

## Study of Micromechanical Properties of PPy/SWCNT/PVA Composites Using Vicker's Microhardness Testing

PRAGYESH KUMAR AGRAWAL<sup>a</sup> and PRIYANKA PARMAR\*

Department of Physics,  
Sarojini Naidu Govt. Girls P.G. College (Autonomous), Bhopal, M. P. (India)

\* Department of Electronics and Computer Maintenance,  
St. Aloysius College (Autonomous), Jabalpur, M. P. (India)

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### Abstract

Authors have been investigating the electronic and mechanical properties of PPy/SWCNT/PVA composites keeping the probable use of this material in making supercapacitors in mind. The micromechanical properties of this ternary conducting polymer composite can be inferred from the Vicker's microhardness testing. This paper reports that the  $H_v$  value is found increasing with addition of SWCNT and PPy/SWCNT in PPy and PVA matrices, respectively. It is also observed that the  $H_v$  values increase for all studied materials upto indentation load 160 g, thereafter it becomes almost constant. The maximum  $H_v$  is obtained for the ternary composite having 25 wt% PPy/SWCNT in PVA matrix. This observation confirms the earlier reporting of macromechanical properties of the studied material.

*Key words:* Conducting polymer; Polypyrrole; Single wall carbon nanotubes; Polyvinyl alcohol; Vicker's microhardness.

### 1 Introduction

Polymer composites are intensively studied for the new properties which are originated by combination of properties of both polymer matrix and filler, respectively. In order

to dissipate electrostatic charges and to prepare materials with antistatic properties conductive particles such as carbon or carbon allotropes are dispersed in the polymer matrix<sup>1</sup>. Conductive filler/insulating polymer composites become conductors when the filler content

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<sup>a</sup>. Corresponding author: Pragyesh Kumar Agrawal, Email: dr\_p\_agrawal@hotmail.com.

The address of actual workplace is Department of Electronics and Computer Maintenance, St. Aloysius College (Autonomous), Jabalpur-482001, M.P. (India)

reaches a critical value and their electrical conductivity show a sharp increase (percolation threshold) and at this value the continuous bulk network structure is formed<sup>2</sup>.

The microhardness of a substance is an important parameter to analyze the mechanical strength of its material. It is basically related to crystal structure of the material. It also provides information of the way in which atoms are packed and the electronic factors operating to make the structure stable<sup>3</sup>. Physically speaking, hardness is the resistance offered by crystal for movement of dislocations and practically it is the resistance offered by crystal for localized plastic deformation. Hardness testing provides useful information about mechanical properties like elastic constants, yield strength etc. of materials. Micro indentation hardness has emerged in recent years as a new method for the evaluation of the mechanical properties of polymers and polymer composites<sup>4-6</sup>.

The micro hardness tests are used to determine the resistance of a material to deformation. These tests can be performed on a macroscopic or microscopic scale. The metals indentation hardness correlates linearly with tensile strength. This important relation permits economically important non destructive testing of bulk metal deliveries with lightweight, portable equipment, such as automatic Vickers micro hardness testers.

Growing demand for portable electronic devices such as digital communication devices has motivated researchers to develop supercapacitors with high power storage and long life cycle<sup>7,8</sup>. The main constituents of supercapacitors are:

- i. High surface area activated carbons;
- ii. Redox metal oxides, and
- iii. Conducting polymers<sup>9,10</sup>.

Among these possible candidates conducting polymers emerge as most promising materials due to their high specific capacitance, easy synthesis and low material cost<sup>11-13</sup>.

The main drawback of supercapacitors based on conducting polymers is poor life cycle due to the change of volume during the doping and dedoping processes. It is, therefore, necessary to strengthen the electrochemically active sites of conducting polymers by the addition of large surface area carbon materials such as carbon nanotubes (CNT). CNTs have been attractive materials for making the electrodes of supercapacitors due to their high electrical conductivity, high accessible surface area and chemical as well as mechanical stabilities. The composites of conducting polymers and CNTs have been synthesized for making mechanically and electrochemically improvised electrodes to be used in supercapacitors<sup>14-17</sup>.

Conductive polymers such as polypyrrole (PPy) exhibit unique chemical and electrochemical properties. PPy is attractive as an electrically conducting polymer because of its relative ease of synthesis. Bulk quantities of PPy can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents<sup>18</sup>. The reaction of pyrrole with aqueous ferric chloride is very rapid and the product is a black powder which is insoluble in all common solvents. Iron (III) salts provide a convenient means for oxidative polymerizing pyrrole and incorporating their anions as dopant

ions<sup>19</sup>.

The present paper aims at an investigation of the micromechanical property of composites of polypyrrole/single wall carbon nanotube (PPy/SWCNT) with polyvinyl alcohol (PVA) as revealed by micro indentation hardness. PVA is used as the polymer matrix because of its high strength, flexible molecular chains and good adhesion to electrodes. Balancing electrical conductivity with desirable mechanical behavior is one of the largest challenges for the use of filled polymer composites in various applications. In this work we focus on the effect of filler concentration on the mechanical behavior of the PPy/SWCNT/PVA composite system prepared from the in-situ polymerization technique.

