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ABSTRACTS BOOK

Editors:

Dr N. Ali (UK) & Dr R. Polini (Italy)

that for the thin film colourization carbon compounds were responsible. Moreover, on the surface images performed by atomic force microscopy (AFM) the particles adsorbed between nanocrystalline grains were also observed.

NS335: Polyisoprene – multi wall carbon nanotube composite structure for flexible pressure sensor application

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Materials for practical smart sensor applications are attracting serious interest over last few years. The major problem of conventional rigid sensor materials are difficulty to integer them into soft flexible structures. Polyisoprene/nanostructured carbon composite appears as promising materials for such application. Previous research approved nanostructured carbon black filled composites as finger pressure sensitive piezoresistive materials [1]. The change of tunneling currents between carbon aggregates causes rapid change of composite electrical conductivity under applied external load. Thus current phenomena can only be achieved if high structure carbon blacks (DBP apsorption is 380ml/100g) are used as conductive filler. Single and multi wall carbon nanotubes (CNT) originate with variable length to width ratio and high electric conductivity in longitudinal direction of tube. The specific properties mentioned above should make it possible to obtain electric percolation in polymer-CNT composites at very low loads of filler. However our recent experience [2] shows quite high value of percolation threshold but still good sensing properties in the vicinity of percolation region, if the CNT has been dispersed by “roll in” method. In this work an attempt to reduce percolation threshold of polyisoprene/multiwall CNT composite by sonicated and stirred dispersion of CNT in chloroform solution is presented. The percolation threshold and the excellent piezoresistive behavior of polyisoprene/multiwall CNT composite have been determined as well.

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NS336: Microstructure and biocompatibility of titanium oxides produced on nitrided surface layer under glowdischarge conditions

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It is fact that native titanium oxide possesses good biocompatibility, however is too thin to prevent of metal ions release. Therefore various methods of surface treatments among them plasma nitriding and oxynitriding are extensively applied to functionalize the implant surface. Since nitrided surface layer produced by plasma treatments is of high biocompatibility and protects against ions release into biological

POLYISOPRENE – MULTI WALL CARBON NANOTUBE COMPOSITE STRUCTURE FOR FLEXIBLE PRESSURE SENSOR APPLICATION

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INTRODUCTON Frequent use of compressive and strain sensors requires new materials to be designed for particular application. Usually pressure and strain sensor are rigid structures connected with difficulties to integrate the sensor into structure being monitored. Attempts were made to design a flexible pressure and strain sensors made of filled polymer or elastomer. But these structures exhibited the lack of reversibility and linearity. Recent research approved polyisoprene-nanostructured carbon black (CB) composite (PNCBC) to be a prospective materials for current needs. At certain concentrations of conductive filler both composites shows remarkable reversible tenso and piezoresistive effect [1]. This is explained by sharp change of tunneling currents between filler particles, caused by mechanical deformation. In this work we present an attempt to use polyisoprene – multi wall carbon nanotube (MWCNT) composite (PCNTC) as a perspective material for flexible pressure sensor indicators. We have estimated and compared the electrical percolation thresholds for various piezoresistive composites, depending on filler and dispersing technique used. We believe that our research will lead to a new kind of functional sensor composite material, which could be used for intelligent sensing in robotics and other smart structures.

THE CONCEPT According to concept of piesoresistivity, in the sharpest region of the percolation threshold the composite should be more sensitive to external mechanical action (Fig.2). This means, to gain more piezoresistive sensitivity, the steepest possible percolation threshold should be acquired with lowest possible fraction of conductive filler. The MWCNT appeared to be perspective filler due to their entangled geometrical structure and good longitudinal electric conductivity. On other hand, high aspect ratio leads to certain difficulties to disperse them properly. Previous research by using MWCNT dispersed by mechanical stirring with small grass beads leaded to poor or negative piesoresistive behavior at large concentrations of filler [2]. This leaded to conclude, that more effective method of dispersion should be used. The sedimentation of mechanically dispersed WMCNT into chloroform clearly showed the poor defragmentation of larger MWCNT aggregates compared with US dispersed ones (Fig.3). Using wet mixing with US we can achieve much better MWCNT dispersion than in previous attempts (Fig.4) when mechanical stirring was used . As a result of better filler distribution, the piezoresitive properties of composites should become better.

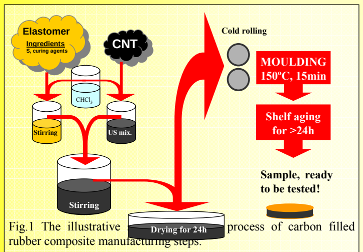


Fig.1 The illustrative process of carbon filled rubber composite manufacturing steps.

