of their different dispersion characteristics in a polymeric matrix. The degree of interfacial interaction between the filler and polymeric matrix is also modeled using the B parameter.

1. Introduction

Composites are unique materials consisting of a mixture or combination of two or more microconstituents mutually insoluble and differing in form and/or material composition [1]. Composites exhibit properties superior to those of their constituents. In recent years, many researchers have dealt with composite materials, because they display improved mechanical

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properties. Achievements in using these materials are documented in several recent reviews [2-5]. The improved characteristics of composites mostly depend on the type, the degree of dispersion, and amount of each constituent in the matrix together with their production method and mixing time. The type of auxiliary additives, such as compatibilizing agents and antifoamers, also affects the ultimate structure [6-7].

In recent years, most investigations have been related to the introduction of layered silicates into various polymeric matrices for improving their mechanical properties [8-14]. As such, the most widely used layered silicate in polymer composites is the clay mineral "montmorillonite," commercially known as bentonite. Its chemical formula can be written as $M_x(A1_{14-x}Mg_x)Si_8O_{20}(OH)_4$. The crystal structure of bentonite consists of layers made of two silica tetrahedral layers and an edge-shared octahedral sheet of either aluminum or magnesium hydroxide.

The layer thickness is about 1 nm, and the intervals between the layers may vary from 30 nm to several μm and even more, depending on the particular layered silicate [15]. The regular distance between the layers, or the so-called interlaminar spaces, are mostly determined by the weak Van der Waals forces. In addition, bentonite is characterized by a relatively high surface charge (known as the cation exchange capacity, CEC in meq/100 g), which also affects such properties as the swelling index and the distance between layers. The layer charge can be easily controlled by introducing cations with different charges, such as Ca^{2+} and Na^+. It should also be noted that the type of exchangeable cations also effects the swelling character and, by the way, the interlayer spacing between layers. In addition, depending on the layered structure, the interaction between the clay mineral and the polymeric matrix is determined by the distance between layers, known as intercalation and exfoliation. On the other hand, the polarity compatibility between the polymer and the clay mineral is another critical point, because, in their natural state, clay minerals can be combined only with hydrophilic substances, where polymers are usually hydrophobic. To overcome this polarity incongruity, the first method is to modify clay particle surfaces with organic substances so as to make them organophilic and compatible with the polymeric matrix [16]. The second method is to modify the polymer with auxiliary additives to match it with clay. Otherwise, particles would agglomerate and act as typical dispersed inorganic fillers in a polymeric matrix, where small amounts of additions will not effectively improve the characteristics of the composite material [17]. On the other hand, colemanite is a boron mineral with the chemical formula $Ca_2B_6O_{11}\cdot 5H_2O$. Contrary to montmorillonite, colemanite has a monoclinic crystal structure and can be found in different forms in nature such as cleavable massives, granular and most commonly in a nodular form. Colemanite has not a layered structure, and thus it will not undergo intercalation or exfoliation in a polymeric matrix. Therefore, in order to obtain a homogeneous dispersion of colemanite, auxiliary additives, such as dispersing agents, are used. As already mentioned, the main differences between colemanite and calcium bentonite is in their crystallographic structure, which also affects their dispersion characteristics in a polymeric matrix. In other words, colemanite can be accepted as a commercial filler, but introduced in small amounts into a polymeric matrix, forms agglomerates and negatively affects the mechanical characteristics of composites. The layered structure of bentonite provides better dispersion characteristics and, by the way, better properties at a lower rate of addition.

Styrene-co-butyl acrylate copolymer (SBA) is a thermoplastic polymer obtained by emulsion polymerization of styrene and butyl acrylate monomers. Since SBA is nontoxic, nonpollutant, and water-borne, it is being widely used in latex paints, coatings, carpet back fillers, and adhesives [18]. SBA/filler composites have aroused great interest, and their performance has been studied using different mineral fillers and SBA [10, 17, 19]. However, there are no investigation results in the literature for the interaction between SBA and colemanite.

