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RESPONSE OF FLY ASH-REINFORCED FUNCTIONALLY GRADED RUBBER COMPOSITES SUBJECTED TO MECHANICAL LOADING

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Keywords: *functionally graded material, fly ash, rubber composite, Young's modulus, finite-element analysis*

A novel approach to estimate the Young's modulus of a functionally graded rubber composite (FGRC) from the damping ratio is demonstrated with the examples of unreinforced and fly ash-reinforced materials. FGRC coupons were prepared using the conventional casting technique. The occurrence of gradation in the specimens was attributed to the variable density of particles present in the fly ash, settling at different depths. The technique of free vibrations was used for experimentation. The damping response of the FGRC specimens was studied. The results obtained from the experiments showed that, with growing filler weight fraction, the Young's modulus of the composite increased. The empirical model developed to predict the magnitude of the modulus turned out to be in good agreement with experimental data.

1. Introduction

Many of the modern technologies require materials with unusual combinations of properties which cannot be met by the conventional metal alloys, ceramics, and polymers alone. This is especially true for materials which are needed for aerospace, underwater, and transportation applications. With a knowledge of the various types of the composites and an understanding of the dependence of their behavior on the characteristics, relative amounts, and distribution of the constituent phases, it is possible to design materials with property combinations that are better than those found in the conventional ones. Polymer-matrix composites are becoming promising materials for a variety of structural and automotive applications, because they possess favorable combinations of mechanical properties [1].

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As a result of marked improvements in the mechanical behavior, together with significant economic advantages, rubber reinforced with a filler presents the most widely used and extensively studied polymeric composite [2]. Rubber has played a vital role ushering the modern civilization and is undoubtedly one of the most useful substances in the world [3]. Filled rubber materials are widely used in today's industries owing to their increased stiffness and wear resistance in comparison with their natural (unfilled) forms. Vulcanized rubbers are one of the most remarkable materials, having a wide range of engineering applications, including tires, engine mounts, shock-absorbing bushes, seals, tunnel linings, and wind shoes [4-6]. The incorporation of a filler into a rubbery polymer imparts many interesting and useful properties to the resulting composite material. Considering various factors which are known to influence the mechanical properties of the material, instead of attempting a multiplicity of systems, if a gradient structure could be developed, its response to loading would be different, and hence such an arrangement has to be studied. Keeping this approach in mind, functionally graded materials (FGMs) need to be developed.

FGMs are systems where a material property varies with geometric parameters, such as thickness, length, etc [7, 8]. FGMs have various applications, e.g., in thermal-barriers [9]. As many of the polymeric systems used for developing FGMs are generally associated with the tag of expensiveness, it was decided to examine the gradation in a composite and its damping behavior in the case where the abundantly available fly ash is used as a filler for the naturally occurring elastomer known as "natural rubber".

The introduction of reinforcing additions, such as carbon black, silica, etc., is usually associated with improvements in the mechanical properties of rubber, such as the elastic modulus, hardness, and tensile and tear strength [10]. An important property under dynamic situations is damping. Filled rubbers with gradation in composition could be suitable candidates for damping. The natural rubber is frequently employed in structures because of its high elasticity, high damping ability, and large elongation at failure. A number of studies can be found in the literature pertaining to the behavioral analyzis of rubber composites [11], but the characterization and analyzis of rubber composites with gradient properties is yet to be realized. The prediction of the mechanical behavior of elastomeric materials has been an active research area for many years, and many numerical studies addressing different characteristics of their elastomeric response have been carried out. Thus, the survey of the available literature indicates that a systematic study on the properties of fly ash-reinforced functionally graded rubber composites (FGRCs) is necessary.

It should be emphasized that, at the moment, the number of experimental investigations into the mechanical behavior of FGMs is very limited. In this paper, a model of functionally graded particulate composites is developed. The variation in the Young's modulus of a FGM is determined experimentally. The present study focuses on characterizing the modulus of a FGRC containing fly ash as a filler, which is an industrial waste and pollutant [12]. This paper outlines the details of an experimental approach to estimating the Young's modulus of FGRC specimens from the damping ratio [13] according to ASTM E 756-05 [14]. Furthermore, an empirical model is developed to predict Young's modulus, and its accuracy is verified by the results of a second set of experiments. Finally, the correlation of the experimental data with the results of a finite-element analysis (FEA) is considered.

