FORMATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL–*CO*–VINYL ACETATE–*CO*–ITACONIC ACID)/PLASTER COMPOSITES PART 2. COMPOSITE FORMATION AND CHARACTERISTICS

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Poly(vinyl alcohol–co–vinyl acetate–co–itaconic acid) P(VA–VAc–It), ranging between 0.2 and 2.0 wt.%, were added to β -hemihydrate plaster to form the plaster composites. Compressive and bending strengths of the composites were measured and correlated with their scanning electron microscope (SEM) images. Results indicated that addition of the copolymer up to 1.2 wt.% is improving the mechanical properties while the further addition of polymer decreased them. SEM showed the role of polymer for interlocking among the set plaster grains. The neat set plaster contained comparatively higher porosity and medium interlocking between the set grains; and consequently relatively low mechanical properties were observed. It is suggested that the addition of the copolymer is forming a thin film around set plaster grains which acted to bind set grains, increase the interlocking, and hence improve the mechanical properties of the composites. At an optimum copolymer concentration of 1.2 wt.%, the best interlocking and strength results were thus obtained.

INTRODUCTION

In the past few decades, gypsum-based materials have become one of the most convenient materials of choice for indoor finishing in many countries. Suitable workability and volume stability in addition to the wide abundance of its un-expensive raw materials in different parts of the world have made gypsum plaster a most widely used finishing material in construction for centuries [1,2]. On the other hand, due to the importance of gypsum plaster as a fire resistant material, a number of studies have paid attention to the thermal behavior of gypsum during the dehydration process [3,4].

To increase the mechanical properties of plaster, a number of trials has been attempted to form plaster composites. Combining plaster with synthetic fibers (glass, polyamide) or natural fibers (sisal, waste paper) [5-7] reflected in appreciable toughness values and improved mechanical strength. Moreover, polymers have been used to improve the durability of concrete [8,9]. The effect of latex on the properties of plaster depends primarily on the latex-hemihydrate ratio. The magnitude of the observed effects generally increased proportionally with the increase of the amount added into pure plaster [10,11]. Çolak observed an increase in the flexural strength of the latex modified plaster as

compared with unmodified composition [10]. This was interpreted as due to the reduction in water of workability. The increase in flexural strength was attributed to the formation of polymer within the plaster [12]. On the other hand, the mechanical strength of the plaster was also enhanced by impregnating a polymer into the pores which were produced from the excess amount of mixing water [13].

The present study aims to characterize the poly (vinyl alcohol–*co*–vinyl acetate–*co*–itaconic acid)/ β -hemihydrate plaster composites with different weight percents of the added polymer. The impact of the polymer addition on the mechanical properties of the set plaster composites was investigated and correlated with their microstructures.

EXPERIMENTAL

A commercial grade β -hemihydrate plaster (BPB Formula Gmbh) and poly(vinyl alcohol–*co*–vinyl ace-tate–*co*–itaconic acid) (Aldrich-product 480223) were used. The proportion of the polymer varied between 0.2 and 2.0 wt.% of the solid plaster powder. The percent of distilled water used was previously de-termined as a normal consistency of neat plaster (46 %) [14].

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To measure compressive strength, 2.5 cm³ cubes were tested using a universal testing machine (FPZ100/ /1, HECKERT/THURINGER INDÜSTRIEWERKE, Germany) at a crosshead speed of 0.56×10^{-4} m/s. Bending strength was measured using $17.2 \times 2.3 \times 2.3$ cm bars tested under three-point bending strength universal testing machine (FM250, HECKERT/THURINGER INDÜSTRIEWERKE, Germany) at a crosshead speed of 0.45×10^{-4} m/s and span of 10 cm. Both compressive and bending strengths were measured after one, three, and seven days of aging. The presented mean values were calculated from five specimens per each composite sample.

Microstructural features of Au–Pd alloy-coated samples were investigated by scanning electron microscopy (SEM) (Hitachi, S-4700) equipped with an energy-dispersive X-ray (EDX) unit.

