

# Studies in Effect of Alumina Nanoparticles on the Properties of Unplasticized Polyvinylchloride (PVC)

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## Abstract

Unplasticized polyvinylchloride (PVC)/nano-alumina composites were prepared using high-speed mixer, two-roll mills and compression molding. In the composite, the concentration of nano-alumina was varied from 0 to 7 phr (parts per hundred). The prepared composites were characterized for mechanical, thermal, electrical, crystallinity and morphological properties. Optimal improvement in properties was obtained at 5 phr concentration of nano-alumina in the PVC matrix. Tensile strength, tensile modulus, flexural strength, flexural modulus and shore D hardness were found to have increased by about 46.8, 54.9, 25.1, 37.8 and 11.3% respectively at 5 phr loading of nano-alumina in the PVC. Thermal conductivity and electrical resistivity also increased with increase in concentration of nano-alumina in PVC.

**Keywords:** Polyvinylchloride, nano-alumina, thermal, mechanical, electrical

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## INTRODUCTION

Polymer nanocomposites are prepared by dispersing nanoscopic inorganic particles, typically 10–100 Å in at least one dimension, an organic polymer matrix to dramatically improve the performance properties of the polymer. Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength and outstanding barrier properties [1].

Poly (vinyl chloride) (abbreviated as PVC) nanocomposites are prepared since a very long time. Zhu *et al.* studied the effect of poly (methyl methacrylate)-grafted-nanosilica and a copolymer of styrene, *n*-butyl acrylate and acrylic acid-grafted-nanosilica on the properties of PVC. Poly (methyl methacrylate) and a copolymer of styrene, *n*-butyl acrylate and acrylic acid formed an adhesive interface between nanosilica and PVC significantly improving its tensile strength and elongation at break [2]. Xie *et al.* investigated the

polymerization of vinyl chloride in the presence of calcium chloride nanoparticles to prepare PVC nanocomposites. Optimal improvement in tensile strength, tensile modulus, impact strength and toughness were obtained at 5 phr loading of calcium carbamate nanoparticles [3]. Wan *et al.* used organically treated clay nanoparticles as reinforcing material in PVC matrix. There was found an appreciable improvement in mechanical properties and processability of PVC on addition of the organically modified clay below 5 wt% concentration [4]. Wang *et al.* investigated the thermal degradation and charring characteristics of PVC/clay nanocomposite using X-ray photoelectron spectroscopy. They found decreased chain stripping of the PVC macromolecules due to the presence of clay nanoparticles [5]. Sanz *et al.* prepared magnetopolymeric nanocomposite using nearly spherical Co<sub>80</sub>Ni<sub>20</sub> of around 65 nm diameter, adding it in concentrations from 0.5 to 50 wt% having combined magnetic and polymeric properties [6]. Awad *et al.* investigated the properties of nanoclay PVC composites prepared using tallow-triethanol-ammonium ion (a less basic amine) modified nanoclay, producing intercalated and

exfoliated systems [7]. It was found, to our best knowledge, that no study is reported of using nano-alumina as a reinforcing material in unplasticized PVC matrix.

The present study deals with the use of nano-alumina as a reinforcing material in unplasticized PVC. The prepared nanocomposites were investigated for mechanical (tensile, flexural, impact), thermal (thermal conductivity), morphological (scanning electron microscopy), and electrical (surface and volume resistivity) properties.

## EXPERIMENTAL

### Materials

PVC (K57 suspension resin, bulk density:  $\sim 0.53 \text{ gm/cm}^3$ , particle size:  $\sim 200$  mesh, inherent viscosity:  $\sim 0.72$ ) was procured from Vansh Polyvinyl India Pvt. Ltd., Mumbai, India. Lead-based one pack stabilizer was obtained from Ala Chemicals, Mumbai, India. Nano-alumina (99.8% purity, specific surface area  $\sim 70 \text{ m}^2/\text{g}$ ,  $\alpha$  phase, white color, rod-shaped, 120–200 nm diameter and 650–850 nm length) was procured from Reinste Nano Ventures, New Delhi, India. All chemicals were used as obtained without any purification or modification.