2. Material and Methods

2.1. Materials

The matrix used was a natural latex supplied by the Karnataka Forest Development Corporation Ltd. (KFDC), Rubber division, Sullia, Karnataka, India. Its density was found to be 1060 kg/m^3. The filler used, i.e., fly ash, was procured by the Raichur Thermal Power Plant, Raichur, Karnataka, India. This ASTM class 'C' fly ash, with a bulk density of about 900 kg/m^3, was a mixture of solid and hollow spheres of assorted sizes. Silica (63%) and alumina (26%) particles were found to be its main constituents [12]. The gradation in the composite obtained was caused by the slightly varying density of the filler owing to the existence of different morphologies of ash particles (plerospheres, cenospheres, or composite ones).

2.2. Processing

Test specimens were prepared by using the conventional casting technique. A pre-weighed amount of fly ash and measured quantities of natural latex, sulphur (vulcanizer), and zinc oxide (catalyst) [15] were mixed together with gentle stirring for about one hour. The mixture obtained was slowly decanted into a 200 × 45 × 10 mm mold, which was completely covered on all sides with a Teflon sheet coated with a silicone releasing agent for easy removal of the cast sample. The mixture was left to cure in an oven at 90°C for about 5-6 h. The cured sample was withdrawn from the mold, and its edges were trimmed. Using a similar procedure, FGRC samples with a varying amount of filler (10, 20, and 30) were cast.

Test specimens of dimensions of 180 × 10 × 4 mm were cut from the trimmed cast specimens by using a diamond-tipped cutting machine.

2.3 Test for gradation

A separate 10 × 10 × 10 mm slab was cut from each specimen for the test of gradation. Four slices of dimension 10 × 10 × 2.5 mm were cut from the slab. Each slice was weighed. Subsequently each slice was heated in an electric bunsen till the sample turned white. The sample was then immersed in tetrahydrofuran to dissolve the rubber component. As the solvent evaporated, the residual fly ash was weighed. The weight fraction of fly ash in each slice was calculated by

$$\text{wt.\% of fly ash} = \frac{\text{weight of residue}}{\text{weight of slice}} \times 100\%.$$

Five replicas of the 10% fly ash sample were tested, and the average of the measured values was calculated. A similar procedure was performed for specimens with 20 and 30 wt.% of filler. Thereafter, the specimens of FG rubber were wrapped in a silver foil, gold-coated under vacuum in an ion sputtering unit at an ionizing current of 10 mA to make them conducting, and then examined in a JOEL JSM 6380 LA SEM.

3. Constitutive Model

The literature on the modeling of rubbers is huge [16, 17]. A number of constitutive models have been developed to address the steady-state, rate-dependent behavior of rubber under cyclic loading [18]. Most commonly, hyperelastic constitutive models are used to describe the nonlinear elastic behavior of rubber. Hyperelastic models are capable of representing a nonlinear elastic stress–strain relationship independent of the prior strain history. Such models are especially appropriate for characterizing unfilled, vulcanized rubbers [19]. Constitutive models that capture this effect are not yet in widespread use, although there appear to exist some promising recent developments [20]. Many researches have worked on different hyperelastic constitutive models and have captured the stress–strain behavior of rubber [21-25].

Despite the fact that rubber is used in a wide range of industrial and consumer products, we still do not have a complete understanding of its mechanical behavior, and we lack constitutive models to accurately simulate some of its responses. This is particularly true for products made of functionally graded filled rubber compounds that operate under dynamic loads. Although the models elaborated and described in the available literature are shown to capture the behavior of filled elastomers, the effect of fillers is not explicitly taken into account in any of properties of the material. To the best of author's knowledge, no literature is available for the constitutive modeling of FGRCs. There has been no attempt to evaluate Young's modulus from the damping ratio with account of filler content by using a theory of composite materials.

