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Strain Sensors Based on Graphite Fillers

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ABSTRACT

In this research, producing a particulate conductive composite is being investigated. The composites are made of ethylene-vinyl acetate (EVA) and polyvinyl choloride (PVC) as matrix and graphite as filler. There are two different procedures applied: dissolving the polymer matrix in a suitable solvent and then add the filler to the solution, which does not work out for PVC because phase separation takes place between the melt mixing of the matrix and filler. The solvents used were toluene for EVA and THF for PVC. The composites were prepared in different volume fractions. After having the composites prepared they were compression moulded into the shape of dumbbells when two extreme sides were covered with a conductive coating. Electrical resistance of the samples before and during applying the strain was measured. Then, gauge factor (strain sensitivity factor) for each sample was calculated and finally the sample with higher gauge factor was chosen.

Key Words:

strain sensor; graphite; piezoresistivity; electrical resistance; conductive composite.

INTRODUCTION

Any device measuring the dimensional changes of an object due to mechanical or thermal stresses or combination of both is called a strain gauge or strain sensor [1].

Strain sensors have various applications, such as controlling sys-

tems of different structures (e.g., bridges, buildings, dams, and containers), calibrating the accuracy of the laboratory devices which measure mechanical properties of material, and totally any other application in which measuring and controlling

(*)To whom correspondence should be addressed. E-mail: ebrahimn@modares.ac.ir the strain is considered [2,3]. Strain sensors are divided into four groups; optical fibre sensors, shape memory alloys (SMA), piezoelectric ceramics and electromechanical strain gauges [2]. Polymer composites are in the electro-mechanical strain sensor group. Piezoresistivity is one of the bases of strain measurement in these sensors. Generally, any material in which the electrical resistance is a function of internal strain is called piezoresistive. The most common piezoresistive material is composites containing a polymer matrix and a conductive filler [1]. Mostly used fillers include metal powder, carbon fillers, semi-conductive metal oxides (e.g., V₂O₃, TiO₂) or non-conductive powders with their surface modified using different methods [3-8]. Among them carbon fillers are used mostly in order to achieve composites with desirable mechanical properties, corrosion resistant, light weight and conductive. Carbon black (CB), graphite (G) and carbon fibres (F), that differ from each other structurally, are in this category [5,8]. In these sensors any polymer with suitable elasticity and toughness can be used [3]. As the deformation of matrix and fillers is not in the same scale during the applied stress, the strain induced, increases the distance between the filler particles dispersed in the matrix and results in piezoresistive effect [9]. Strain sensitivity or gauge factor is defined as the aspect of electrical resistance value to dimensional changes:

$$G = (dR / R) / (dL / L) = (\Delta R / R0) / \varepsilon$$
⁽¹⁾

In these sensors the resistance changes due to the strain is non-linear. Besides they do not show much sensitivity to small values of strain, therefore, they are not applicable in such cases [1,3,9,10].

Electrical resistance of a conductive composite depends on the filler volume fraction. At a distinct temperature an insulator-to-conductor transition occurs in the composite. When the filler content is very low, the electrical resistance of the composite is very similar to the matrix's, but in a certain volume fraction, the resistance reduces suddenly, which is called percolation threshold [8,9]. After that point, the electrical resistance reduces until the volume fraction reaches its critical value, at this point all the fillers particles are covered with a very thin layer of matrix, and adding another filler particle is similar to adding a third part to the system and can cause misleadings in the trend of changes in the property of the composite [11]. These also include electrical properties. This critical value, named critical percolation volume concentration (CPVC), can be calculated using the oil absorption (\overline{OA}) value of the filler [11,12].

$$CPVC = \frac{1}{1 + (\frac{\rho_{poly}}{993.5} \times \overline{OA})}$$
(2)

Where, ρ_{poly} is the polymer density and \overline{OA} is defined as the grams of oil in 100 g of powder which can make the paste-like particle [11,12].