### Composite Preparation

PVC, one pack stabilizer (5 phr of PVC. phr is an abbreviation for parts per hundred) and nano-alumina (as per formulation) was dry blended in a high-speed mixer for 10 min. Melt blending was performed using a two-roll mill at  $190^\circ\text{C}$  for 20–30 min, until all the mix got converted into a uniform molten mass. To prepare samples for testing, the molten mass was compression moulded using an upward stroke compression-moulding machine having upper and lower platen temperature as 185 and  $190^\circ\text{C}$ , and 15 MPa pressure was applied. Before compression moulding, material obtained from two-roll mill was pre-dried in oven for 3–4 h at  $70^\circ\text{C}$ , to remove any adsorbed or absorbed moisture. Pressure and heat was applied for 15–20 min during the compression stage, followed by cooling to room temperature which took about 30–45 min. The sheet ( $20 \times 20$  cm, 2 sheets) obtained was then cut to get samples for mechanical, thermal, morphological and electrical testing. Cut samples were conditioned for 48 h before testing. The quantity of nano-alumina in each batch was calculated on the weight basis of PVC. Formulations prepared are shown in Table 1.

**Table 1:** Prepared PVC/Nano-alumina Composites.

Sr. no.	Sample name	Polyvinyl chloride (PVC)		One pack stabilizer	
		%	gm	phr	gm
1.	PVCC	100	500	5	25.0
2.	PVC1	75	375	5	18.8
3.	PVC3	50	250	5	12.5
4.	PVC5	25	125	5	6.3
5.	PVC7	0	0	0	0

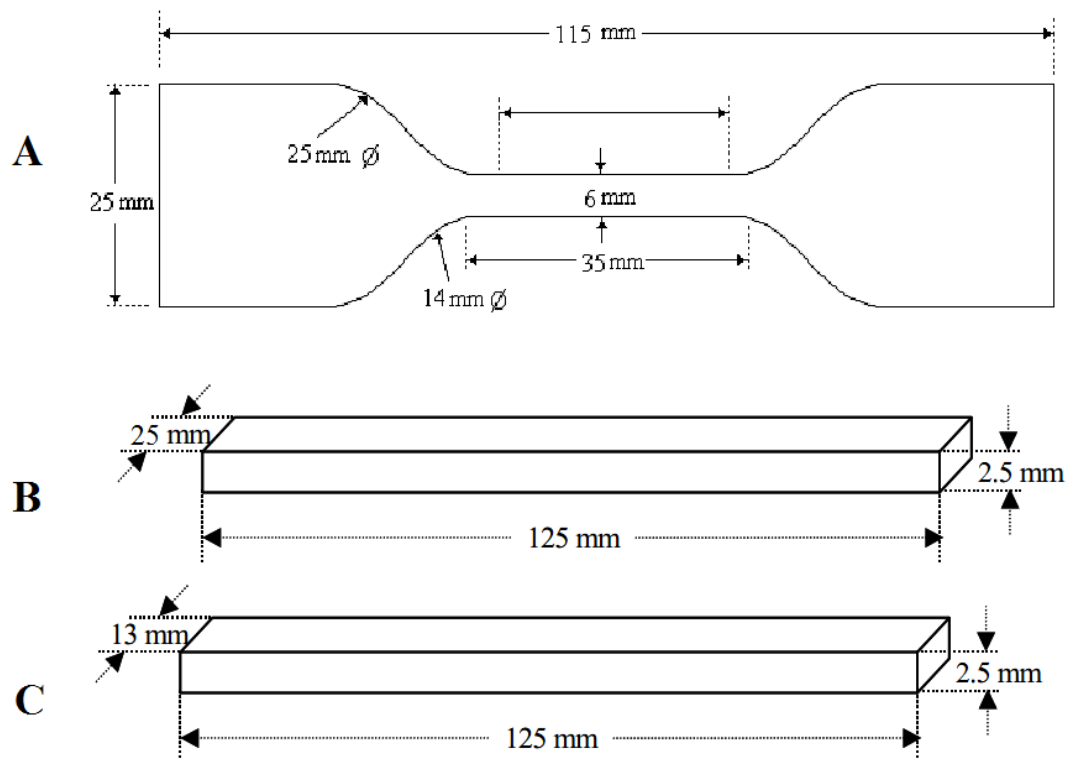
### Characterizations

#### Mechanical Properties

Tensile properties; tensile strength, tensile modulus and elongation at break and flexural properties; flexural strength; and flexural modulus were measured at ambient condition using a universal testing machine (LR-50K, Lloyds Instrument, UK), according to ASTM procedures D638 and D790 at a crosshead speed of 50 and 2.8 mm/min respectively. Charpy impact strength was determined at ambient condition according to ASTM D6110

standard, using impact tester (Avery Denison, UK) having striking velocity of 3.46 m/s employing a 2.7 J striker.

