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Electrical properties and longitudinal modulus of superconductor/polymer $NdBa_2Cu_3O_{7-\delta}$/PVC composites

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High temperature superconductor $NdBa_2Cu_3O_{7-\delta}$/poly(vinyl chloride) (Nd123/PVC) composites have been prepared by cold press and hot press methods. Addition of PVC resulted in increase of the electrical resistivity with percolation occurring between 0.3 and 0.5 Nd123 volume fraction for both preparation methods. Although the samples showed some form of magnetic levitation at liquid nitrogen temperature, they do not show any zero-resistance temperature indicating the lack of effective superconducting percolative path. The density deviates from the linear calculated value with increasing Nd123 content at 0.3 volume fraction for the cold press and at 0.6 for the hot pressed samples due to increasing porosity. X-ray powder diffraction patterns suggest that the Nd123 crystals tend to align when the composites are prepared by hot press method. A resistance anomaly is observed at 90 K in the hot press composites indicating improved electrical contact between the aligned Nd123 grains. The longitudinal modulus increases as Nd123 content is increased.

1. Introduction
The discovery of superconductivity at around 90 K in $YBa_2Cu_3O_{7-\delta}$ (Y123) has opened up new horizons in the field of superconductivity [1]. This is followed by the discovery of other high temperature superconductors (HTSC) such as the bismuth, thallium and mercury systems with transition temperatures above the boiling point of liquid nitrogen.

Y123 ceramic superconductors are porous and have poor mechanical properties. The effects of secondary phase materials to improve its physical properties have been widely investigated. Several studies on superconductor/polymer composites with the aim of improving the mechanical properties have been reported [2, 3]. Generally these studies indicate that although the diamagnetic property of the superconductor/polymer composites is preserved, the electrical resistance does not show any superconducting transition or zero-resistance temperature. It is interesting to investigate further the electrical and elastic properties of such composites.

From the materials processing point of view $NdBa_2Cu_3O_{7-\delta}$ (Nd123) has been of great interest because it has a wider solidification range and exhibits a much higher peritectic decomposition temperature than the widely studied Y123 [4, 5]. The structure and the superconducting properties of Nd123 with various oxygen contents have also been reported [6]. Nd123 also showed high transition temperature (up to 95 K) and sharp transition when prepared by melt processing in air [7, 8].

In this paper we report the effect of poly(vinyl chloride) (PVC) on Nd123 with volume fraction of Nd123 between 0–1.0. Most of our samples with substantial Nd123 content showed magnetic levitation effect at liquid nitrogen temperature similar to previous reports on Y123. In this work we report on the electrical resistivity of Nd123/PVC composites together with the elastic modulus, microstructure and X-ray diffraction results.

2. Experimental details
Superconducting powder of Nd123 was obtained by mixing Nd_2O_3, $BaCO_3$ and CuO (purity ≥99.99%) with starting composition $NdBa_2Cu_3O_{7-\delta}$. The powders were mixed, ground and calcined in air at 920 °C for 48 hours with several intermittent grindings followed by oven cooling at 60 °C per hour. The powders were reground and pressed into discs of ∼12.5 mm

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diameter and 2 mm thickness. It is then sintered at 920 °C for 24 hours and slow cooled to room temperature at 60 °C per hour.

The Nd123 discs were then reground and mix with PVC powder with volume fraction 0.0 to 1.0. In this paper volume fraction refers to volume of Nd123 with respect to PVC. The size of the PVC powder is between 50–100 μm. The mixed powders were then cold pressed and hot pressed into discs with ∼12.5 mm diameter and 2 mm thickness. In the cold press method, the powders are cold pressed into discs before heating in air at 170 °C for 1 hour and labeled as Nd123A. In the hot press method, Nd123 and PVC powders are pressed into discs while simultaneously heated at 170 °C for 1 hour and labeled as Nd123B.

X-ray powder diffraction patterns were recorded using a Siemens D5000 diffractometer with Cu K_α radiation in the 2θ range 2°–60°. The room temperature dc electrical resistivity is measured by using the Van der Pauw's four point-probe method. The dc electrical resistance versus temperature measurements were carried out using the standard four point-probe method with silver paste contacts in conjunction with a closed cycle refrigerator from CTI Cryogenics (model 22), a temperature controller from LakeShore (model 330), and constant current source (Keithley 220). The microstructure of the fractured samples was recorded using a Philips XL 30 scanning electron microscope (SEM). Ultrasound velocity at room temperature is measured by a Matec 7700 pulsed echo overlap system in conjunction with a quartz transducer in the longitudinal mode at 10 MHz. Nonaq grease is used to bond the sample to the transducer.