Some of the factors affecting the electrical resistance of the composite are: shape and dimensions of the filler particles. For instance in the spherical fillers, smaller diameter particles cause lower percolation threshold, or for the fillers in which L/D ratio is more than one, more extensive distribution values of L/D result in the reduction of percolation threshold. Wetting is another affecting parameter on the percolation threshold, which depends on the difference between surface energies of the matrix and filler. Better wetting of filler particles using polymer matrix, reduces the connection between particles, and causes a reduction in the total resistance and also in the percolation threshold of the composite. That is why a difference in surface energies of the polymer and filler seems desirable [8].

Piezoresistive Model

When the stress is applied to the composite, its electrical resistance changes due to the change of distance between particles. According to the model introduced by Zhang et al. [9,10], assuming that the distance between two particles changes from S_0 to S, relative resistance (R/R₀) is calculated by:

$$R/R_{o} = (S/S_{o}).exp[-\gamma(S-S_{o})]$$
⁽³⁾

Where, R_0 is the initial resistance and S_0 is the initial distance between particles, and γ is defined as:

$$\gamma = (4\pi/h) \times \sqrt{(2m\phi)} \tag{4}$$

Where, m is electron mass; h , the Plank s constant; and φ , the potential barrier height [9,10].

As the modulus of polymer is much less than the

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modulus of the filler, the deformation of filler particles under strain can be ignored. So, the changes occurring in the distance between two particles across the electrical conduction path can only be CPVC= due to the deformation of polymeric matrix. So the distance S after uniaxial compression would be:

$$S = S_{0}(1 - \varepsilon) = S_{0}(1 - \sigma/M)$$
(5)

and if the stress is extensional, then:

$$S = S_{0}(1+\varepsilon) = S_{0}(1+\sigma/M)$$
(6)

where, ε is the matrix s strain, σ is the stress being applied and M is the polymer modulus. Assuming that the filler particles dispersion has a cubic lattice array, the initial distance between two particles, S_o, would be:

$$S_{0} = D[(\pi/6)^{1/3} \times \theta^{-1/3} - 1]$$
⁽⁷⁾

Relative resistance, the most important parameter in piezoresistive effect, will be achieved by replacing eqns (6) and (7) in eqn (3):

$$R / R_0 = (1 + \sigma / M) \times \exp[-\gamma D[(\pi / 6)^{1/3} \times \theta^{-1/3} - 1] \times \epsilon]$$
(8)

. . .

Using eqn (8), the effect of stress (σ), composite modulus (M), filler particle s diameter (D), filler volume fraction (θ) and potential barrier height (ϕ), on the piezoresistivity can be investigated [9,10].

EXPERIMENTAL

The materials used in this research are as following: ethylene vinyl acetate (EVA) with 18 wt% of vinyl acetate, melting point 88 C, and density 0.9 g/mL, plasticized polyvinyl chloride (PVC), with 50% DOP (plasticizer) and density 1.14 g/mL, graphite powder with particle size of 25-38 microns, and density 1.25 g/mL.

In this research, the production of composites using both EVA and PVC matrices by dissolving and melt mixing procedures was desired, but because of the existence of DOP in plasticized PVC, the prepared solution prepared separated into two phases and so the solution mixing procedure was not applicable in this case.



Figure 1. Dumb-bells moulded from the composites [3].

In solution mixing procedure, EVA was dissolved in toluene at 75 C so that a 35 wt% concentration solution was obtained. Then the calculated amount of graphite was added, and it was stirred at a rate of 400 rpm rate for 1 h. Then the mixture was transferred into teflon pans so that their solvent content would be evaporated after 24 h. After that samples were completely dried in the oven, at the temperature of 115 C for 16 h. The samples showed no electrical conductance before being dried in the oven. Then the dried composites were chopped and compression moulded into the shape, shown in Figure 1.