As the focus of the present study is the behavioral analysis of FGRC, at the heart of our constitutive model is the theory governing FG reinforced materials, according to which [26]

$$E = f(z) = E_f V_f(z) + E_m(1 - V_f(z)), \tag{1}$$

where, E is the Young's modulus of composite, E_f is the Young's modulus of filler, E_m is the Young's modulus of matrix, and V_f is the volume fraction of filler, which varies along the z axis (the gradation axis). Equation (1) is a preliminary relationship based on the rule of mixtures, lacking in accuracy. For a FG beam of length L, width b, and thickness h, Young's modulus E, varying continuously in the thickness direction (in the z-axis direction – across the thickness), can be written in the form [27]

$$E(z) = E_m + (E_f - E_m)\left(\frac{2z+h}{2h}\right)^k, \tag{2}$$

where $k \geq 0$, and m and f stands for the matrix and filler, respectively.

Equation (2) is modified considering the concept of matrix overstrains in networks with colloidal highly structured fillers [10]. The resulting expressions is written as

$$E(z) = E_m\left[1+\left(1+\frac{2.5\varphi_{eff}}{1-2\varphi_{eff}}\right)\left(\frac{2z+h}{2h}\right)^k\right],$$

where, φ_{eff} is the effective volume fraction of filler, which takes into account all less deformable parts of the rubber matrix [28].

For describing the reinforcing effect of colloidal fillers on elastomers, Guth and Gold [29] several decades ago introduced a quadratic term on the basis of the Smallwood–Einstein equation to take into account the interaction between filler particles and obtained the equation

$$E = E_m\left(1+2.5\varphi+14.1\varphi^2\right), \tag{3}$$

where φ is the volume fraction of filler.

Equation (3) is only applicable to elastomers filled with a certain amount of spherical particles. If the filler concentration is higher than 10 vol.%, the modulus increases much more rapidly than Eq. (3) would predict. Guth [30] later developed a new equation by introducing a shape factor α (length/breadth), namely

$$E = E_m\left(1+0.67\alpha\varphi+1.62\alpha\varphi^2\right). \tag{4}$$

Due to adaptability of the Guth equation to rubber composites, Eq. (2), as applied to FGRCs, is written in the form

$$E(z) = E_m\left[1+\left(1+0.67\alpha\varphi+1.62\alpha\varphi^2\right)\left(\frac{2z+h}{2h}\right)^k\right].$$

4. Experimental Program

FGRC specimens cut to the shape required were pasted on an Oberst bar by using a Chemlok 205/220 adhesive. The surface of specimens was previously made rough to increase the adhesion and was thoroughly cleansed with toluene. Alternate coats of a primer and the adhesive were applied thrice to the specimens by a brush and dried at room temperature. The drying time typically varied from 30 to 45 min for the primer and from 45 to 60 min for the adhesive. Immediately after the last coat had been applied, a precut specimen was pasted under a moderate pressure sustained for about half an hour at 60°C.

4.1. Test setup

Figure 1 shows the arrangement of the experimental setup with an Oberst bar and a specimen in position. The complete experimental setup with a fast Fourier transform (FFT) analyzer is shown in Fig. 1b.

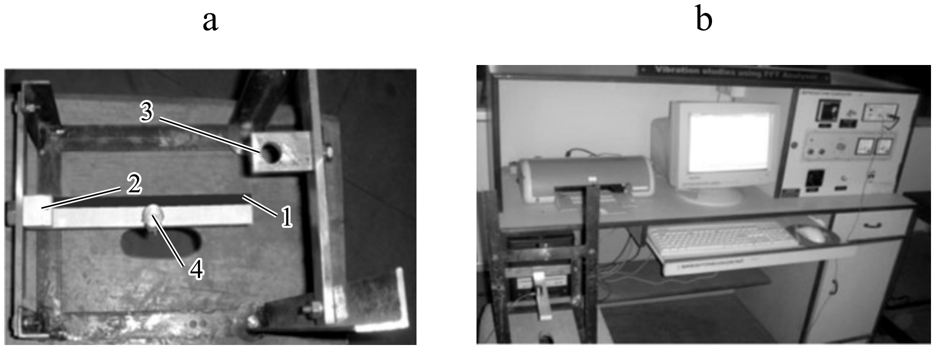

Fig. 1. FGM specimen (1) on the Oberst bar (2), mass droping arrangement (3), and accelerometer (4) (a) and the experimental setup (b).