3. Results

3.1. Cold pressed Nd123A

X-ray diffraction (XRD) patterns of Nd123A show that the orthorhombic structure is preserved with the addition of PVC. Not much change in the X-ray diffraction pattern of the Nd123 component is detected with increasing PVC content except for the change in the baseline suggesting increase in the amorphous structure of the composite.

Fig. 1 shows the density of Nd123A composites and compared with the calculated theoretical value. The theoretical density is determined by using the formula $\rho = v\rho_s + (1-v)\rho_p$ where ρ, ρ_s and and ρ_p are the densities of composite, superconductor powder and polymer matrix respectively, v is the volume fraction of Nd123 in the composite. The density increases with increasing volume fraction of Nd123 but deviates from the linear (calculated theoretical) value above 0.3 volume fraction indicating the increase of porosity. SEM micrographs of Nd123A containing 0.95, 0.90, 0.70 and 0.40 volume fraction shown in Fig. 2 indicate that the grain size increases together with increasing PVC content.

The resistance versus temperature curves of all samples containing PVC showed insulating behaviour within the temperature range investigated (50 K–300 K). Fig. 3a shows the normalized resistance versus temperature curves of Nd123A for samples with 0.95 and

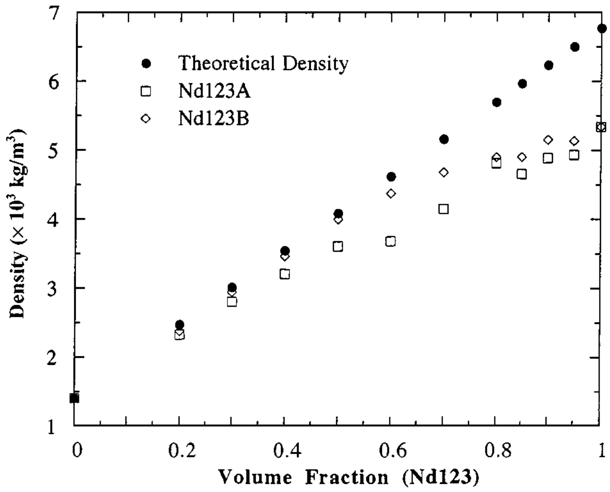

Figure 1 Measured density and calculated theoretical density of Nd123A and Nd123B composites.

0.80 volume fraction. Fig. 4 shows the room temperature electrical resistivity versus volume fraction. The resistivity shows insulating behavior and percolation occurs at around 0.30–0.50 volume fraction (where the resistivity drops abruptly). This indicates that above 0.50 volume fraction, Nd123 particles start to form better contacts with each other and electrically conducting chains start to form.

3.2. Hot pressed Nd123B

X-ray diffraction patterns of Nd123B indicate no observable change in the Nd123 component as PVC is added, similar to the case of the cold pressed samples. For example Fig. 5 shows the X-ray diffraction pattern for samples with 1.0 and 0.80 volume fraction. The orthorhombic structure is preserved throughout the entire PVC range with no change in the lattice parameter. This indicates the oxygen content is stable [6] and not affected by PVC. No evidence of chemical reaction between Nd123 and PVC is observed and the two components remain segregated. This shows that hot pressing does not result in any change in the structure of Nd123.

Changes in the relative intensity of the XRD peaks in the composites are observed which suggests that the crystals were aligned during the hot pressing. Such alignment is only observed in the hot pressed samples. In addition, changes in the baseline of the pattern indicates that the amorphous structure increased when the PVC content is increased.

The density increases with increasing Nd123 but deviates from the linear (calculated theoretical) value above 0.60 volume fraction. Fig. 6 shows the SEM micrographs of Nd123B with volume fraction (a) 1.0, (b) 0.90, (c) 0.70 and (d) 0.40. The density of Nd123B is slightly higher than Nd123A because less air is trapped in Nd123B due to hot pressing. The micrographs show that the grain size increases slightly with increasing PVC content.