The purpose of this study is to delineate the effect of colemanite and calcium bentonite as fillers in SBA-based composites, considering the effect of minerals with different crystal structures, on their mechanical indices. Mineral/polymer interactions are also modeled using the interfacial interaction parameter B.

2. Experimental

2.1. Materials

The styrene-co-butyl acrylate copolymer (SBA) was kindly provided by Organik Kimya (Turkey) under the trademark ORGANO PST5010. The content of the solid matter of latex, found according to ISO 1625 and DIN 53189, was 50%. The glass-transition temperature of the copolymer, determined by a differential scanning calorimeter, was 5°C. Colemanite was supplied by Eti Maden (Bigadiç, Turkey) under the trademark ETI42, but calcium bentonite (CB) — by SOMAS (Silivri, Turkey). An aqueous solution of ammonium polyacrylate (38 wt.%), under the trademark Ardewatt A (600 cP), was used as a wetting/dispersing agent, and Elementis Dapro DF7010 was utilized as an antifoaming agent. Calcium bentonite was purified in a hydrocyclone process [20], while the other materials were used as received.

2.2. Composite production method

The wetting and antifoaming agents were first added to the SBA latex in order to prevent the aggregation of mineral fillers and the formation of bubbles in the latex, which could adversely affect the properties of composite films. Then, all the content was mechanically stirred for 5 min at 800 rpm for homogenization of the mixture. The mineral fillers were slowly added to the mixture at different weight ratios for a period of 20 min under constant stirring at a rate of 1000 rpm.

A series of composite films were prepared with mineral fillers at ratios varying from 1 wt.%, up to 9 and 15 wt.% for the colemanite and calcium bentonite, respectively. Finally, the mixtures prepared were poured into Teflon molds and allowed to dry for 72 h at 30°C.

2.3. Mechanical characterization

The mechanical properties of the composites obtained were evaluated on a Devotrans FU Universal Test Machine at a constant tension rate of 0.2 mm/min and ambient temperature [21, 22]. Measurements were repeated five times for each series of specimens (90 × 20 × 2 mm) to get their average value.

2.4. Interfacial adhesion strength

Many researchers have proposed semiempirical models for a quantitative characterization of interfacial adhesion between the fillers and matrix [16, 23-25].The most important parameter appearing in these models is the parameter B charactering the degree of interfacial interaction. This parameter can be found from the tensile strength by using the equation [26]

$$Q_{yc} = Q_{ym}\left[\left(1-v_f\right)/\left(1+2.5v_f\right)\right]\exp\left(Bv_f\right),$$

or from the relative tensile strength Q by the equation

$$Q = \left(\frac{Q_{yc}}{Q_{ym}}\right)\left[\left(1+2.5v_f\right)/\left(1-v_f\right)\right],$$