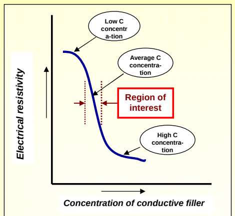
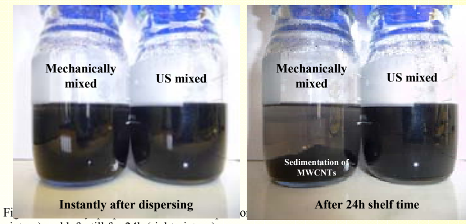


Fig.2 The illustration of the percolation threshold for carbon filled conductive composites.



Fi… picture) and left still for 24h (right picture).

Fig.4 Hielscher UP200S ultrasound homogenizator, used for dispersing of CB and MWCNT filler into solutions.

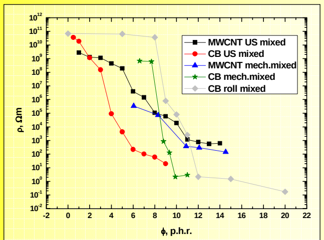


Fig.5 The percolation thresholds for differently prepared polyisoprene - CB or MWCNT composites.

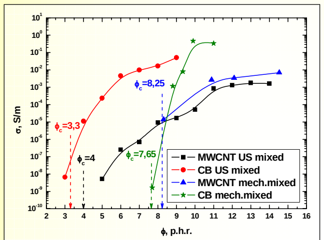


Fig.6 The regions of percolation thresholds, used for Φc determination for differently prepared polyisoprene - CB or MWCNT composites. The indicated Φc values were fine tuned later by proper fitting of each experimental data.

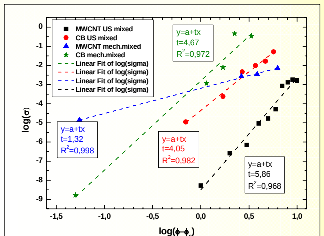


Fig.7 The fitting of percolation thresholds for differently prepared polyisoprene – CB or MWCNT composites. The coefficient *t* in equations represents the critical coefficient of each percolation.

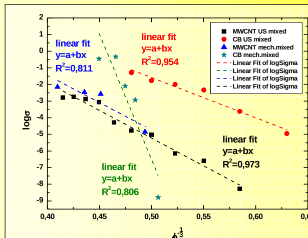


Fig.8 The fitting of percolation thresholds with linear trend line, proving the direct influence of tunneling currents, especially for composite samples prepared using US homogenization.

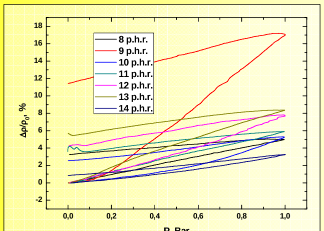


Fig.9 The piezoresistive behavior (relative change of electrical resistivity versus operational pressure) of polyisoprene MWCNT composites with different concentration of conductive filler prepared using US mixing.

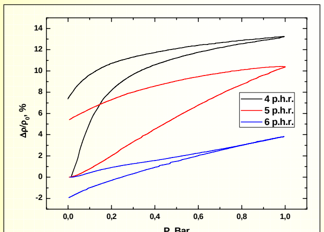


Fig.10 The piezoresistive behavior of polyisoprene CB composites with different concentration of conductive filler prepeared using US mixing.

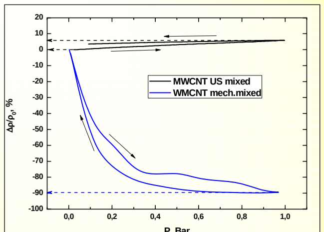


Fig.11 The piezoresistive behavior of polyisoprene MWCNT composites in the saturated region of percolation threshold – sample prepared using mechanical mixing versus sample prepared using US mixing.

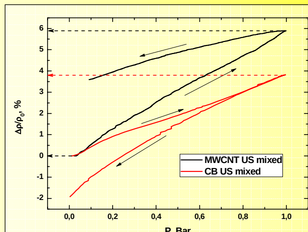


Fig.12 The piezoresistive behavior of polyisoprene MWCNT composite versus piezoresistive behavior of polyisoprene - CB composites in the saturated region of percolation threshold. Both samples prepared using US mixing.