RESULTS AND DISCUSSION

Results of both compressive and bending strengths of the composite samples containing different copolymer concentrations after aging for 1, 3, and 7 days are shown in Table 1. The compressive strength results are graphically presented in Figure 1. It is obviously clear from Figure 1, that the strength of both neat plaster and different composite samples increased sharply by aging from 1 to 3 and 7 days; which is a normal phenomenon met with all binding and cementing materials [15]. Compressive strength of the tested composites increased with the copolymer content up to 1.2 wt.%, at which value it reached maximum, and then started to decrease with further addition of polymer. Generally, the compressive strengths of the composite samples tested after 3 and 7 days are more than twice their corresponding samples tested after one day. Comparing the compressive strength values of the samples tested after 3 and 7 days demonstrates a slight increase in the strength of the composites tested after 7 days in comparison with those samples tested after 3 days, as shown in Figure 1.

The improvement in the compressive strengths of both the neat plaster and composite samples with aging for 1 up to 3 days could be attributed to the increase in the extent of hydration of plaster in the polymer-free as well as plaster-polymer samples with time; reaching its highest value after 7 days [15]. On the other hand, the existence of extra amount of water used for workability is decreasing the strength by aging to 3 and 7 days due to its normal evaporation leaving behind open pores. The net result of these two factors is the observed increase of the compressive strength with aging time.

Results in Figure 2 show that the addition of poly (VA–VAc–It) up to 1.2 wt.% increases the compressive strength of the composite samples. Further addition of the copolymer causes the decrease of the strength. It is suggested that the added copolymer is forming a thin film coating the set plaster grains and is increasing the interlocking among them, hence enhancing the strength of the composite. The extent of a thin copolymer film on the grain boundaries of the set plaster is linearly increasing until the grains are fully covered. Further addition of the copolymer starts to form polymer aggregates resulting in a drop of the complymer on the strength is increasing with the polymer addition up to 2.0 wt.%, the upper limit of the observed concentration range.



Figure 1. Compressive strength of plaster composites with aging time. The presented points are the mean values of 5 experimental values with standard deviation not more than 0.25 MPa.



Figure 2. Compressive strength of plaster composites with polymer concentration wt % at x-axis. The presented points are the mean values of 5 experimental values with standard deviation not more than 0.25 MPa.

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Polymer	Compressive Strength (MPa)			Bending Strength (MPa)			
(wt.%)	One Day	3 Days	7 Days	One day	3 Days	7 Days	
0.0	8.5±0.21	17.7±0.18	18.2±0.16	2.3±0.16	6.7±0.19	8.7±0.23	
0.2	8.8±0.05	19.2±0.14	19.7±0.10				
0.4	9.2±0.11	19.9±0.15	20.8 ± 0.08				
0.6	9.5±0.16	20.2±0.05	21.5±0.09				
0.8	9.9±0.07	20.7±0.11	21.7±0.05				
1.0	10.1±0.06	21.6±0.09	22.3±0.11	$2.4{\pm}0.05$	$6.4{\pm}0.08$	8.6±0.11	
1.2	10.4 ± 0.07	23.1±0.00	23.2±0.25	3.1±0.09	7.1±0.05	9.2 ± 0.08	
1.4	9.3±0.06	20.4±0.13	21.4±0.11	$2.9{\pm}0.09$	6.7 ± 0.06	8.7±0.11	
1.6	9.1±0.05	19.9±0.08	20.9 ± 0.06				
2.0	8.0±0.05	17.9±0.07	19.1±0.11				

Table 1. Mechanical properties of different polymer/plaster composites.

This behavior shows that there was an adverse effect that took place in the composites when the percent of polymer used was increased over the critical percentage of 1.2 wt.%. In the presence of 1.2 wt.% of the polymer, this was a sufficient concentration to cover and bind all plaster grains causing the formation of glued block of a composite, explaining its highest compressive strength. Increasing the polymer concentration over this critical value, it appeared that the extra polymer concentration remained at the interfaces between these previously formed glued grains, hence weakening their interfaces and consequently causing them to fail at lower loads. On the other hand, the evaporation of the free water of workability with time on aging for up to 7 days, helped in the progressive improvement of the strength of these composites.

Bending strength results of the neat plaster and some selected composites are given in Table 1. It is evident from Figures 3 and 4 that the presence of 1.2 wt.% of the polymer also gave the highest values of bending strengths amongst all compositions. The increase of bending strength of all composites with time is also evident and could be attributed to the reasons discussed above.

