Effect of Filler-Filler Interactions on Mechanical Properties of Phenol Formaldehyde Based Hybrid Composites

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Abstract. Mechanical properties of phenol formaldehyde (PF) based hybrid composites reinforced with molybdenum disulphide (molykote; MC), copper (Cu), graphite (Gr) and antimony (Aty) particles in micron size, having different shape and aspect ratio, are studied. Incorporation of MC, Cu and Gr enhanced the hardness, compression and flexural properties of PF based hybrid composites. A slight decrease in density was observed in MC + Gr (A5) reinforced PF based hybrid composites, making these composites suitable in weight susceptible applications. The investigations showed that the control sample A1 without MC/Cu/Gr/antimony (control sample) exhibited poorer mechanical properties. Addition of Cu, MC and Gr to the control sample resulted in moderate improvement in the mechanical properties. However, hybridization of the control sample with Gr + Aty (A6) showed lower mechanical properties compared to that of composites filled with MC and Gr (A4 and A2) respectively. This decrease was ascribed to the tendency of non-uniform dispersion, deprived bonding of Aty particles as well as poor filler-matrix adhesion. When Aty was replaced with Gr + MC (Sample A5), filler-filler with matrix interaction appears to be increased, resulting in increased strength and modulus. The developed PF based hybrid composites have exhibited improved mechanical properties and these composites with detailed thermal and tribostudies may be recommended for railway braking applications.

1. Introduction

Polymeric materials with apt filler/matrix interaction and suitable fiber together with new methods to develop hybrid and multiphase polymer matrix composites (PMCs) is having prospective applications in automotive, aerospace and constructions industries. To cope with the obvious limitations of polymers, for example, low stiffness and low strength, and to expand their applications in different sectors, inorganic particulate fillers, such as micro-/nano-SiO₂, glass, Al₂O₃, Mg (OH)₂ and CaCO₃ particles, carbon nano tubes (CNTs) and layered silicates, are often added to develop newer PMCs, which normally combine the advantages of their constituent phases [1-3]. Particulate fillers modify the physical and mechanical properties of PMCs in many ways [4]. Among them one of the methods to use multi ingredient and multiphase polymer systems is related to controlling the physical and chemical interactions at the interface to improve the mechanical properties.

Phenolic formaldehyde (PF) resins possess exceptional bonding properties and have high stiffness, dimensional stability, outstanding heat and fire resistance due to a highly cross linked aromatic structure [5]. The major drawbacks of the PF resins which prevents its widespread applications are high brittleness and shrinkage. This properties are surmounted by inclusion of micron sized particulate fillers and load bearing synthetic fibers or elastomeric materials [6-11]. PF resin generates chemical bonding with synthetic fibers/surface modified fillers, leading to strong

forces between fiber/particulate and resin. Thus, a high compatibility in the system between synthetic fiber/filler with PF resin is achieved. It is reported that copper, graphite/CNTs/carbon fiber is a potential reinforcement for phenolic resins [12-15].

Especially in automotive brakes and clutches, Non-asbestos organic (NAO) based friction materials are used, which are essentially multi ingredient systems (containing more than 10 ingredients, in general) in order to achieve the desired amalgam of performance properties [16-20].

The four categories of ingredients, viz. binders, fibers, friction modifiers and fillers based on the major function they perform apart from contributing towards friction and wear performance are selected. Binders mainly from phenolic or modified phenolic provide mechanical integrity to the friction material while fibers, such as mineral, ceramics, organic and metallic types provide mainly the strength. Friction modifiers, such as abrasives and solid lubricants are used to achieve the desired range of friction. Fillers the fourth class is again subdivided as functional fillers (to enhance the specific function, such as resistance to fade, thermal conductivity, etc.) and space fillers/inert fillers (just to cut the cost without any adverse effect on performance properties) [21]. Each of these ingredients is contributing their part to synergistic effect; however properties imbibed by particular ingredient may affect properties of other ingredients which in turn determine total synergistic effect.