THE SAMPLES The piesoresistive polyisoprene – multi wall carbon nanotube composite (PCNTC) is is made from polyisoprene natural rubber, necessary curing ingredients and multi wall carbon nanotubes (MWCNT) (Fig.1). For current compositions comercially available MWCNTs were used with outer diameter 40-60nm and average lenghts ranging 0,5-500μm. Curing ingredients are mixed into polyisoprene matrix using cold rolls. To reduce the viscosity of the raw rubber mixture it is swelled and solved into chloroform by mixing for 24h. Then desired electroconductive filler is dispersed into chloroform using Hielscher UP200S ultrasound homogenizator for 5 minutes. Specific power – 1W/ml. Afterwards the filler dispersion in chloroform is added to raw rubber solution and stirred in room temperature for another 24h. Then solution is poured onto Petri dishes and let for another 24h for chloroform to evaporate. Acquired films are then homogenized using cold rolls. The PCNTC samples were made by curing in hot mould for 15 minutes at 150ºC. The sandpaper polished brass foil mould inserts were used to acquire good electrical connection for piezoresistance measurements. Before any electrical measurements the samples were shelf aged in room temperature for at least 24h.

EXPERIMENTAL The composite samples were made using hot steel mould and thermostated press Rondol™. The samples were shelf aged before each test at least 24h at room temperature. The electrical resistivity of the samples was measured using Agilent A34970A digital multimeter/multiplexer and Kethley Model 6487 Picoammeter/Voltage source. The mechanical tests were provided using Zwick/Roell Z2.5 universal material testing machine, coupled and synchronized with Agilent A34970Amultimeter mentioned above. The evaluation of results and trend line fitting was done using Origin8 data analysis and graphing software solutions.

EVALUATION OF THE RESULTS The investigations of electrical conductivity percolation in all prepared nanocomposites have been attempted at first. The Fig.5 and Fig.6 represents the percolation thresholds of experimentally obtained electrical resistivity and conductivity respectively. One can see that “sonicated” PNCBC has an obvious shift of percolation threshold to lower values in comparison with roll mixed PNCBC and within solution mechanically mixed PNCBC. On contrary the percolation threshold of “sonicated” PCNTC has been less obviously affected (Fig 5.). Only after careful fitting of experimental results by statistical percolation theory predicted dependence of conductivity on filler concentration, so called scaling law

$$\sigma = \sigma_0(\Phi - \Phi_C)^t, \qquad (1)$$

the correct values of Φ_c have been evaluated (Fig.6. and Fig.7.). Experimental results was fitted by plotting *log*σ versus *log*$(\Phi\text{-}\Phi_c)$ (Fig.7.) by incrementaly varying of Φ_c until the best linear fit was obtained [3]. In such way the notable reduction of Φ_c also has been found for “sonicated” PCNTC (Fig.7.). During the fit of experimental results the non-universal critical index *t* values were stated for “sonificated” PNCBC (*t* = 4.05) and PCNTC (*t* = 5.86) as well as for solution mechanically mixed PNCBC (*t* = 4.67). Obtained results can be explained basing on different distribution and dispersion scenarios [4]. In our case the solution mechanical mixing gives good distribution of nanostructure aggregates and agglomerates but solution sonification leads to both good distribution and good dispersion of primary nanostructures and aggregates. Balberg [5] reported that if tunneling is present, the non-universality of the t gives rise to higher values then expected. So in our case, if solution was simply mechanically mixed the good distribution of CNT bundles (agglomerates) but pour distribution of nanostructure aggregates had been achieved, that means, most of distances between adjacent nanostuctures (CNT bundles) were to wide to tunneling currents to occur. Inside the bundles direct touches of CNT are possible due to pour dispersion. Therefore t = 1.32 for solution mechanically mixed PCNTC. In other three composites good nanostructure distribution and dispersion is achieved that leads to enhancement of tunneling currents (large values of t). The impact of tunneling currents on conductivity of the all tested composites is evaluated in Fig.8. According to Bauhofer [6] tunneling between CNT separated by an isolating layer should lead to a dependence of the form

$$\ln \sigma_{DC} \propto \Phi^{-\frac{1}{3}} \qquad (2)$$

The best fit of experimental results with equation (2) was for “sonicated” PNCBC and PCNTC. This is in good agreement with mentioned *t* values.
Afterwards the MWCNT and CB composite samples both prepeared with US mixing were tested for piezoresistivity. The results for operational pressures up-to 1 Bar are shown in Fig.9 and Fig.10. When compared with piezoresistive character of PCNTC made by mechanically mixing of MWCNTs, the effect shows quasi-linear positive behavior and moderate hysteresis, thus it is more suitable for pressure sensing than indication (Fig.11). Although, for small operational pressures the PCNTC are more effective than PNCBC, as they show sharper piezoresistive response (Fig.12). This can be explained with improved distribution of conductive filler, using more effective US mixing. This leads to more dominant role of tunneling currents in conductivity mechanism of the composite structure. This statement is although proved by linear fitting of percolation threshold data in Fig.8.

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