## 2 Experimental

The PPy and PPy/SWCNT composites were synthesized by chemical oxidation method using FeCl<sub>3</sub> as oxidant. Details of this method have been reported in earlier paper<sup>20</sup>. SWCNTs amounting to 0.5wt% of PPy were added to prepare the optimized<sup>20</sup> PPy/SWCNT composite.

The digital microhardness tester DHV 1000 supplied by Vaisheshika Electron Devices, Ambala, India was used for measuring the Vicker's microhardness ( $H_v$ ).  $H_v$  was calculated using formula

$$H_v = 1.854 \times L / d^2$$

where L is load applied in kgf, d is mean of the two diagonals,  $d_1$  and  $d_2$  in mm and  $H_v$  is Vickers microhardness. Dwell time of every indentation was 10 seconds.

## 3 Results and Discussion

Figure 1 shows variation of Vicker's microhardness  $H_v$  with respect to load applied at the time of indentation. It is observed that the microhardness increases gradually upto 160 g indentation load, thereafter it becomes almost independent of load. It is also revealed that  $H_v$  value increases with increasing weight percentage content of PPy/SWCNT composite in PVA matrix. The addition of 25 wt % of PPy/SWCNT in PVA raises its microhardness almost four times. It can be concluded from these observations that PPy/SWCNT acts as a hardner for PVA.

Behaviour of the conducting PPy/SWCNT in PVA can be considered similar to that of metallic filler in a polymeric medium<sup>17</sup>. The addition of PPy/SWCNT to PVA leads to a decrease in it's inter chain distance. This leads to decrease the vacancies in polymer matrices which make polymer less brittle thereby increasing its microhardness. Figure 1 also shows that below a particular concentration of PPy/SWCNT in PVA, the hardness values of the material are less sensitive to filler content and particle size. It can be imagined that at low filler concentrations, the PPy/SWCNT particles dispersed within the amorphous matrix are easily displaced under the indenter. Above a particular concentration of filler content the PPy/SWCNT particles contribute to material resistance to plastic deformation. This again confirms the observations earlier reported by the authors<sup>20</sup> regarding the tensile strength of the composites.

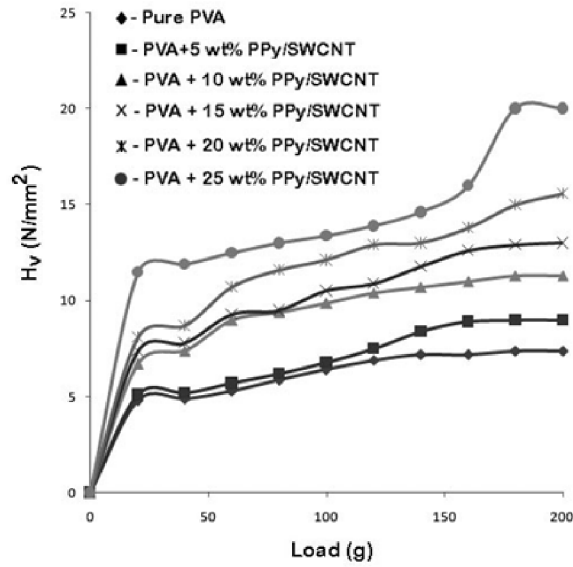


Figure 1. Variation of  $H_v$  versus load of indentation for pure PVA and its composites with PPy/SWCNT

Figure 2 presents a comparative study of the microhardness of pure PPy, pure PVA and PPy/SWCNT as well as PPy/SWCNT/PVA composites. This figure also confirms the increment in microhardness of ternary composite as compared to the individual constituents or binary composites.

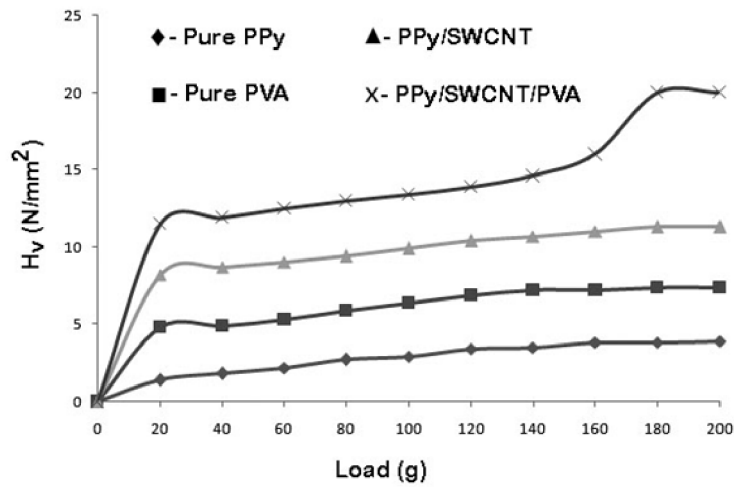


Figure 2. Variation of  $H_v$  versus load of indentation for pure PPy, pure PVA, PPy/SWCNT and PPy/SWCNT/PVA composites

#### 4 Conclusions

Variations in the Vicker's microhardness of various materials with respect to applied load and percentage composition have been reported in this paper. It is observed that addition of PPy/SWCNT in PVA matrix increases  $H_v$  of PVA matrix in general. It can be concluded that the ternary composition having 25 wt% PPy/SWCNT in PVA matrix offers maximum microhardness and hence, can be suitably used for making supercapacitors.

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