To the best of our knowledge, although investigations on PF based hybrid composites have been conducted so far by several researchers, evidences of the overall effect conferred by micro-size copper, molybdenum disulphide and graphite incorporation on physico-mechanical of PF based composite in any previous study are relatively scarce [22-26]. The mixture of PF, binders and fillers has been pulverized for 45 min to have a better dispersion of the fillers into PF and other binders. Such kind of pulverization is not usually followed during PF based multiphase composite fabrication. Generally, addition of functional fillers can provide PF with specific properties but sometimes triggers problems such as loss of some mechanical properties, degradation of the polymer matrix, etc., aspects that need to be taken care when considered for braking applications.

Based on the above cited literature, effects of different micro-sized fillers to PF based multiphase composite for disclosing microstructure and mechanical properties relationship of the resulting composites is of high interest and is the main aim of this investigation. It is expected that molykote and/graphite filled PF based hybrid composites can enable superior mechanical properties.

2. Materials and Methods

2.1. Materials

Phenol formaldehyde (PF, containing 9.2 wt. % hexamethylenetetramine) powder with the average particle size of 35 μm , was considered as primary binding material along with the other secondary binding elements such as cashew nut oil, fire clay (average particle size of 200 μm), linseed oil and plaster of Paris (average particle size of 30 μm) are used to enhance the binding effect with the fillers. Friction dust (average particle size of 15 μm), rubber powder (average particle size of 18 μm) and hexamine (average particle size of 35 μm) are used as fillers, which improves the manufacturability resulting in reduction of cost. Molybdenum disulfide, a lubricating filler commercially known as Molykote (MC) with average particulate size of 50 μm , copper (Cu), graphite (Gr) and antimony (Aty) all in powder form with corresponding average particulate size of 25 μm , 50 μm and 135 μm are selected as primary frictional additives. Further, ferrosilicon, barium sulphate, silicon carbide, and carbon in powder form with corresponding average particulate size of 18 μm , 10 μm , 25 μm and 20 μm are used as secondary frictional additives. They are used to reduce the wear and to improve the coefficient of friction. Short glass fiber with average diameter and length of 10 μm and 6 mm were used as reinforcing element to improve strength and friction performance in the present investigation. Table 2 presents the role of ingredients in the intended composites.

The source and the selected properties of the materials used to prepare the brake composites in the present investigation are listed in Table 1.

Table 1. Materials used in the Present Investigation.

Sl. No.	Polymer/Filler	Density (g/cm ³)	Suppliers
01	PF Powder	1.05	Claro India Pvt. Ltd, Chennai
02	Barium sulphate	4.48	
03	Antimony	6.68	
04	Hexamine	1.33	
05	Cashew nut oil	0.95	Sathya Cashew Chemical Ltd, Chennai, India
06	Friction dust	0.45	
07	Linseed oil	0.93	
08	Fire clay	2.40	Mysore Pure Chemicals, Mysuru, India.
09	Rubber powder	0.91	
10	Molykote	4.80	
11	Carbon powder	1.80	
12	Plaster of Paris	2.70	Murugan Hardware, Erode, India
13	Ferrosilicon	2.34	Kumar Hardware, Coimbatore, India
14	Copper powder	8.90	Metal Powder Company (MEPCO) India PVT Ltd, Sivakasi, India
15	Graphite	2.26	Gowtham Chemicals, Chennai, India
16	Silicon carbide	3.20	Carborundum Universal Ltd (CUMI), Cochin, India
17	Fiber glass	2.54	Mukthagiri Industrial Corporation, Mumbai, India

Table 2. The ingredients and their role in the composites [27].