$$Q = \exp(Bv_f).$$

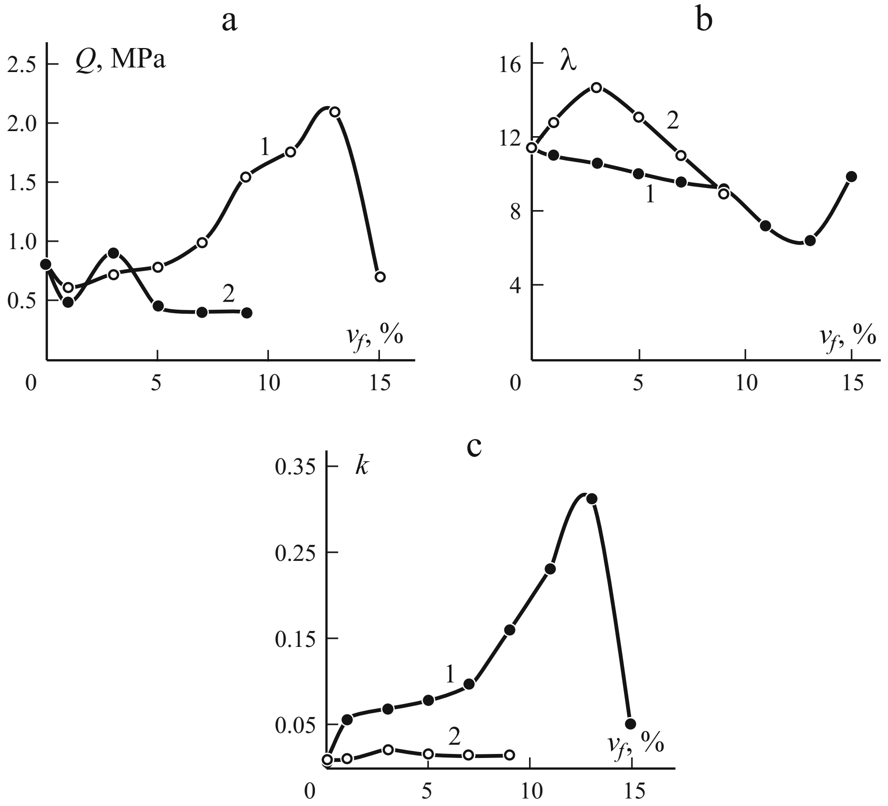

Fig. 1. Tensile strength Q (a), stretch ratio λ (b), and elasticity index k (c) of SBA/filler composites vs. content of filler v_f; with calcium bentonite (1) and colemanite (2).

Here, Q_{yc} is the tensile strength of the composite with a filler, Q_{ym} is the tensile strength of the pure polymer composite, and v_f is the volume fraction of filler in the polymeric matrix. The integral interfacial interaction parameter B of composites with different fillers can be obtained from the $\ln Q$ versus v_f diagram.

3.Results and Discussion

3.1. Mechanical properties of SBA composites

Micron-sized inorganic fillers have been used in industry to improve the mechanical indices and lower the cost of the products [27]. In our study, the mechanical properties of composites were revealed in order to understand the effect of colemanite and calcium bentonite addition on the ultimate structure.

The tensile strengths of composites containing these fillers are presented in Fig. 1a. As can be seen, colemanite provides a higher tensile strength than calcium bentonite at the same weigt content. This fact can be explained by the structural differences between the fillers, which also reflect the interaction of the fillers with polymer and the level of interfacial adhesion.

As indicated in [10], in the case of SBA/bentonite composites, polymer penetrates into bentonite layers and increases the distance between them. This increase continues until the layered structure collapses by forming agglomerates in the matrix; in our study, this maximum point corresponded to 13 wt.% of bentonite addition. As mentioned in the literature, the particle size of a filler is another important parameter for explaining the effect of filler addition on the mechanical and other characteristics of composites [27]. In this study, the mean size of dry bentonite particles was approximately 53 μm, whereas that of

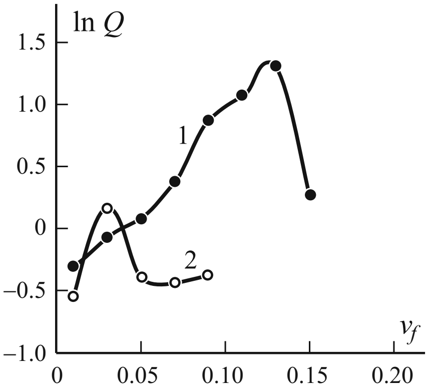

Fig. 2. Calculation of the parameter B for composites with calcium bentonite (1) and colemanite (2) fillers.

colemanite ones was 5 μm. Despite this size difference, the better properties of calcium bentonite in comparison with those of colemanite can be attributed to a better dispersion of polymer matrix in bentonite layers rather than to the effect of particle size.

The mechanical properties of composites with commercial fillers like calcium carbonate have been studied intensively [1, 27-28]. The mechanical indices of this type of composites exhibit maxima at filler additions lower than in the cases of any type of a layered silicate, such as bentonite. This can be explained by structural differences between these fillers. In the literature and also in our study, it is shown that higher mechanical indices can be obtained with the bentonite filler at higher concentrations owing to its more homogeneous distribution in the polymeric matrix and the resulting greater interfacial area, as a consequence of which the distance between particle layers increases.