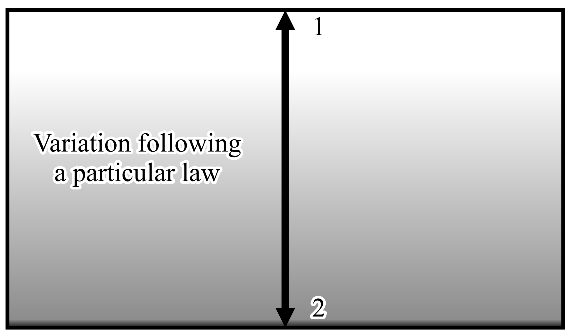

Fig. 2. Variation in specimen properties in the rubber-up configuration.

A single-channel FFT analyzer with a frequency range of 0-10,000 Hz, coupled with an accelerometer having a frequency range of 1-6000 Hz, was used for signal pickup. A FGRC specimen, along with the Oberst bar, was set in free vibration. The tests were carried out for two different orientations of specimen — with rubber up (Fig. 2) and ash up.

In each trial, five replicates were tested and the average of the measured response was considered for analysis. The test results provided by the system were in the form of acceleration vs. time plots, which were then converted to plots of displacement vs. time. The damping ratio and modulus were estimated from displacement–time data.

4.2 Determination of Young's modulus from the damping ratio

The damping ratio can be found from a displacement–time plot, as shown below.

The logarithmic decrement δ is expressed as [23]

$$\delta = \ln \frac{Y_m}{Y_{m+n}},$$

where Y_m and Y_{m+n} are vibration amplitudes.

For small values of the damping ratio ξ, the formula

$$\xi \cong \delta / 2\pi$$

is valid.

The Young's modulus or stiffness of FGRC is then computed from the experimentally estimated damping ratio, which in turn is calculated from the damped natural frequency w_d found from the amplitude vs. frequency plot. The stiffness k of the entire system (a specimen with the Oberst bar) is estimated by the formula

$$k = \frac{w_{\mathrm{d}}^2 (m)}{1-\xi^2}.$$

Knowing the stiffness k_{Oberst} of the Oberst bar, the stiffness k_{FGM} of a FGM specimen is computed from the formula

$$k_{\mathrm{FGM}} = k - k_{\mathrm{Oberst}}.$$

The Young's modulus of FGM specimen is computed from k_{FGM} by using the relation [31]

$$E_{\mathrm{FGM}} = \frac{k_{\mathrm{FGM}}\, L}{A}, \tag{5}$$

where E_{FGM} is the Young's modulus of FGM, A is the cross sectional area of the FGM specimen, and L is its length.

Equation (5) is utilized for calculating the Young's modulus of rubber and rubber-like materials, because their stress–strain curves are linear up to strains of about 10%. At higher strains, they become nonlinear. The linear portions of the curves are used to determine the Young's modulus of the elastomers [32].

4.3 Empirical model for Young's modulus

A linear regression model (empirical model) [33] has been developed for both the rubber-up and the ash-up cases to establish a correlation between the weight fraction of fly ash and Young's modulus. According to the model,

Young's modulus for the rubber-up condition (YM-RU) is given by

$$\text{YM-RU} = 0.955 + 0.178W \tag{6}$$

and for the ash-up condition (YM-AU) by

$$\text{YM-AU} = 1.07 + 0.187W, \tag{7}$$

where W is the wt.% of fly ash.