Sl. No.	Description of Material	Role in the composition
1.	Phenol Formaldehyde	<p>This is a derivative of Phenolic resin and available in powder form. It is used for binding all the other ingredients as solid piece at elevated temperature. This powder melts and flow freely in between the granular structure of the fillers at 128 °C and integrates the composite mixture into one homogeneous block taking the required shape of the die.</p> <ul style="list-style-type: none"> • Withstand high temperature. • Wear resistant.
2.	Barium sulphate	<ul style="list-style-type: none"> • Wear resistant. • High thermal stability.
3.	Antimony	<p>It is an inert material (metal), available in powder form.</p> <ul style="list-style-type: none"> • Improving the density. • Dissipating the frictional heat generated on account of braking. • Providing bearing characteristic. • Providing anti-wear properties.
4.	Hexamine	<ul style="list-style-type: none"> • Acts as a catalyst and speed up polymerization. • Improve hardness of brake blocks.
5.	Cashew Nut Shell oil	<p>It is derived from cashew nut shell, used as a binder and friction modifier. It also possess good refractoriness, which can withstand up to 400 °C.</p>

6.	Cashew Friction Dust	It is derived from cashew nut shell, and has the following characteristics. <ul style="list-style-type: none"> • Mould ability. • Good friction properties. • Refractoriness i.e. to withstand elevated temperature. • Environment friendly.
7.	Linseed oil	Natural oil used as an additive for improving bonding.
8.	Fire Clay	This is used as a filler for providing adequate frictional characteristics.
9.	Rubber Powder	This is added in granular form to facilitate wear resistance and improves cushioning properties to withstand the impact during braking.
10.	Molykote	As a solid lubricant additive in brake lining applications <ul style="list-style-type: none"> • Excellent lubricating properties • Reduction of friction and wear • Resistant to oxidation • Extreme pressure resistance. • Wide service temperature range.
11.	Carbon Powder	It is used as hardener.
12.	Plaster Of Paris	It is used a filler and benefitted with good mould ability, refractoriness and improves the mechanical properties like density and crushing strength.
13.	Ferrosilicon	A metallic compound of iron and silicon, and helps in improving the non-sticking characteristic at elevated temperature, density and compactness.
14.	Copper powder	It reduces wear and prevent scoring, possess high thermal conductivity and forms uniform frictional film.
15.	Graphite Powder	This, when combined with rubber gives the brake block, a smooth surface in order to give maximum bedding of the brake blocks. It also possesses anti-sticking properties and stabilizes coefficient of friction (μ).
16.	Silicon carbide	It possess high hardness, strength, good chemical and thermal stability, high melting point, oxidation resistance and high wear resistance.
17.	Fiber Glass	They are used as reinforcements for the composites.

2.2. Methods

2.2.1. Composite Fabrication: The Phenol Formaldehyde (PF) multi phased composite samples were prepared by hot compression moulding technique. The various PF composites, their ingredients and proportions are presented in Table 3. The process includes mixing, hydraulic pressing, curing and post curing. Initially the particulate fillers were mixed using mechanical plough type shear mixer followed by the addition of fibers to ensure homogeneous distribution. The mould was preheated to 80 °C. Hardening of the composite made of several different materials is referred as curing. This can be achieved by heating, chemical additive or ultraviolet radiation. To relieve the frozen-in stress and cure the residual resin post curing is done. This method also increases heat resistance, better chemical and mechanical properties and cross link of the polymer. The mixture was filled into the mould cavity and closed hydraulically at a temperature of 135°C and load of 50 tonnes for 40 min, with three intermittent breathings were given in between to expel the volatile gases. The test samples were prepared as per ASTM standards.

Table 3. Constituents of the phenol formaldehyde hybrid composites for the present study.

Composites *	Composite Constituents					
	Binders (wt. %)	Fillers (wt. %)	Molykote (wt. %)	Copper (wt. %)	Graphite (wt. %)	Antimony (wt. %)
A1 = B + F	60 [^]	40 [§]	---	---	---	---
A2 = B + F + MC	55	40	05	---	---	---
A3 = B + F + Cu	55	40	---	05	---	---
A4 = B + F + Gr	55	40	---	---	05	---
A5 = B + F + (Gr+MC)	55	40	2.5	---	2.5	---
A6 = B + F + (Gr +Aty)	55	40	---	---	2.5	2.5
*B – Phenol formaldehyde and other binders as listed below, F – fillers as listed below, MC – Molykote, Cu – Copper, Gr – Graphite, Aty – Antimony [^] Binders includes PF Powder 30 wt. % + Cashew nut oil 10 wt. % + Fire clay 10 wt. % + Friction dust 05 wt. % + Rubber powder 02 wt. % + Hexamine 01 wt. % + Linseed oil 01 wt. % + Plaster of Paris 01 wt. % [§] Common fillers includes Ferrosilicon 25 wt. % + Barium sulphate 10 wt. % + Silicon carbide 02 wt. % + Fiber glass 02 wt. % + Carbon powder 01 wt. %						