Shore D hardness was determined in accordance with ASTM standard D2240 (test sample dimension: 2 cm x 2 cm x 0.2 cm). On an average of ten tests were performed to report the average hardness of samples. Sample dimensions for tensile, flexural and impact testing are shown in Figure 1.



**Fig. 1:** Sample Dimensions for (A) Tensile, (B) Flexural and (C) Impact Testing.

#### **Thermal Properties**

The thermal conductivity (W/mK) was calculated by the product of the thermal diffusivity ( $\text{mm}^2/\text{s}$ ), specific heat (J/gK) and density ( $\text{g}/\text{cm}^3$ ), using Unitherm 2022 (Anter Corpo, USA) thermal conductivity tester according to ASTM E 1530.

#### **Morphological Properties**

Scanning electron microscopy (SEM) analysis was performed with JEOL 6380 LA (Japan). Samples were fractured under liquid nitrogen to avoid any disturbance to the molecular structure and then sputtered with platinum before imaging.

#### **Crystallinity Properties**

XRD analysis was carried out to determine the percentage crystallinity of the prepared systems. A normal-focus copper X-ray tube was operated at 30 kV and 15 mA. Sample scanning was done from  $2.0^\circ$  to  $80.0^\circ$  at the rate of  $2.00^\circ/\text{min}$ . The data processing was done using the Jade 6.0 software. The X-ray of the Cu  $K_\alpha$  radiation filtered by a Ni filter has a wavelength of  $1.54178 \text{ \AA}$ .

#### **Electrical Properties**

Electrical properties like surface resistivity and volume resistivity were measured using Million Meghometer (LS-3B, Siva Instruments, India), according to ASTM standard D257. Ten samples were tested.

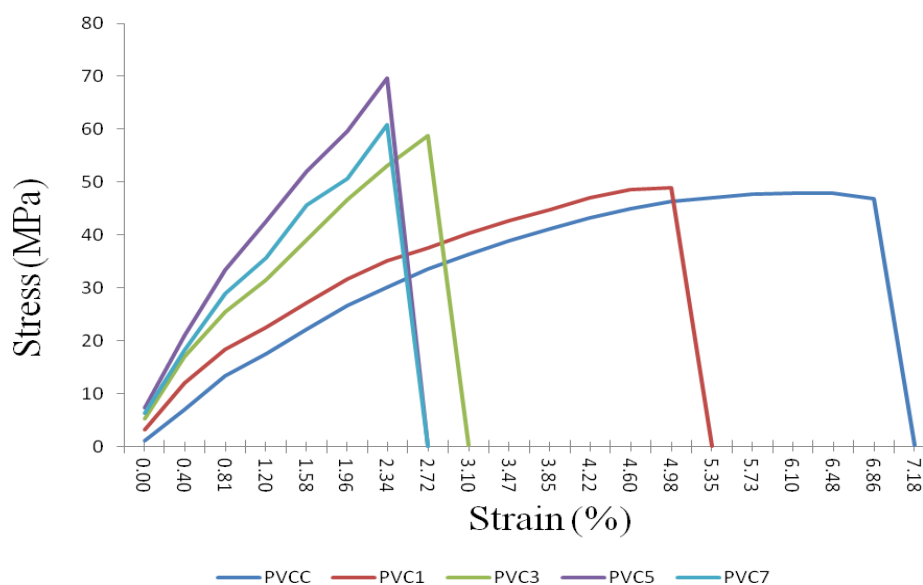
## **RESULTS AND DISCUSSION**

#### **Mechanical Properties**

Tensile strength, tensile modulus, elongation at break (%), flexural strength, flexural modulus, impact strength and shore D hardness values obtained for the PVC/nano-alumina composites are listed in Table 2 whereas the tensile stress-strain curves are shown in Figure 2. It was observed that tensile strength, tensile modulus, flexural strength, flexural modulus and shore D hardness increased with increase in concentration of nano-alumina in the PVC matrix, but upto the concentration of 5 phr, above which they remained nearly constant or decreased. Contrasting trend was observed for elongation at break (%) and impact strength properties. 5 phr is the optimized concentration for addition in the unplasticized PVC matrix.