4.4 Simulation of FGRCs by using ANSYS

Young's modulus of a FGRC specimen was evaluated using a finite-element analysis and then utilized to validate experimental results. ANSYS 5.4, a commercially available software package, was employed for the analysis. A modal analysis was performed for a specimen modeled as a two-dimensional SOLID45 element having1991 nodes and 1800 finite elements. The edge length of the element was taken to be one. At the contact surfaces of layers and between the layers, rigid contact conditions were specified to eliminate the relative movement of layers with respect of each other. Furthermore, nodes were merged at the interface, thus securing a proper coupling between the layers and interfaces. The possible variations owing to the gradation considered in the present FE analysis are uniform (U), linear (L) and piecewise linear (PL) ones, as shown in Fig. 3.

To provide an input into the FEA, Young's modulus for each layer was calculated from Eq. (4) at $\alpha = 1$, since the filler particles were spherical:

$$E = E_{\mathrm{m}} \left(1 + 0.67\varphi + 1.62\varphi^2\right).$$

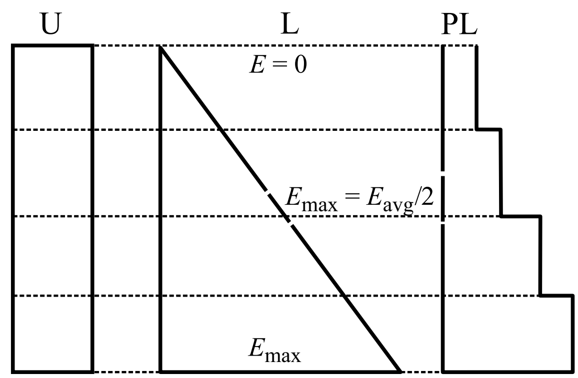

Fig. 3. Gradation across the specimen thickness: uniform (U), linear (L), and piecewise linear (PL).

TABLE 1. Properties Used in the FEA for Modeling the FG Core

Wt. % of fly ash	Layer No.	Layerwise wt.% of fly ash	Young's Modulus, GPa	Density, kg/m^3
10	1	1	0.63	1041.9
	2	2	0.65	1043.6
	3	3	0.68	1044.7
	4	4	0.71	1045.9
20	1	2	0.65	1043.6
	2	4	0.71	1045.9
	3	6	0.79	1047.1
	4	8	0.88	1051.3
30	1	3	0.68	1044.7
	2	6	0.79	1047.1
	3	9	0.94	1052.3
	4	12	1.15	1056.3

The values of E obtained from this equation are shown in Table 1, where the densities estimated using the rule of mixtures are also listed.

The FEA was carried out for all these different cases of gradation with rubber-up and ash-up configurations, as mentioned before.

5. Results and Discussion

5.1. Gradation characterization of the FG core

Figure 4 presents SEM photographs of the rubber with 10 wt.% of filler and the results of the burn-out test (as mentioned in Sect. 2.3). In the four slices shown in the figure, the test gave the weight percentages of fly ash 0.81 against 1, 1.78 against 2, 2.75 against 3 and 3.80 against 4 from top to bottom, respectively, where 1, 2, 3, and 4 were the notional filler concentrations