The flow chart in Fig. 1 reveals the major stages of preparation of PF based composites. Multi phased PF composites (A2, A3, A4, A5 and A6) comprising of molykote, copper, graphite and antimony possess 5 wt. % of fireclay reducing the binder content from 60 wt. % in former (i.e. A1) to 55 wt. %.

Figure 1. Process Chart for the Fabrication of PF based Hybrid Composites.

2.2.2. Characterization of Phenol Formaldehyde Composites: The experimental density of multi phased PF composites were determined by Archimedes principle using Sartorius make (Model – BSA224S-CW) densometer. The weight of the sample in air was noted and then immersed in distilled water at room temperature, a small holder was utilized to ensure complete sink of the sample and density was determined. The hardness was determined by Barcol impresser (Make – VERTEX). Hardness test was investigated as per the standard procedure using Barcol impresser. This test characterizes the indentation hardness through the depth of penetration of an

indenter, loaded on a material sample and compared to the penetration in a reference material. Barcol hardness testing is a method of measuring the hardness of reinforced and non-reinforced rigid plastics. The hardness value is arrived at by assessing the plastic materials resistance to being penetrated by indenter. The specimen is placed under the indenter of the Barcol hardness tester and a uniform pressure is applied to the specimen until the dial indicator reaches maximum value. Later the depth of penetration is converted in to absolute Barcol numbers. The compressive and flexural properties were determined on Universal Testing Machine (Make – JJ Lloyds, London, UK, capacity 1-20 kN). The test (specimen size = 25mm length and 12.5mm diameter cylindrical pin, speed 2 mm/min, and load range of 10 kN) was carried out using Kalpak universal testing machine (Model KIC, serial number 121101) according to ASTM D 3410. Flexure test were carried out by changing the jaws of the set up and the specimen acts as simply supported beam subjected to point load at the middle by considering span length of 50mm. The flexural strength and flexural modulus were determined at the rate of 2 mm/min as per ASTM D 790.

2.2.3. Microstructure of Phenol Formaldehyde Composites: The surface morphologies of the selected PF based multiphase composite specimens were studied by a scanning electron microscope (SEM) (JSM-6510 LV, JEOL, Japan) with a maximum operating voltage of 20 kV. Specimens were mounted on aluminium stubs with carbon tape and sample-surface was coated with a thin gold layer by a sputtering unit prior to SEM measurements.

3. Results

3.1. Microstructure of PF Based Hybrid Composites

Figs. 2a, 2b, 2c, 2d, 2e and 2f show the microstructure using SEM of control composite sample (A1), molykote (A2), copper (A3), graphite (A4), graphite + molykote (A5) and graphite + antimony (A6) filled PF based hybrid composite, respectively. From Fig. 2a, it is clearly shown that the adhesion of the various binders, glass fiber and fillers (Table 2) with the PF matrix in the interfacial region is poor. The void spaces between various fillers, glass fiber with the binders and PF matrix are also shown, which indicate poor impregnation of fillers, glass fiber in the PF matrix. This poor impregnation and left out space between the constituents increased the void percentage in the A1 composite.

Figs. 2b and 2c show photomicrographs of the MC and Cu filled PF based hybrid composites respectively. It can be seen from the corresponding figures that the MC and Cu particles and other fillers including short glass fibers were closely embedded in PF matrix with other binding materials and at some regions micro spaces (comparatively less than the former) exist at the interfacial province between the fillers and the matrix, which resulted in good filler-filler and matrix interaction. Lower voids and good bonding strength between fillers and binders enhanced the mechanical properties of the PF based MC and CU filled composites (A2 and A3) which are discussed in details in the subsequent sections.