Figure 5 shows SEM micrographs of some selected Poly(VA-VAc-It)/plaster composites aged for 7 days. All SEM micrographs showed the formation of well developed set plaster interlocked crystals, leaving behind a high porosity produced from the evaporation of the excess water used for workability, which amounted to about 28 %. These pores are clearly appearing with the polymer-free sample as shown in (Figure 5a). The amount of these pores decreased with the addition of the copolymer content, accompanying the formation of a copolymer thin film that is coating the set plaster grains. As a result, it gives a structure with a lower porosity for the 1.2 wt.% composite (Figure 5b). Addition of the copolymer is slightly decreasing porosity and gradually increasing the interlocking in the same time of thin film formation among the interlocked set plaster grains. The further increase of the copolymer content



Figure 3. Bending strength of plaster composites with aging time. The presented points are the mean values of 5 experimental values with standard deviation not more than 0.23 MPa.



Figure 4. Bending strength of plaster composites with polymer concentration wt % at x-axis . The presented points are the mean values of 5 experimental values with standard deviation not more than 0.23 MPa.

more than 1.2 wt.% helped in polymer clusters formation (Figure 5c) which is accompanied with the increase of pores and consequently a noticeably decrease in the mechanical properties. It is clear from Figures 5a,b that the edges sharpness of the plaster needle-like crystals decreased with the presence of copolymer, which is attributed to the formation of the thin film. Higher amount of polymer (above 1.2 wt.%, Figure 5c) results in higher amount of polymer clusters (compared with Figure 5b). These SEM micrographs therefore confirm both the strength results and the suggested model, regarding the cementing of the set plaster grains by the copolymer thin films.

CONCLUSION

The influence of addition of poly(vinyl alcohol-covinyl acetate-co-itaconic acid) P(VA-VAc-It) to a commercial β -hemihydrate plaster has been investigated. Different concentrations of the copolymer ranging from 0.2 to 2.0 wt.% were used. Mechanical properties of the formed composites after aging for 1, 3, and 7 days revealed the increase in the compressive strength of the formed composites with increasing of the copolymer content up to 1.2 wt.% then decreased at higher polymer contents. Compressive strength results of neat plaster (18.2 MPa) was remarkably improved after the addition of 1.2 wt.% poly(VA-VAc-It) achieving 23.2 MPa after one week of aging. On the other hand, bending strength slightly increased from 8.7 MPa to 9.2 MPa, for the same compositions and aging time. This increase in both compressive strength (27 %) and bending strength (5.8%) was attributed to the formation of thin layers of the polymer around set plaster grains, adhering and binding them, hence increasing their interlocking, and consequently improving the mechanical properties of the composites.

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a)



b)



c)

Figure 5. SEM micrographs of needle-like structure of (a) neat plaster; and polymer/plaster composites containing (b) 1.2 wt.% (c) 2.0 wt.% of poly(VA-VAc-It) aged for 7 days.

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PŘÍPRAVA A CHARAKTERIZACE KOMPOZITŮ SÁDRY A POLY(VINYL ALCOHOL–*CO*–VINYL ACETATE–*CO*–ITACONIC ACID) ČÁST 2. PŘÍPRAVA A CHARAKTERIZACE KOMPOZITŮ

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Byl sledován vliv přídavku poly(vinyl alkohol-co-vinyl acetate-co-itaconic acid) P(VA-VAc-It) v rozmezí od 0.2 do 2.0 wt. % do β-hemihydrátové sádry. Pevnost vzniklých kompozitů v tlaku a v ohybu byla měřena a korelována s texturou získanou pomocí rastrovacího elektronového mikroskopu (SEM). Výsledky ukazují, že přídavek kopolymeru až do hodnoty 1,2 hm. % zlepšuje mechanické vlastnosti, avšak další přídavek polymeru je už zhoršuje. Pevnost v tlaku nemodifikované sádry (18,2 MPa) byla významně zlepšena přídavkem 1,2 hm. % poly(VA-VAc-It) a dosáhla hodnoty 23,2 MPa. SEM ukázal úlohu polymeru při propojování sádrových krystalů. Čistá sádra vykazovala zřetelně vyšší porositu a střední stupeň propojení mezi krystaly sádry; důsledkem čehož byly pozorovány relativně nízké pevnosti. Bylo navrženo, že přídavek kopolymeru vytváří na krystalech sádry tenký film, pomocí kterého se jednotlivé shluky krystalů propojují, čímž se zvyšuje celkové propojení a tedy i zvyšuje pevnost. Při optimální koncentraci kopolymeru 1,2 hm. % vykazuje kompozit nejvyšší stupeň propojení a tedy i nejvyšší pevnost.