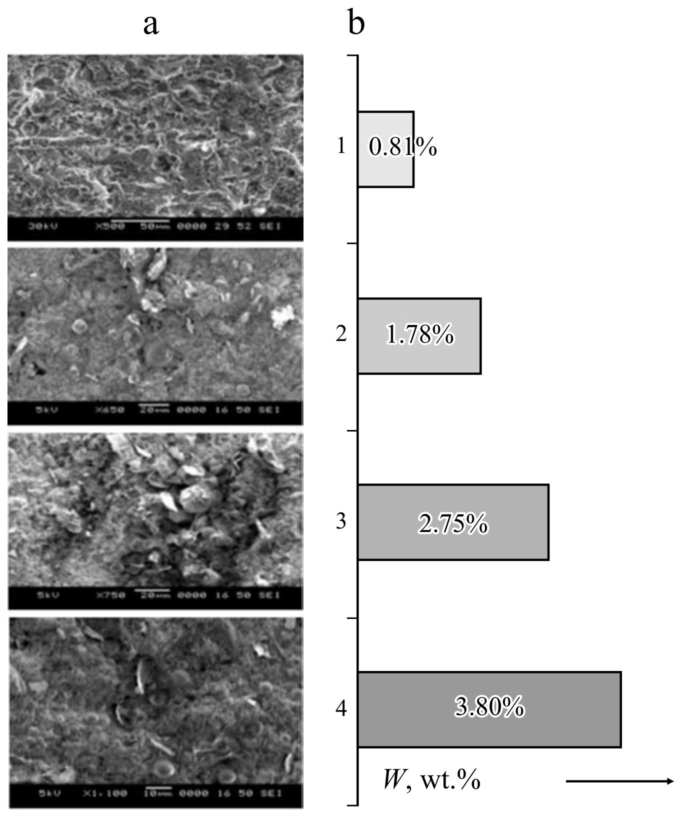

Fig. 4. SEM photographs of a FG rubber with 10 wt.% of fly ash (a) and concentration of the filler in four slices of the rubber (b) in the rubber-up configuration.

TABLE 2. Values of Young's Modulus (YM)

Fly ash, wt.%	YM from the damping ratio		YM from the tensile test at RU, GPa
	Rubber up (RU), GPa	Ash up, GPa	
0	1.02	1.06	0.97
10	2.51	2.56	1.80
20	4.79	4.99	3.25
30	6.21	6.59	5.16

in the FG sample. The actual filler weight content had boiled down to 9.14% against 10%. This difference could be attributed to the loss of filler during the burn-out process (residual separation) and to the loss of some its particles during weighing.

The gradation is evident from the distribution of fly ash particles in different slices of the sample, as illustrated in Fig. 4.

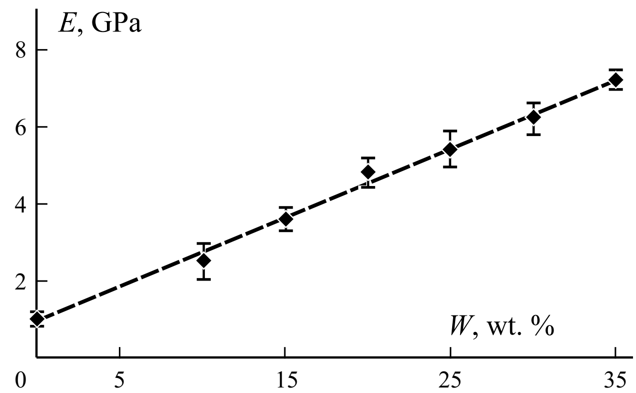

Fig. 5. Comparison of experimental (◆) and predicted (– – –) Young's moduli E for the rubber-up configuration.

5.2. Young's modulus

The Young's moduli of all FGM specimens estimated from the experimentally evaluated damping ratio (as discussed in Sect. 4.2) are listed in Table 2. Table 2 also shows Young's moduli obtained using the conventional tensile testing methodology.

The increase in the modulus is in line with expectations for a hard reinforcement such as fly ash (E = 70 GPa [34]), in a soft rubbery matrix (E = 1 GPa [3]). The high-modulus fly ash particles were expected to increase the modulus based on their volume/weight fraction, shape and aspect ratio [35]. This question has been studied extensively both theoretically and experimentally [35, 36]. The moduli determined by the present technique were compared with those found from the conventional tensile test (Table 2). As seen, they are in close agreement with each other. Thus, we can conclude that the indirect way of determination of the modulus E from a damping analysis also yields sensible results.

A significant observation in the present study is the increase in E, even with relatively small additions of fly ash. With introduction of 10, 20, and 30 wt.% of the filler, Young's modulus increased by the factors of 2.5, 4.7, and 6 compared with that of the unfilled rubber for the rubber-up configuration and 2.7, 4.7, and 6.2 times in the ash-up case. This might be because of the fact that, with increase in filler content, the stiffening effect creeps in, causing constrained straining of the matrix. This clearly suggests that the fly ash network becomes more and more prominent with growing weight fractions of the filler. The presence of a network aided by gradation results in a much more progressive modulus as compared with those of the neat counterparts. One more obvious reason could be the high surface-to-volume ratio of ash particles.