All PVC containing samples showed insulating behaviour and no superconducting transition is observed. The room temperature resistivity drops abruptly

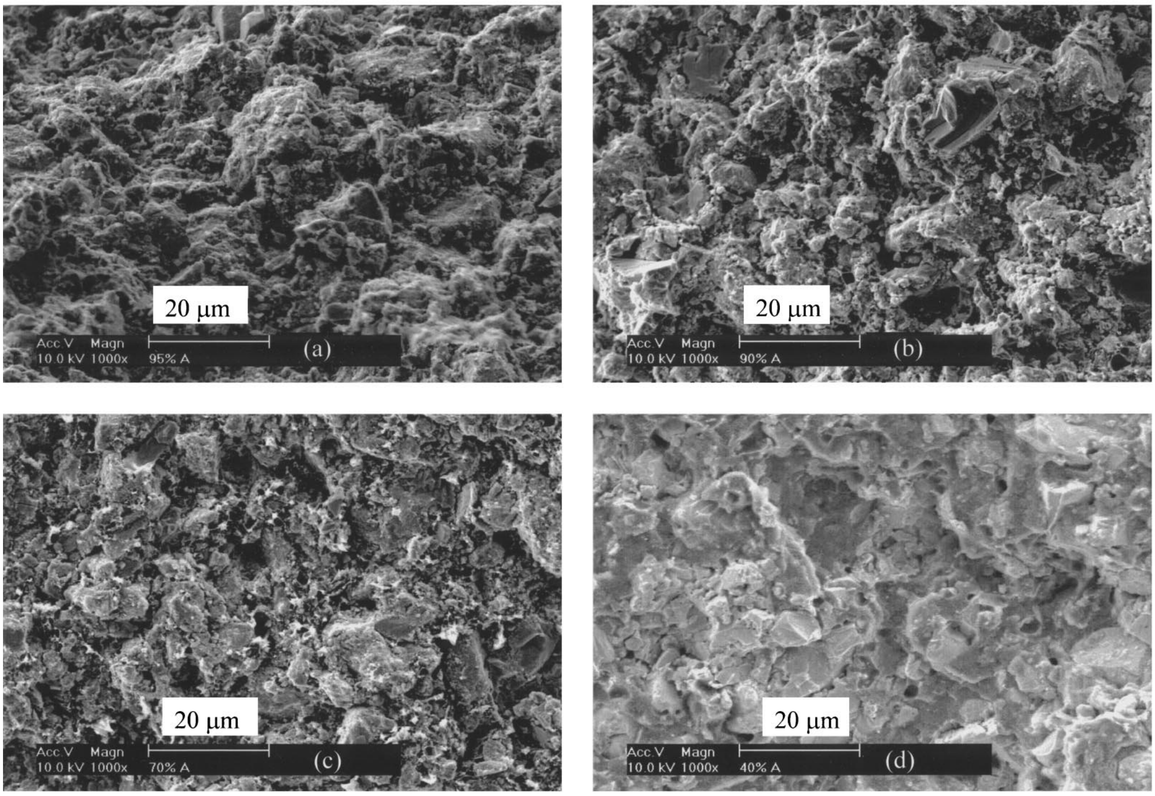

Figure 2 SEM micrographs of Nd123A composite with (a) 0.95, (b) 0.90, (c) 0.70 and (d) 0.40 volume fraction.

