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## PREPARATION AND CHARACTERIZATION OF POLY VINYL ALCOHOL - ALUMINA COMPOSITES

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**Abstract:** Poly vinyl alcohol-alumina hybrid materials were synthesized in aqueous medium by the sol-gel method using hydrochloric acid (HCl) as catalyst and aluminum butoxide as alumina precursor, respectively. Transparent, flexible thin film composites of homogenous thickness were obtained at room temperature after drying for 5 days. The hybrid composites were characterized by Scanning Electron Microscopy (SEM) and Energy X-rays Diffractometry (XRD).

SEM micrographs revealed that alumina was dispersed in the PVA matrix without the large-scale aggregation of particles. EDX studies confirm the presence of alumina in the form of homogeneous dispersion in the polymer matrix. The amount of alumina is shown to be increasing with increase in aluminum butoxide. XRD patterns of pure PVA and PVA- alumina composite point out the wide bulge among 16 and 22 of 2- $\theta$  degree, and this is connected to amorphous field in Poly Vinyl Alcohol thin film polymer. It was found that the extent of crystalline domain of composite Poly Vinyl Alcohol has improved with addition of alumina. The crystalline movement is amplified with segment wise shift of Poly Vinyl Alcohol mass among sites of coordination and relaxation of confined structure raise the crystallinity with increase of alumina.

**Keywords:** Sol-Gel, Polyvinyl Alcohol, Aluminum butoxide, Alumina, Hybrid Organic-Inorganic Composite, SEM, EDX, XRD,

### Introduction

Polymeric composites are emerging as potential candidates for technological applications. Many investigations (Wen and Wilkes, 1996) regarding the development of the incorporation techniques of the particles into the polymeric matrices have been published. In most of the cases (Tasi et al. 1997), such combinations require blending or mixing of the components, taking the polymer in solution or in melt form. Resulting composites have found successful applications in versatile field's i.e. battery cathodes (Nazar et al. 1992), microelectronics (Vassilion et al. 1990), nonlinear optics (Beecroft and Ober, 1999), sensors (Cao et al. 1992) etc. In polymeric composites, the incorporation of inorganic material in organic polymer moiety is pursued to build devices with higher electronic, optical and magnetic properties (Jiu et al. 2005).

Sol-gel method has been widely employed in recent times for the synthesis of hybrid organic-inorganic composite materials (Dimitriev et al. 2008; Ellsworth and Gin, 1999). The versatility of sol-gel chemistry in polymers affords a measure of control

over the nature of organic-inorganic interface and a convenient method for the introduction of newer properties such as catalysis (Pierre and Sayed 1987), Biomedical (Pal et al. 2007) and nonlinear optical properties (Kobayashi, 1989) into the resulting material. One important area of recent interest in the field of polymer-inorganic composites has been the synthesis of materials having hydrogel behaviour.

Poly vinyl alcohol (PVA) is commonly used constituent of biodegradable polymeric compounds due to its water solubility (Homann et al. 2003). A film can be simply made from it and used like optically apparent malleable contact lenses (Patents, 2007).

PVA/silica system has received interest due to the known hydrogel behaviour of PVA (Cauich et al. 1996 a, b). The synthesis of an artificial heart valve stent from PVA was reported (Wan, 2003). There are also reports about a PVA/layered silicate composite for potential application in drug delivery (Gianellis, 2008). Due to the gentle reaction condition of silicon alkoxide (as tetraethoxysilanes, TEOS) is the mainly used metal alkoxide (Huang et al. 1987; Bandyopadhyay et al. 2005).

The remarkable decrease in degree of swelling in hybrid membranes of poly(vinyl alcohol) (PVA) and tetraethylorthosilicate (TEOS) was observed with increasing TEOS content in membranes and is attributed to the formation of hydrogen and covalent bonds in the membrane matrix (Kariduraganavar et al. 2005).

Pereira et al. (2000) have investigated the production and reactivity of PVA/silica hybrids obtained via the sol-gel method. The composites were prepared from PVA and tetraethyl orthosilicate (TEOS) with further modification of the inorganic phase with "bioactive" soda-lime phosphate silicate glasses. The preparation of PVA/silica hybrid having possible applications as water perm selective membrane or immobilization carriers for a biocatalyst, from polyvinyl alcohol and tetraethyl orthosilicate in aqueous medium by the sol-gel method was reported by Nakane et al. (1999). Other reports of PVA/silica synthesis include those by Hsu et al. (2000). Where PVA (average Mw  $1.5 \times 10^5$ ), TEOS and a mixture of dimethyl sulphoxide (DMSO), water and alcohol were used to form the sol-gel mixture and by Sharp et al. (1995), where formic acid played a dual role of catalyst and solvent to form the sol-gel mixture from PVA and TEOS.

The work on alumina-polymer composites are pursued with great interest in different laboratories of the world. Alumina is an important inorganic material, which is cheap and abundantly available. We are reporting the SEM and XRD studies on PVA- Alumina composites in a comprehensive manner.

## Materials and Methods

### Materials

Poly vinyl alcohol (PVA, MW= 72000, polymerization degree = 1600, hydrolyzed= 98%) has been purchased from Applichem GmbH, Darmstadt. Aluminum butoxide, (ABO, density = 960 kg/m<sup>3</sup>) was procured from Fluka, Germany and concentrated hydrochloric acid (AR grade) was from Merck. All the solutions were prepared in deionized water.