Young's modulus is an increasing function of filler content, although the increase in it at 20 wt.% of the filler is not considerable. This increase might be due to the constraint imposed on matrix deformation by the presence of the rigid particles. A similar observation was reported by Guo et al. [37] in the case of vinyl ester resin reinforced with functionalized alumina particles and has also been mentioned in several other studies [38]. However, there might exist a critical composition at which these characteristics undergo an inversion in their trends.

Young's modulus for the ash-up configuration is recorded to be on the higher side than that for its counterpart (within 4%). As this difference is small, it can be safely neglected owing to material nonlinearity.

5.3. Empirical model

By taking different values of filler weight fraction in Eqs. (6) and (7), Young's modulus can be calculated for both the cases configurations mentioned. The positive coefficients of the equations suggests that the modulus of FGRC increases with the weight fraction of fly ash for the tested range in both the configurations.

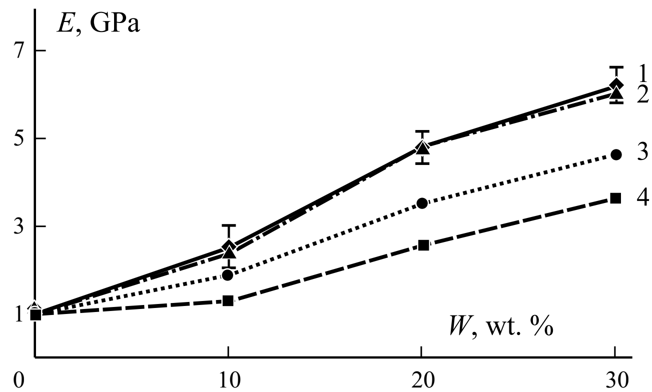

Fig. 6. Young’s modulus E vs. the weight percent W of fly ash for the rubber-up configuration: experimental (1), FEA-PL (2), FEA-U (3), and FEA-L (4).

Control tests were also performed at 15, 25, and 35 wt.% of fly ash. The experiments were conducted with five replicates each. Figure 5 compares the results predicted by the empirical rule (Eq. (6)) with experimental data for the rubber-up configuration. A similar picture was also observed in the case of ash-up configuration.

As one can see, the empirical results agree well with the experimental ones. The calculated error varies within 1% for the rubber-up configuration and within 1.6% for the ash-up one. This indicates that the regression equation derived above describes the evaluation of the modulus in the FG samples with a very good degree of approximation.

5.4. Finite-element Simulation

A comparison of Young’s moduli obtained by the indirect experimental approach (from the damping ratio) and the FE method, at different weight fractions of fly ash, is presented in Fig. 6 for the rubber-up configuration.

It is evident from Fig. 6 that the FEA results for uniform (FEA-U) and linear (FEA-L) gradations deviate to a large extent from the experimental results. In contrary, the experimental data closely agree with the FEA results obtained for the piecewise linear gradation (FEA-PL). This fact once agains confirms the existence of piecewise linearity of the filler across the thickness in the specimens prepared. This could be a breakthrough in the present study, because the FG samples were casted in a single go.

6. Conclusions

The preparation and mechanical characterization of a functionally graded material have been undertaken. A graded particulate composite comprising spherical particle of fly ash and a rubber matrix was developed using the gravity casting technique. A method for determining Young’s modulus from a damping analysis of the FGM was elaborated. This paper deals with some key issues related to the functionally graded filled rubber composite. The following conclusions are drawn from the behavioral analysis of the FGRC.

The results of burn-out test clearly point to an increasing weight fraction of fly ash across the thickness of test specimens. This fact confirms the presence of gradation in the FGRC.

The Young’s modulus of FGRC can be evaluated from the damping ratio found experimentally in free-vibration tests.

The empirical model developed for predicting the Young’s modulus of FGRC is in very good agreement with experimental data. The gradation achieved closely agrees with FE results if the gradation is assumed to be piecewise linear.

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