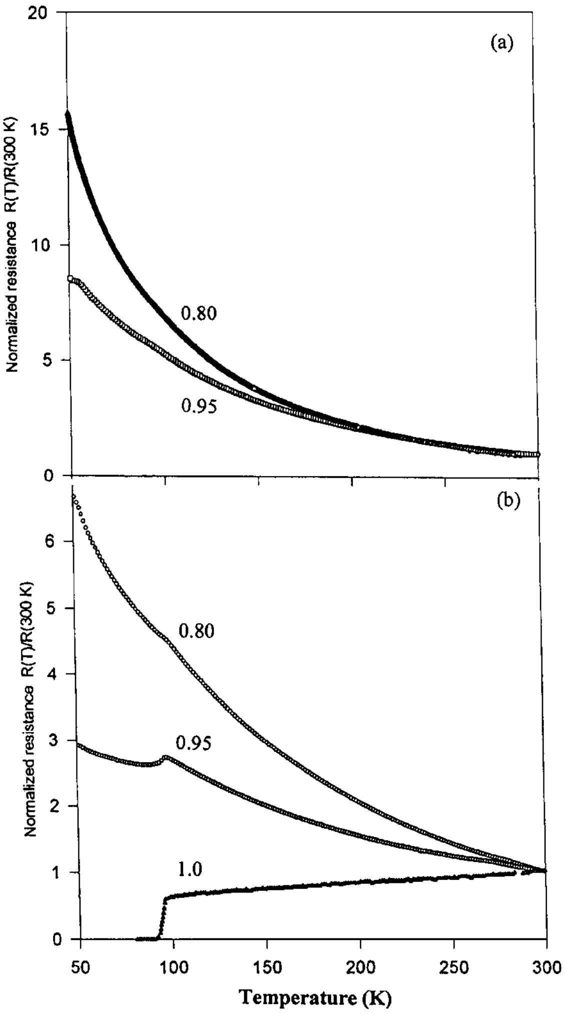

Figure 3 (a) Normalized resistance versus temperature of Nd123A with 0.95, and 0.80 volume fraction. (b) Normalized resistance versus temperature of Nd123B with 1.0, 0.95 and 0.80 volume fraction.

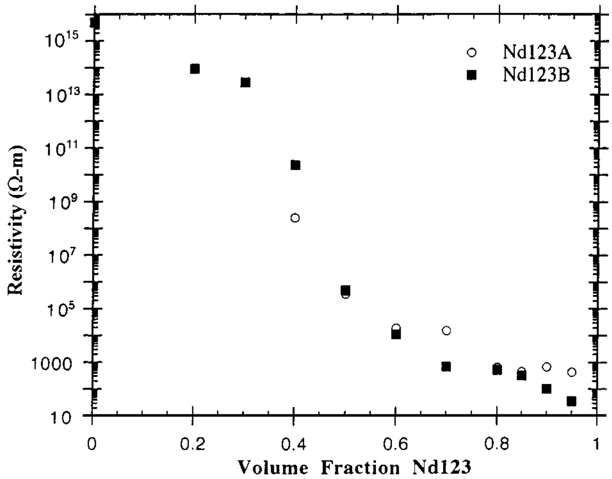

Figure 4 Room temperature electrical resistivity versus volume fraction of Nd123A and Nd123B.

between 0.30 and 0.50 volume fraction (Fig. 4), similar to the cold pressed sample. This suggests that the superconducting grains are not contacting each other well because of large gaps and pores below 0.5 volume fraction. The electrical resistance versus temperature curves for 1.0, 0.95, and 0.85 volume fraction of Nd123B shown in Fig. 3b indicates an insulator-like behavior with a resistance anomaly near 90 K for 0.95 and 0.85 volume fraction. This anomaly is not observed in the cold pressed samples indicating better contact between the Nd123 grains is achieved through hot pressing. Improved contact between the grains could have been achieved through the alignment of the Nd123 grains as observed in the XRD patterns. However, zero-resistance temperature is not observed indicating that a complete superconductive path is not formed.

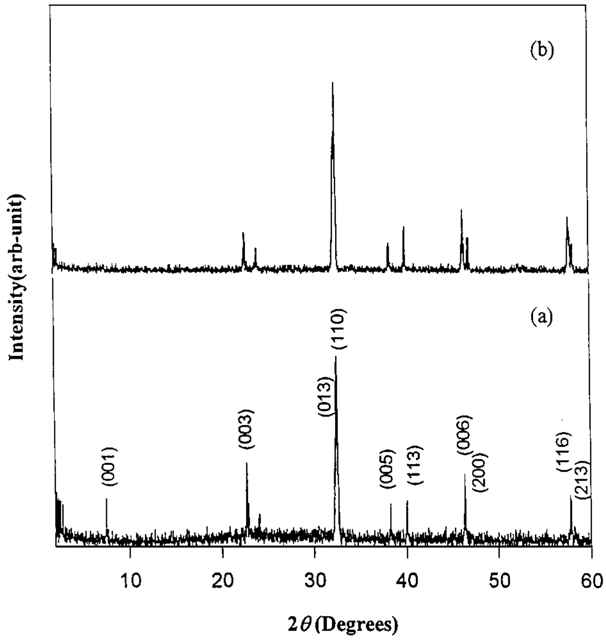

Figure 5 X-ray diffraction pattern of hot pressed Nd123B composite with (a) 0.8 and (b) 1.0 volume fraction of Nd123.