**Table 2: Mechanical Properties Obtained for PVC/nano-alumina Composites.**

Sample name	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/mm)	Shore D hardness
PVCC	46.8 ± 2.3	1589.1 ± 52.8	6.8 ± 0.4	72.9 ± 3.7	8554.0 ± 342.2	1.32 ± 0.08	80 ± 1
PVC1	49.4 ± 2.5	1670.2 ± 54.2	4.9 ± 0.3	79.4 ± 3.9	9156.7 ± 366.3	1.14 ± 0.07	83 ± 1
PVC3	58.4 ± 2.9	1903.2 ± 57.1	2.6 ± 0.2	86.8 ± 3.3	9734.6 ± 389.4	0.81 ± 0.04	87 ± 2
PVC5	69.2 ± 3.4	2462.1 ± 73.9	2.3 ± 0.1	91.2 ± 3.5	11785.3 ± 471.4	0.5 ± 0.03	89 ± 1
PVC7	60.6 ± 3.1	2062.9 ± 61.9	2.4 ± 0.1	87.3 ± 3.2	10783.4 ± 431.3	0.6 ± 0.03	89 ± 1

**Fig. 2: Stress-Strain Curves Obtained for PVC/nano-alumina Composites.**

There are two reasons for the improvement of the properties, first is the better compatibility between the PVC matrix and nano-alumina; second is the uniform dispersion of nano-alumina in the PVC matrix. Alumina has good compatibility with the PVC matrix. Thus, the addition of nano-alumina acted as the reinforcing points in the PVC. Uniform dispersion helped in better interaction between PVC and nano-alumina, acting as a point of physical cross-linking of PVC. This helped in holding the PVC molecules at their fusion position even on application of the load. This also helped in better orientation of the PVC molecules about the alumina nanoparticles, increasing the crystallinity of the matrix PVC, thus improving the above-mentioned properties. Nano-alumina concentration up to 5 phr concentration remained uniformly distributed in the PVC matrix, above which (i.e., at 7 phr) nano-alumina might have formed aggregates, decreasing the total surface area available for bonding with PVC. These

aggregates might also give rise to the stress concentrate points in the PVC, giving easy initiation of the cracks, decreasing the load-handling capacity and thus the above mentioned properties.

As the interaction between PVC and nano-alumina increased up to 5 phr concentration, it became more difficult for the PVC molecules to move about each other decreasing the elongational property.

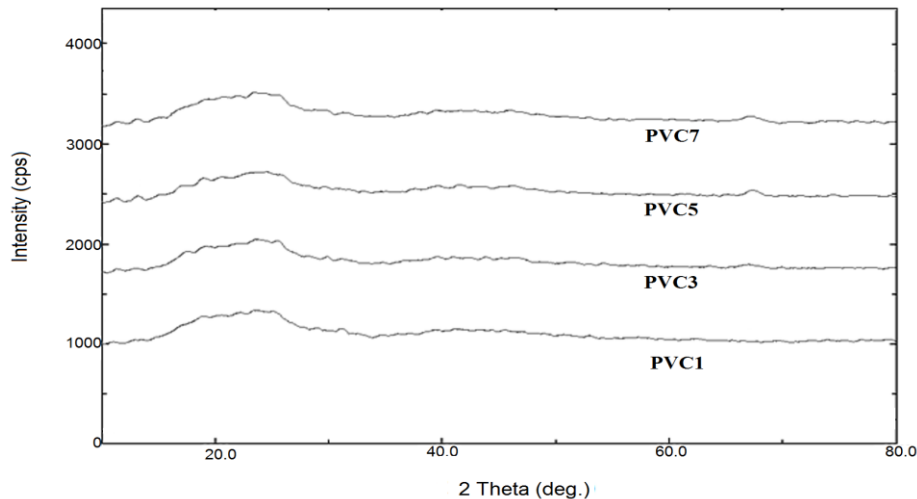
Tensile strength, tensile modulus, flexural strength, flexural modulus and shore D hardness were found to have increased by about 46.8, 54.9, 25.1, 37.8 and 11.3% respectively, which is appreciable for 5 phr loading of nano-alumina in PVC matrix. Elongation at break (%) and impact strength were found to have decreased by 64 and 61.5% for 5 phr loading of nano-alumina in PVC.