Figs. 2d and 2e show photomicrographs of the Gr and Gr + MC filled PF based hybrid composites respectively. More voids, poor dispersion of various fillers and bunching of glass fibers are the features that can be seen from Fig. 2d for Gr filled PF based hybrid composite (A4). However, in case of combined fillers inclusion (sample A5) i.e., Gr + MC filled PF based hybrid composite more or less uniform dispersion and directional orientation of glass fibers, various fillers were distributed uniformly and good interfacial adhesion between fillers, fibers with PF matrix can be seen from Fig. 2e.

Fig. 2f shows microstructure of PF based hybrid composite where in Gr and antimony fillers were included (A6). Non uniform distribution of fillers and more empty spaces left at various regions are observed in Fig. 2f. The void space between fillers and binders is more and hence increased the total void percentage in the final composite (A6). Poor bonding, non-uniform dispersion of fillers within binders and very poor bonding between fillers and binders may be the possible reasons for poor mechanical performance of the hybrid composite (A6) and these mechanical performance data are discussed in sections 3.2 to 3.5.

Figure 2. Microstructure of PF based Hybrid Composites: (a) Control PF composites (A1), b) MC filled PF (A2), c) Cu filled PF (A3), d) Gr filled PF (A4), e) Gr + MC filled PF (A5), f) Gr + Antimony filled PF (A6).

3.2. Density

It is one of the primary characteristics of the polymer composites and majorly depends upon the relative proportion of the matrix and reinforcing elements and their respective density. Agarwal and Broutman [28] have obtained the theoretical density (ρ_{ct}) of composite materials by using the following equation (1)

$$\rho_{ct} = \frac{1}{\left\{ \left(\frac{w_f}{\rho_f} \right) + \left(\frac{w_m}{\rho_m} \right) \right\}} \quad (1)$$

where 'w' is the weight fraction and 'ρ' is the density of the corresponding materials. The suffixes 'f' denotes the filler/reinforcement element and 'm' represents the matrix respectively in a composite with unit filler/reinforcement. However, the present investigation involves eight different types of binders as matrix material and nine various ingredients as filler materials. Hence the above equation (1) has been tailored as follows.

$$\rho_{ct} = \frac{1}{\left\{ \left(\frac{w_{f1}}{\rho_{f1}} + \frac{w_{f2}}{\rho_{f2}} + \dots + \frac{w_{f9}}{\rho_{f9}} \right) + \left(\frac{w_{m1}}{\rho_{m1}} + \frac{w_{m2}}{\rho_{m2}} + \dots + \frac{w_{m8}}{\rho_{m8}} \right) \right\}} \quad (2)$$

where the suffix $f_1, f_2 \dots f_9$ denotes the nine various fillers and $m_1, m_2 \dots m_8$ stands for eight various binding elements as matrix material. The actual densities (ρ_{ca}) of the prepared composites are determined by Archimedes principle in accordance with ASTM standard as mentioned in Table 3. The voids (v) present in the prepared composites is calculated by using the following equation

$$v = \frac{\rho_{ct} - \rho_{ca}}{\rho_{ct}} \quad (3)$$

Table 4 presents the theoretical and experimentally measured densities along with the corresponding voids in the PF based hybrid composites. Reduction of fire clay to 5 wt. % from 10 wt. % and inclusion of Cu by 5 wt. % (A3) in PF composite has escalated the density by 17.8 % compared with that of reference composite (without fillers A1). This is due to the density of Cu, found to be the highest among the selected filler in the study group. Molybdenum disulphide (MC) filled PF composite (A2) exhibited slightly higher density by 7.9 % compared to A1 composite and lower density by 8.37 % compared to A3 composite. This is attributed to the reduced density of MC.

Table 4. Mechanical properties of phenol formaldehyde hybrid composites.