Meanwhile, in SBA/colemanite composites, the interaction of colemanite with polymer was similar to that to calcium carbonate, and the maximum point obtained at a 3 wt.% addition can be explained by an earlier agglomeration and weaker interfacial adhesion with the matrix.

Most of the literature data for SBA/bentonite [29-31] refer to bentonite samples modified with quaternary amine salts in order to overcome the polarity incongruity. However, in our study, the polymer was modified with auxiliary additives for obtaining a polarity similar to that of the polymeric matrix. On the other hand, the maximum growth in stress can be explained by the deformational hardening, i.e., deformations increase up to the point of rupture [10]. At that point, the superior behavior of calcium bentonite to that of colemanite could also be explained by a better dispersion of filler particles in the film.

The stretch ratio λ and elasticity index k of the composites as functions of filler concentration are shown in Fig. 1b, c. These results show that the addition of filler particles increased the tensile strength, but decreased the elongation. This phenomenon can be attributed to the growing rigidity of the composite film, which increased proportionally to the increasing filler content until the interfacial adhesion between filler particles and the polymer was broken. The behavior of elongation characteristics of the composites can be ascribed to the weak zones created by broken filler particles or by the formation of aggregates in the matrix.

Therefore, it can also be understood why, as in the tensile hardening, the dispersion of filler particles was homogeneous up to 13 wt.% for calcium bentonite and up to 3 wt.% for colemanite.

Unlike the pattern observed in the tensile strength shows in Fig. 1, the elongation exhibited a reverse trend with increasing filler addition, pointing to the hardening of the composite and thus to lower values of λ. The elasticity properties showed in Fig. 1c reveals that an increasing filler content in the matrix results in a higher elasticity of both the fillers. Similar dependences for the elastic modulus have been reported in various studies for various filler/polymer systems [32-35].

3.2 Interfacial adhesion strength

The mechanical properties, especially the tensile strength, of composites are significantly affected by the interfacial adhesion between filler particle and the matrix [23]. If there is no interfacial adhesion, any external load can be carried only by the matrix, because the filler will not offer any resistance to the load [36]. The interfacial adhesion between the filler and polymer is affected by particle size, preparation method, and structure of the filler material.

Figure 2 shows the calculated tensile strength as a function of volume fraction of fibers v_f for colemanite/SBA and calcium bentonite/SBA composites. The values of the interfacial interaction parameter B, calculated from the slopes of corresponding plots, were 1.28 and 8.63 for colemanite and calcium bentonite, respectively.

The higher value of B for the calcium bentonite filler is caused by its better distribution in the same polymeric matrix.

A decrease in the interfacial adhesion parameter begins at $v_f = 0.13$, which can be explained by a decrease in the cross-sectional area of the composites to bear additional loads. In other words, only a small amount of stress can be transferred from the matrix to filler particles. Evidently, such mechanical properties as the tensile strength, elongation, and elasticity are affected by the filler fraction and the interfacial adhesion between filler particles and the matrix. The improved interfacial adhesion also implies that higher stresses can be transmitted to the particles from the matrix, which results in a higher tensile strength. However, in the case of weak interfacial adhesion, the microcracks forming along the interface between the matrix and filler particles reduce their ability to prevent the formation of cracks.

Conclusions

A polymer composite was obtained by mixing an aqueous polymer emulsion with two different fillers — colemanite and calcium bentonite. The main findings are summarized below.

- Addition of a rather small amount of a colemanite or calcium bentonite filler considerably improved the mechanical properties of composites. The optimum filler concentrations are found to be 13 and 3wt.% for calcium bentonite and colemanite, respectively.
- At filler concentrations higher than the optimum ones, a significant decrease was observed in the mechanical properties of both composites. This situation is likely to be induced by increasing agglomeration of the fillers in the polymeric matrix.
- The parameter B showed that the interfacial interaction between the polymeric matrix and filler was higher when calcium bentonite instead of colemanite was used, which can be explained by different crystal structures of the minerals.

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