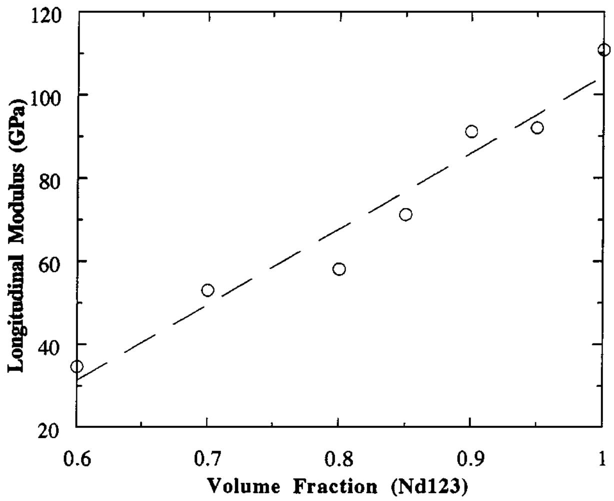

Figure 7 Ideal longitudinal modulus of Nd123B (hot pressed) with 0.6 to 1.0 volume fraction. Dashed line is use for eye-guide only.

Fig. 7 shows the ideal longitudinal modulus for the hot pressed samples with 0.6 to 1.0 volume fraction. Longitudinal modulus (C_L) can be calculated from the longitudinal velocity (v_L) by the equation $C_L = \rho_m v_L^2$ where ρ_m is the measured density. For an isotropic elastic medium the ideal longitudinal modulus (C_{Li}) can be approximated by $C_{Li} = \rho_I v_{Li}^2$ where ρ_I is the ideal density and v_{Li} is the ideal longitudinal velocity with $v_{Li} = (\rho_I/\rho_m)^{1/2} v_L$ [9]. A general trend of increasing longitudinal modulus with Nd123 content is observed. For samples with volume fraction 0.5 and less, the materials became highly attenuative where no ultrasonic echo can be observed to measure the longitudinal velocity. Elastic percolation can be interpreted as the formation of a complete network of springs in the material [10]. Above 0.6 volume fraction, the assembly of "springs" in the composite system forms a complete network. It is possible that the elastic percolation is below 0.6 volume fraction of Nd123, similar to the electrical percolation. This is expected because Nd123 is the