Property	ASTM Test	Phenol Formaldehyde composites					
		A1	A2	A3	A4	A5	A6
Density (g/cm ³), theoretical	Rule of mixture	1.63	1.72	1.90	1.62	1.68	1.69
Density (g/cm ³)	D 792	1.52	1.64	1.79	1.52	1.62	1.58
Voids (%)	-----	6.74	4.65	5.78	6.17	3.57	6.50
Barcol hardness number	D 2583	27	36	35	30	40	38
Compressive strength (MPa)	D 3410	14.37	26.11	21.05	22.92	34.84	19.32
Compressive modulus (MPa)		94.68	190.42	140.86	158.94	242.57	146.35
Flexural strength (MPa)	D 790	14.55	20.59	19.87	21.54	25.34	16.86
Flexural modulus (MPa)		58.99	80.58	77.22	84.52	100.55	63.42

The measured density of hybrid composite with Gr and MC (A5) in PF demonstrated the density of 1.6 g/cm³ which is less by 10.5 % compared with A3 composite (Fig. 2). This is due to reduced density of Gr with 2.5 wt. % content in the composite. Graphite and antimony filled PF (A6) composite demonstrated reduced density by 11.7 % compared to Cu filled PF (A3) composite. This is due to the inherent density property exhibited by the Gr and antimony fillers compared to that of Cu filler. Further, Gr (5 wt. %) filled PF composite (A4) and A1 composite demonstrated the equivalent density. This is due to the replacement of 5 wt. % of fire clay by Gr, and these materials possess density values closer to each other. Further, it may be noted that the theoretical density of the composite deduced by the equation (2) are slightly higher than the experimentally measured

value. This is attributed to the presence of voids in the composites. The presence of voids depends upon the packing factor of the filler and matrix materials. The shape and size of the particulates plays a vital role on the packing factor. Particulates with higher size and irregular geometries results in lower packing factor, thus leading to increase in void contents. The reference PF composite (A1) possess maximum voids of 6.74 % in the study group. The presence of 10 wt. % fire clay with irregular geometry and having average particle size of 230 μm , has reduced the packing factor with increase in void fraction. The irregular geometry and the larger particle size have increased the distance between the consecutive particles, thus providing more space for formation of voids. PF composite with graphite and antimony (A6) showed 6.5 % of void. The Gr and antimony used in the investigation has fine and coarse flaky structure with average particle size of 50 and 135 μm respectively, resulting in increased void fraction of the composite. Filler like Gr and MC in PF composite (A5) possess lowest void percentage (3.57 %) in the study group. The particle sizes are comparatively lower and this has reduced the space for void formation and thus resulted in lower void fraction.

The PF based hybrid composites had calculated density values based on the actual density of the micron sized fillers used. There was variation of percentage voids from 3.57 to 6.74 between the PF based hybrid composites (Table 4). PF based composite with MC and Gr showed that there was marginal difference in density values. It can be also concluded that the PF based composite manufacturing procedure has meticulously performed, which is of a great importance to obtain the hybrid composites having homogeneous performance in the study group.

3.3. Hardness

The hardness of the PF based hybrid composites are listed in Table 4 and in the form of bar chart shown in Fig. 3. It is evident from the Table 4 and Fig. 3 that the PF composite with Gr and MC has demonstrated better hardness in the study group. This is attributed to lower voids and improved adhesion of filler-filler with the PF matrix material. Suresha et al. [29] observed as compared to C-E, graphite filled C-E posses higher density, hardness and tensile strength. Further, MC and antimony has higher average molecular weight followed by Cu and Gr in the study group. Also antimony possesses higher hardness followed by Cu, Gr and MC. The presence of these fillers enhanced the hardness of the PF based hybrid composite comparatively.

Figure 3. Hardness (Barcol) and density of Phenol formaldehyde-based multiphase composites.