The above-mentioned supposition can be confirmed using X-ray diffraction analysis and scanning electron microscopy.

### Crystallinity Properties

X-ray diffractograms obtained for the

PVC/nano-alumina are shown in Figure 3 and the values obtained are listed in Table 3. It was found that the crystallinity increased with increase in the concentration of nano-alumina in the PVC matrix.



**Fig. 3:** X-ray Diffractograms Obtained for PVC/nano-alumina Composites.

**Table 3:** Crystallinity Values Obtained for PVC/nano-alumina Composites.

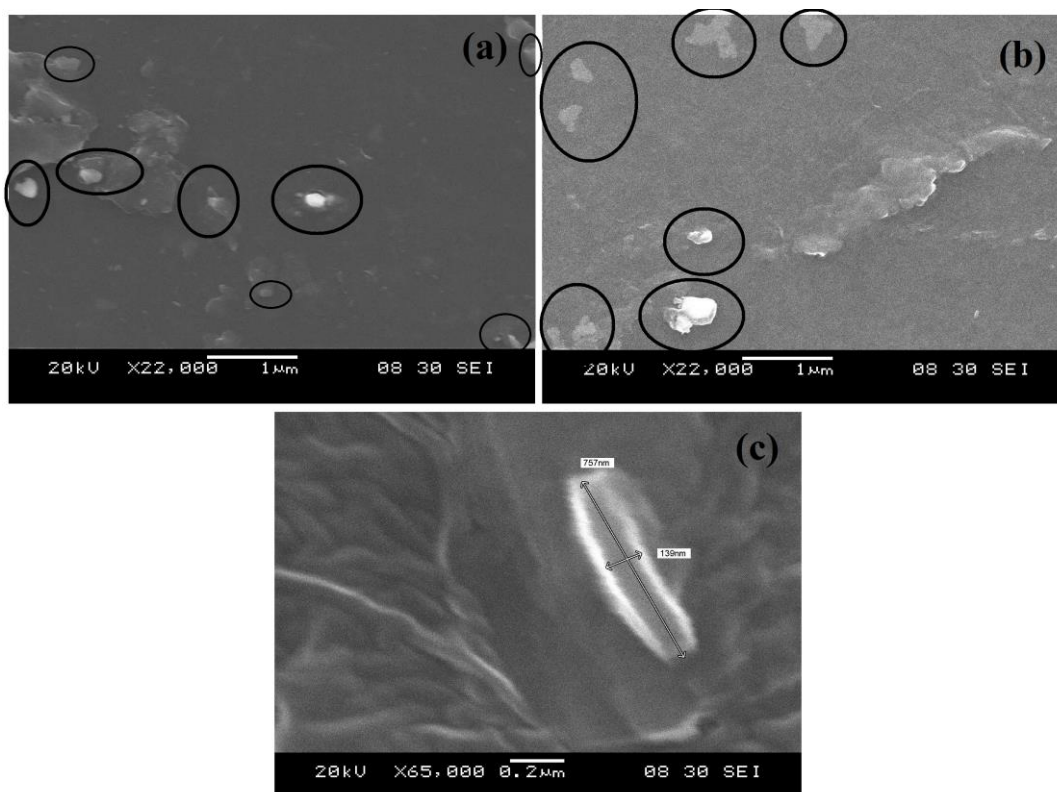
Sample name	Crystallinity (%)
PVCC	$5.9 \pm 0.5$
PVC1	$7.8 \pm 0.4$
PVC3	$8.2 \pm 0.3$
PVC5	$8.9 \pm 0.3$
PVC7	$8.8 \pm 0.2$

Better interaction of nano-alumina with PVC and uniform dispersion of nano-alumina in PVC matrix are the major reasons for the increase in the crystallinity, and is in complete coordination with the obtained mechanical properties. Crystallinity was similar for 5 and 7 phr nano-alumina-loaded PVC samples. This proves of nano-alumina having no appreciable effect in affecting the morphology of the PVC molecular chains above 5 phr concentration, most probably due to the formation of aggregates.