In the melt mixing procedure, mixing was done in a Brabender internal mixer at 150 C for EVA and 190 C for PVC, for 30 min. Then the mixtures were also compression moulded into the shape of Figure 1.

The compositions of the prepared mixtures are described in Tables 1-3.

After preparing dumbbells according to Figure 1, the specified areas on the Figure, were covered with a conductive coating (which could be a silver paint, or aluminium foil, etc.). It should also be mentioned here that samples EG1-M and EG1-S were rejected because of no conduction and sample EG6-S was also rejected because of not having enough mechanical strenghth.

Sample	Composition (EVA/graphite)	Graphite (g)
EG1-S	65/35	1.3
EG2-S	60/40	1.6
EG3-S	55/45	2
EG4-S	50/50	2.4
EG5-S	45/55	3
EG6-S	40/60	3.6

 Table 1. Composition of EVA samples (solution mixing).

Somolo	Composition	EVA	Graphite
Sample	(EVA/graphite)	(g)	(g)
EG1-M	70/30	30.9	18.4
EG2-M	65/35	28.7	21.4
EG3-M	60/40	26.5	24.5
EG4-M	57.5/42.5	25.4	26
EG5-M	55/45	24.3	27.6
EG6-M	50/50	22.1	30.6

Table 2. Composition of EVA samples (melt mixing).

Table 3. Composition of PVC samples (melt mixing).

Comple	Composition	EVA	Graphite
Sample	(EVA/graphite)	(g)	(g)
PG1-M	40/60	33.5	24.5
PG2-M	57.5 / 42.5	32.1	26
PG3-M	55/45	30.7	27.6

The electrical resistance of the samples, before applying the strain and also during that, was measured using a digital multi-meter (KAISE, SK 611). Extension tests were done by an Instron 4466 extensometer.

RESULTS AND DISCUSSION

The initial values of the samples are shown in Figure 2.

As it is shown in Figure 2, the percolation threshold for EVA composites (solution mixed) is around volume fraction of 35-40; EVA (melt mixed), around 30-35; and PVC, around 40-42.5. The other point in the graphs of Figure 2 is another increase in the resistance after percolation. This increase is in volume fraction of 50 for EVA samples and 45 for PVC. It can be said that the mentioned volume fractions are about the critical value (CPVC), calculated theoretically using eqn (2), after measuring \overline{OA} of graphite which is 107.9 g. The values for CPVC of the composites are shown in Table 4.

Comparing the SEM micrographs of EG5-M and

Table 4. CPVC Value for composites of PVC and EVA matrix

 and graphite filler.

Matrix	CPVC (%)
EVA	49.1
PVC	43.2



Figure 2. Resistance vs. filler volume fraction in composite (a) EVA, solution (b) EVA, and PVC melt.

EG6-M (Figures 3 and 4) shows a fluffy structure in EG6-M sample, where EG5-M has more continuous structure. This can further prove the reason why the resistance increases in volume fraction of 50.

Figure 5 shows the electrical resistance vs. strain graphs in composites. To plot these graphs, three dumbbells of each composition were tested, and the most suitable curve was fitted with the data. Figure 6, shows



Figure 3. SEM Micrograph of EG6-M,1000x.



Figure 4. SEM micrograph of EG5-M,1000x.



Figure 5. Resistance vs-strain curves: (a) EVA solution; (b) EVA melt; and (c) PVC melt .



Figure 6. Exponential behaviour of resistancevs-strain curve for sample EG3- M. The equation is related to fitted curve is: $R = 10.187 \text{ exp} (0.5885 \varepsilon).$



Figure 7. Gauge factor vs volume fraction for EVA composites(melt mixing).



Figure 8. Gauge factor vs. volume fraction for EVA composites (solution mixing).

all three series of data in addition to the fitted curve for sample EG3-M.

It is obvious in Figure 5, that the general trend of resistance changes due to strain is exponential, that was expected according to references [5,17,18, 20].