3.4. Flexural Strength and Flexural Modulus of PF Based Composite

The average flexural strength (σ_f) and flexural modulus (E_f) evaluated from three-point bend tests for PF based hybrid composite specimens are shown in Fig. 4. It is seen that σ_f increases with different MC, Cu and Gr fillers except combined filler loading (MC + antimony) in the control sample (A1). The rate of increase of σ_f is different for all the fillers studied, indicating the type, shape and size of the filler importance. The flexural strength value for the control sample is 14.55 MPa, while it increases to a value of 21.54 MPa for PF based composite with 5 wt. % Gr content. On the other hand, contrary to the increase in σ_f value, the strength is found to decrease with the incorporation of graphite and antimony fillers (16.86 MPa, Specimen A6). The minimum value of E_f observed for the unfilled PF composite specimen is 58.99 MPa and the maximum E_f value obtained for PF based multiphase composite specimen of 2.5 wt. % MC + 2.5 wt. % Gr is 100.55 MPa. Therefore, the highest increase in obtained herein E_f is 70 %. Improvement in bending strength of Phenol formaldehyde resin/graphite composite was found by Yin et al. [31].

Among all the filler-filled PF based composites, the lower σ_f of the PF based composite is with Gr and antimony filled ones (A6). It was noticed that flexural strength/modulus was increased for smaller particle size (A2 - A5) and the decreases for the larger particle size (A6). This could be due to a number of reasons, such as weak interfacial bonding at Gr and antimony particles with PF matrix interfaces, agglomeration of micron sized particles, less surface area of antimony particles due to bigger particle size, process-related defects such as porosity and so on. The change in σ_f is also controlled by the particles size of the filler along with molecular weight, flexibility and surface properties of filler and matrix, thus, bigger (120-150 μm) antimony particles filled PF leads to more voids, lesser filler-matrix interaction, thereby showing lower strength as well as modulus. Further, it is worth mentioning that σ_f of a material is the maximum stress exhibited by it under deflection. Under the deflection processes, the position and movement of filler aggregates, matrix molecules and develop pores during fabrication inside the material may affect the resulting interaction among PF-PF molecules, filler-filler aggregates and PF/Filler molecules.

Figure 4. Flexural strength and modulus of PF based hybrid composites.

Figure 5. Stress versus Strain (flexure-mode) of phenol formaldehyde-based multiphase composites.

Dwindling of interaction due to above mentioned facts is assumed to reduce the σ_f of the PF based composites with different compounded filler loading. Moreover, the adsorption of the antimony filler limited wettability in PF matrix phase may result in poor interface adhesion of Gr particles to PF matrix, and inefficient stress-transfer between the particle-matrix interface occurs as long as the load is applied.

The smaller particle size fillers (MC and Cu) tends to agglomerate and hence reduced the flexural strain values by restricting the mobility of matrix chains, which was also supported by the trend of variation in strain at break of PF based composite (A1) filled with MC (A2) and Cu (A3) as shown in Fig. 5. Fig. 5 represents the variation in flexural strain at break of different filler reinforced PF based composite systems.

3.5. Compressive Strength and Modulus of PF Based Composite

The compressive strength of reference PF based composite (A1) and filler reinforced PF based composite systems (A2 - A6) are shown in Fig. 6. Particulate reinforced PF based composites showed higher compressive strength than the unfilled PF composite and when combination of MC and Gr were included to the PF composite (A5), compression strength significantly increased. The compressive strength of A5 composite was found to increase by 142 % in comparison with A1 composite and 82 % with A2 composite. Further, the MC (A2) and Gr (A4) reinforced PF composite compressive strength is higher than Cu (A3) reinforced but lower than that of combined hybrid filler reinforced PF composite (A5). The increase in compressive strength of hybrid PF composite is because of graphite filler content. The variation of compressive strength of MC/Gr and Gr/antimony particulate reinforced hybrid PF composites are also shown in Fig. 6. It is observed that the MC reinforced PF composite with Gr filler addition is exhibiting higher compressive strength. Additionally, compressive strength was found marginal increase (34 %) for hybrid particulates (Gr and antimony) in PF based composite (A6), possibly due to poor quality of the composite, formation of air pockets which may be due to their higher surface energy to adhere among themselves and to larger inter-particle distance between fillers, in which case matrix breakage becomes the prominent failure mechanism. Gautam and Kar [31] found that the composite slabs with filler weight percentage of 35/5/3/exfoliated graphite/carbon black/graphite powder, offered in-plane and trough-plane electrical conductivities of 374.42 and 97.32 S/cm, bulk density 1.58 g/cm³, compressive strength 70.43 MPa, flexural strength 61.82 MPa, storage modulus 10.25 GPa and microhardness 73.23 HV.