### Morphological Properties

Scanning electron micrographs obtained for PCV5, PVC7 and an isolated alumina nano-particle are shown in Figure 4 (a), (b) and (c) respectively. Uniformly and individually distributed alumina nano-particles can be properly seen in the SEM image of PVC5, justifying the explanation given above while in PVC7 aggregates of nano-alumina were seen, with also the points of stress concentrate. SEM image of an isolated nano-alumina shows the dimension of the nano-particle. Nano-alumina is rod shaped having length of about 740 nm and diameter of 130 nm. Nano-alumina has very good interaction with the PVC matrix as seen from the images.





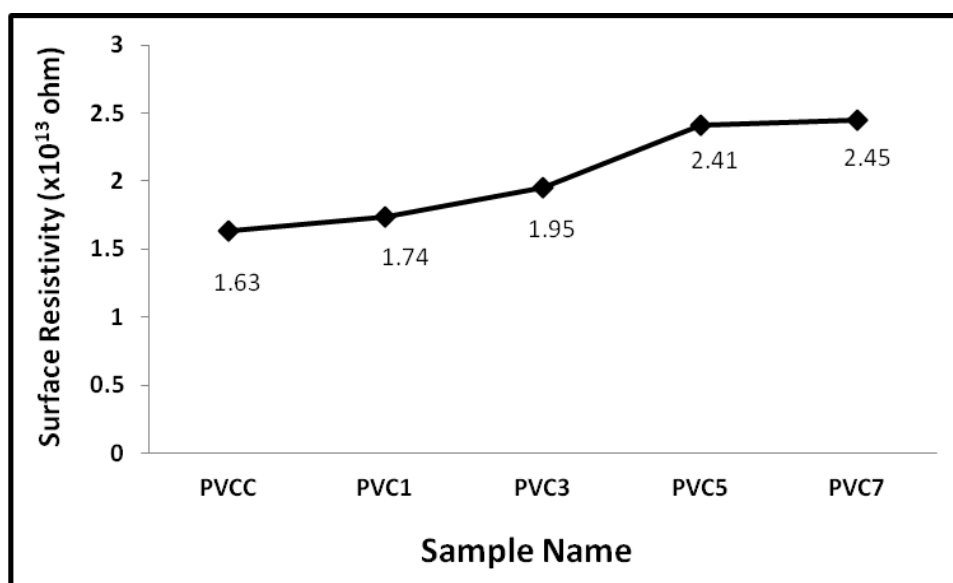
**Fig. 4:** Scanning Electron Micrographs for (a) PVC5, (b) PVC7 and (c) Isolated Alumina Nano-particle.

Thus, better interfacial attraction between nano-alumina and PVC, and uniform distribution of nano-alumina in PVC matrix are the prime reasons for the appreciable improvement in the mechanical properties.

**Electrical Properties**

Surface and volume resistivity values are very

important to understand the electrical properties for a composite material. Surface and volume resistivity values are in the form of graph in Figures 5 and 6. It was found that both surface and volume resistivity increased with increase in concentration of nano-alumina in PVC matrix.