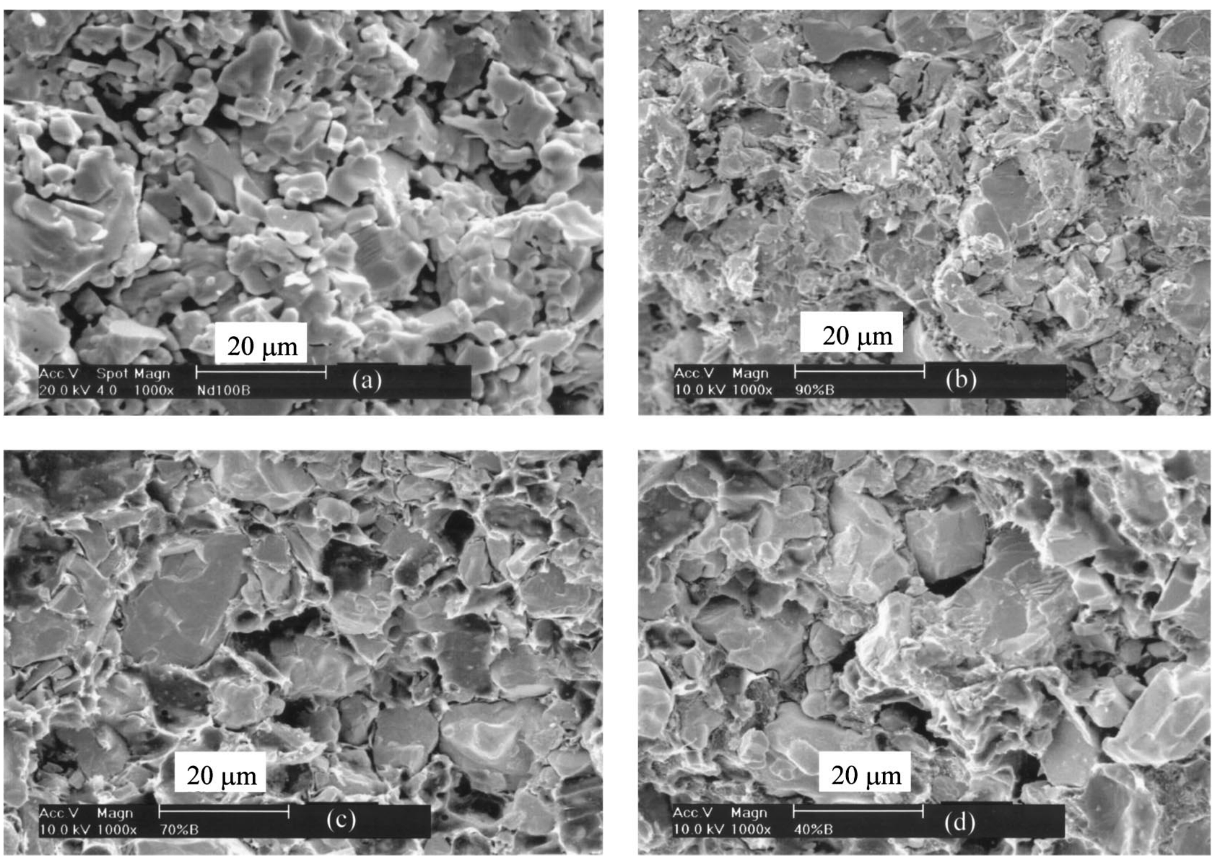

Figure 6 SEM micrographs of Nd123B with volume fraction (a) 1.0, (b) 0.90, (c) 0.70 and (d) 0.40.

dominating component that contributes to conductivity as well as elastic modulus.

4. Discussion

From the above results we make the following observation and remarks:

(i) No noticeable difference between the electrical percolation of the cold pressed and hot pressed samples is observed. Electrical percolation occurs between 0.3 and 0.5 volume fraction for both series of samples. This indicates that although the density of hot pressed samples is higher, it does not necessarily provide a better electrical contact between Nd123 particles for normal current to flow. The amount of Nd123 seems to play as important role as the degree of connectivity between particles for electrical percolation.

(ii) The density of the cold pressed samples deviate from the linear (calculated theoretical) value at 0.3 volume fraction while the hot pressed samples deviates at 0.6 volume fraction. This indicates that hot pressing results in better packing between Nd123 grains and PVC. However, the density of both series of samples tends to saturate at higher Nd123 content (about 0.8 volume fraction). This indicates that hot pressing does not give any significant increase in density at high volume fraction because of increasing porosity due to Nd123 grains.

(iii) No change in purity and lattice parameter of the Nd123 component in both hot and cold pressed samples is observed. This shows that no reaction takes place between PVC and Nd123. This also indirectly indicates that the oxygen content of Nd123 is stable in the composite. Alignment of the Nd123 grains is observed in the hot pressed samples.

(iv) The resistance versus temperature curves does not show any zero-resistance temperature for all PVC containing samples. However, the hot pressed samples with volume fraction equal or greater than 0.85 showed a resistance anomaly near 90 K (i.e. near the transition temperature of pure Nd123). This anomaly is suggested to be due to better contact between the aligned Nd123 grains. The alignment of the Nd123 grains is only observed in the hot pressed samples. Although better contact between the aligned Nd123 grains can result in increase tunneling of supercarriers between neighboring grains, no effective superconducting percolative path is formed for zero-resistance.

In conclusion, cold press and hot press methods have been used in preparing Nd123/PVC composites. Electrical percolation occurs between 0.3 and 0.5 Nd123 volume fraction. No elastic percolation is observed between 0.6 and 1.0 volume fraction. Elastic percolation may occur below the volume fraction we are measuring i.e. in the range of the electrical percolation because the Nd123 grains is the dominant component for electrical conductance as well as the elastic modulus. Although the Nd123/PVC composites generally showed levitation effects at liquid nitrogen temperature, no zero-resistance temperature is observed.

The XRD patterns indicate that the Nd123 grains are aligned in the hot pressed samples and these samples also showed resistance anomaly at 90 K. This indicates that better contact between the aligned superconducting grains can be achieved through this preparation method. Further studies in improving the processing technique for example with pressure and temperature variation may be useful in understanding the missing zero-resistance in this and other high temperature superconductor composites. Improvement in the processing technique will ensure that these composites are not only useful in levitation applications but also for electrical conductors.

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