Figure 6. Compression Strength and Modulus of PF based Hybrid Composites.

Influence of different filler inclusion on compressive modulus of PF based composites are as shown in Fig. 6. The modulus of the PF based composite (A1) was increased by 101% due to the incorporation of MC filler within the PF matrix (A2). Further, addition of 2.5 wt. % Gr particles to A2 composite, the result was quite interesting and the compressive modulus was significantly enhanced by 156 % as compared to A1 composite. There was an improvement of 68 % in the modulus for the addition of Gr filler into the PF matrix was recorded (A4). The modulus of A4 composite was decreased by 13 % with further addition of 2.5 wt. % of antimony filler (A6). These results thus proves that the compressive strength and modulus to the PF based composite (A1) was improved due to the addition of MC, Cu, Gr and their hybrid particles within the PF matrix.

The rule of mixture equation (4) was applied to randomly distributed particulate/short fiber reinforced polymer composite materials;

$$E_{Comp} = K \times (E_m \times w_m + E_p \times w_p) \quad (4)$$

where E_{Comp} = modulus of the polymer matrix composite, E_m , E_p are the modulus of the matrix and particulate/fiber materials; w_m , w_p are the weight fraction of matrix and particulates/fibers. K is the constant called as reinforcing material efficiency parameter. However, filler loading constitutes to 40 wt. % and is constant for all the PF composites, and hence equation (4) reduces to equation (5) as below:

$$E_{Comp} = K \times (E_p \times w_p) \quad (5)$$

Further the values K was determined using equation (5) and are noted in the Table 5. Flexural modulus of PF = 7.5 GPa, Molykote = 9.31 GPa and Graphite = 16.8 GPa were considered [32] for calculation.

Table 5. K value of PF composites.

Composites	Flexural modulus of composites (E_{Comp}) in MPa	K
A1	58.99	0.0131
A2	80.58	0.0175
A3	77.22	NA
A4	84.52	0.0170
A5	100.55	0.0210
A6	63.42	NA

Fig. 6 shows that the values of K have the close proximity for the MC and MC + Gr reinforced PF composites (A2 and A5). This value is in higher side for the MC filler and intermediate values for the Cu and Gr reinforced PF composite materials (Table 5).

4. Conclusions

Combined effect of filler-filler interaction on mechanical properties of phenol formaldehyde based hybrid composite systems were investigated and the following conclusions can be drawn from experimental results:

- The microstructure observed with SEM, revealed that fillers like molybdenum disulphide and copper strongly improved the adhesion and compatibility with other fillers as well as with various binders in PF based hybrid composites.
- Molykote/copper/graphite loading influenced the density and hardness of PF based composite systems (A2, A3, A4 and A5) and they showed increased tendency as compared with reference PF composite (Sample A1) and hybrid filler (graphite + antimony; A6) loaded composite systems. Samples of A3 (5 wt. % Cu) showed highest density whereas A5 (Gr + MC) showed the highest hardness.
- The MC/Cu/Gr filled PF based hybrid composites showed good compressive and flexural strengths as well as modulus compared to the control sample (A1).
- The hybridization of MC + Gr in PF based composite increased the mechanical properties, which was highest for B + F + (Gr +MC) PF based hybrid composite (A5) among all the PF based composites studied in the group.

Conflict of Interest

Authors are hereby making humble note about not making complete disclosure of formulation of Materials system and methods followed to fabricate Composite Brake Block (CBB) specimens. Since, it is treated as confidential matter by South Western Railway, Office of the CWM, Central workshop, Mysore South, Karnataka. However, with the consent of South Western Railway authority, authors bring out the sufficient details required for technical understanding of present investigation and for publication.

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