**Fig. 5:** Surface Resistivity Values Obtained for PVC/nano-alumina Composites.

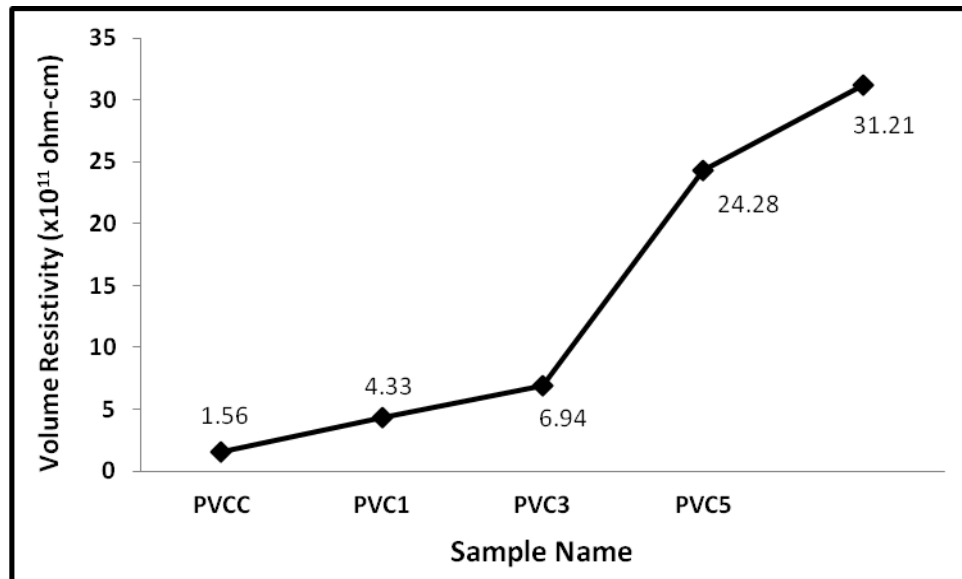


Fig. 6: Volume Resistivity Values Obtained for PVC/nano-alumina Composites.

Alumina is an electrically insulating material. Addition of nano-alumina in PVC induced this property in it, increasing the resistance to current flow. Also, the increased molecular interaction of PVC with the alumina nanoparticles decreased the polar sites available for transmission of electricity. Thus, surface resistivity and volume resistivity increased with increase in concentration of nano-alumina in PVC. This will be very helpful in making

plastic parts with the prepared material having electrical applications.

#### Thermal Properties

Thermal conductivity values obtained for the prepared PVC/nano-alumina composites are plotted in Figure 7. Thermal conductivity was found to have increased with increase in concentration of nano-alumina in PVC matrix.

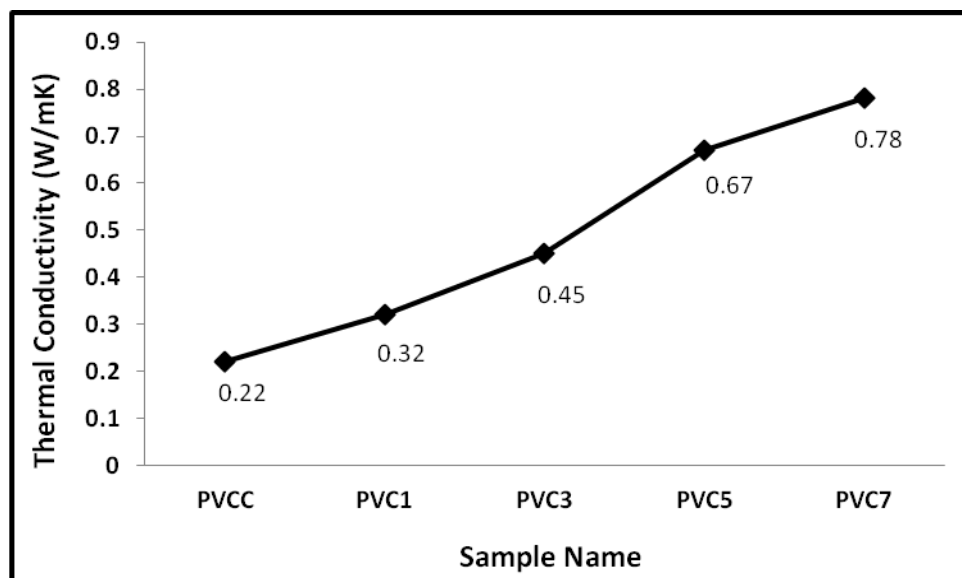


Fig. 7: Thermal Conductivity Values Obtained for PVC/nano-alumina Composites.

Alumina is a thermally conducting material, inducing this property into the composite. Increase in thermal conductivity will help in

increasing the thermal stability of the composite, making the composite to be processed at higher temperature range.

## CONCLUSIONS

PVC/nano-alumina composites were successfully prepared and characterized for mechanical, thermal, electrical, morphological and crystallinity properties. Nano-alumina was found to have better interaction and uniform dispersion in the PVC matrix as seen through scanning electron micrographs. Tensile strength, tensile modulus, flexural strength, flexural modulus and shore D hardness were found to have increased by about 46.8, 54.9, 25.1, 37.8 and 11.3% respectively. Appreciable improvements were also observed in thermal conductivity and electrical resistivity values on addition of nano-alumina. Optimal improvements in the properties were observed at 5 phr concentration of nano-alumina.

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