Figures 7-9 show the values of gauge factor (G) vs.



Figure 9. Gauge factor vs. volume fraction for PVC composites(melt mixing).



Figure 10. Piezoresistive model check for EG5-M sample.

volume fraction of the filler for each composite(o is the middle point).

The values of (G) were calculated using the data of Figure 5 and eqn (1). Assuming a middle point at each volume fraction, shows that EG5-M has the highest value and so this is the optimized sample.

Finally, to check the piezoresistive trend of the samples with the model explained by eqn (8), γ values where calculated, using the electrical resistance and strain values at each point for all data series of each composition. Then the average values of γ were substituted in eqn (8) and the theoretical equation achieved was plotted for each sample. It should be noticed that as the filler particle s sizes change in the range of 25- 35μ , the theoretical graph was plotted twice for each sample. Comparing the theoretical graphs with experimental data it was shown, that sample EG5-M has the best fitting with the model. This is shown in Figure 10.

The theoretical equations gained according to eqn (8) are shown in Table 5.

Table	5.	Theoretical	equations	describing	piesoresistive
behavi	iour				

Sample	Particle size(mic.)	Equation
EG3-M	25	$R/R_0 = (1 + \epsilon) \exp (30.7 \epsilon)$
203-101	38	$R/R_0 = (1 + \varepsilon) \exp (39.82 \varepsilon)$
EG4-M	25	$R/R_0 = (1 + \epsilon) \exp (39.12 \epsilon)$
	38	$R/R_0 = (1 + \varepsilon) \exp (39.06 \varepsilon)$
EG5 M	25	$R/R_0 = (1 + \varepsilon) \exp(59.7 \varepsilon)$
EG3-W	38	$R/R_0 = (1 + \varepsilon) \exp(60.11 \varepsilon)$
EG6-M	25	$R/R_0 = (1 + \varepsilon) \exp(8.62 \varepsilon)$
200-101	38	$R/R_0 = (1 + \varepsilon) \exp(6.04 \varepsilon)$
EG2-M	25	$R/R_0 = (1 + \varepsilon) \exp (20.19 \varepsilon)$
L02-W	38	$R/R_0 = (1 + \varepsilon) \exp (20.2 \varepsilon)$
EG2 M	25	$R/R_0 = (1 + \epsilon) \exp (53.24 \epsilon)$
EG3-W	38	$R/R_0 = (1 + \varepsilon) \exp(53.22 \varepsilon)$
EC2 S	25	$R/R_0 = (1 + \varepsilon) \exp (43.79 \varepsilon)$
E02-3	38	$R/R_0 = (1 + \epsilon) \exp (42.88 \epsilon)$
EG3-S	25	$R/R_0 = (1 + \varepsilon) \exp(54.89 \varepsilon)$
E03-3	38	$R/R_0 = (1 + ε) \exp (45.77 ε)$
EC4 S	25	$R/R_0 = (1 + \varepsilon) \exp(16.89 \varepsilon)$
EG4-3	38	$R/R_0 = (1 + \varepsilon) \exp(17.67 \varepsilon)$

CONCLUSION

The samples with the volume fraction of 40 to 60 filler content were prepared. The electrical resistance of the samples showed another increase, after percolation volume fraction, around 50% for EVA and 45% for PVC matrices. The composites prepared by dissolving mixing procedure had much lower electrical resistance than the samples prepared by melt mixing. This is because the shear applied in melt mixing procedure results in better dispersion of filler particles in the matrix which reduces the possibility of conductive network formation.

Investigating the graphs of electrical resistance vs. strain approves an exponential behaviour. Comparing these graphs with the piezoresistive model, it can be shown that the samples EG5-M and PG3-M are best fitted with the model. Whereas, the sample EG5-S does not fit at all. The sample EG5-M was recognized to be the best composition to be used as strain sensor, because it has the most gauge factor (G).

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