### Methodology

#### *Preparation of Sol-Gel Mixtures from Poly Vinyl Alcohol-Aluminum Butoxide*

A 5% aqueous solution of poly(vinyl alcohol) (PVA) was prepared by distributing 50 g of poly(vinyl alcohol) into about 900 mL deionized water and then kept at a temperature of 353.16 K in oven for 24 hours. The solution was cooled to ambient temperature (298.16 K) and the volume was made up to 1000 mL with deionized water and stored in a container. 10, 20, 30, 40 and 50, weight percent of aluminum butoxide with respect to 100 g of the polymer each in 5 dissimilar divisions was mixed to the PVA solutions in stirring circumstances to form a homogenous mixture at ambient temperature. Table 1 represents the compositions of all the PVA-alumina hybrid composites used in this research. Subsequent to methodical integration for 10 min, the acid catalyst i.e., 0.5 mL of concentrated HCl was added to the resulting polymer solutions so that to maintain the pH of the mixture in the range 1-2. The reaction medium was once more stirred up to 20 min at ambient temperature to carry out the in-situ acid hydrolysis of aluminum butoxide within PVA aqueous solution.

**Table 1. Compositions of the reagents used for preparation of poly (vinyl alcohol)-alumina hybrid composites and their physical properties (alumina content and appearance of the films)**

S. No.	Composite designation	Aluminum butoxide (Wt %)	Alumina (Wt %)	Appearance of the films
1	PVA	0.00	0.00	Transparent
2	ABO 10	10	2.61	Transparent
3	ABO 20	20	4.55	Transparent
4	ABO 30	30	9.61	Transparent
5	ABO 40	40	10.47	Transparent
6	ABO 50	50	12.92	Transparent

### **Preparation of Composite Films from Pva-Alumina Sol-Gel Mixtures**

The sol-gel mixtures were poured into thoroughly cleaned smooth glass petri dishes. The cast films were permitted to gel until they show no weight difference. The completely gelling process of the composite films was completed at ambient temperature within 5 days. Look of every film (typical thickness of 0.31 mm) as noted in Table 1.

### **Characterization of Organic-Inorganic Hybrid Composite Films**

Characterization of resulting composite films was done by using various analytical techniques, which are given below:

#### **Scanning Electron Microscopy (SEM)**

SEM analysis of a number of chosen thin films were carried out using scanning electron microscope SEM (Model JSM-5910-JEOL JAPAN) on thin films of hybrid composites applying an accelerated voltage of 5 kV. The Scanning electron micrographs were obtained at 2500  $\mu$ m magnification.

#### **Energy Dispersive X-rays (EDX)**

The scattering of alumina particles in the PVA medium was investigated by the Energy Dispersive X-rays (EDX) saved in EDX with SEM (JMS 5910) INCA 100/ Oxford instruments, U.K. Thin films were sputter covered by gold so that to oppose the artifacts produced above the surface because of charging.

#### **X-Rays Diffractometry (XRD)**

XRD patterns of the composites were studied by X-ray diffractometer (JDX-3532, JEOL Japan) so that to recognize the phases offered in the films and estimate the crystal orientations. CuK $\alpha$  rays of wavelength  $\lambda = 0.15406$  nm were applied with a voltage adjustment of 40 kV tube voltage and 30 mA tube current. The range of diffraction angle was 10.00 to 70.00 of 2- $\theta$ .

## **Results and Discussions**

### **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) was performed to observe morphology of the PVA, PVA/alumina composite thin films (Fig. 1&2).

Scanning electron microscopic profile of pure PVA Figure 1 shows approximately smooth surface except some of its own bulging. The representative PVA/alumina thin film composite is presented within Figure 2.

The presence of PVA in the mixture does not create any drastic change in reaction conditions for the hydrolysis and condensation of alumina. However, the polymer concentration and viscosity was found to significantly affect the tendency of co-condensation of alumina within PVA. It appears that when the PVA concentration (and hence viscosity) is lower, the alumina has a higher tendency to undergo self-condensation reaction. At intermediate PVA concentration, co-condensation is favoured while at higher concentration self-condensation again becomes the dominant reaction. This was concluded from a study of the SEM of the composites shown for various compositions. Figure 2 (representative SEM for the various composite micrographs) shows the SEM micrograph of composite prepared from ABO 50 i.e. 12.92% alumina in PVA. In this case, there is no large-scale aggregation of alumina particles and the pattern of dispersion is uniform. The SEM micrograph in Figure 2 shows square or rectangular shaped alumina. An explanation for this may be that the extended ramified structure of alumina adopts a square configuration in acidic media. Landry et al. (1992) have reported such a mechanism. In acidic media, the individual squares are small and not densely cross-linked. The observed square shaped morphologies of the alumina domains might be due to collapse of the alumina acidic polymer chains during shrinkage. At low PVA concentration, the number of hydroxyl groups from PVA is low and therefore the condensation mechanism primarily involves linkages between the hydroxy groups from alumina. At intermediate concentrations of PVA, the number of hydroxy groups is sufficiently large to allow for a co-condensation mechanism and therefore we get homogenous sol-gel dispersions and uniformly dispersed alumina. At higher concentrations of PVA, self-condensation and co-condensation seem to proceed at equal rates because hydroxy groups from PVA might show an increasing tendency to form linkages among themselves (Nakane et al. 1999).



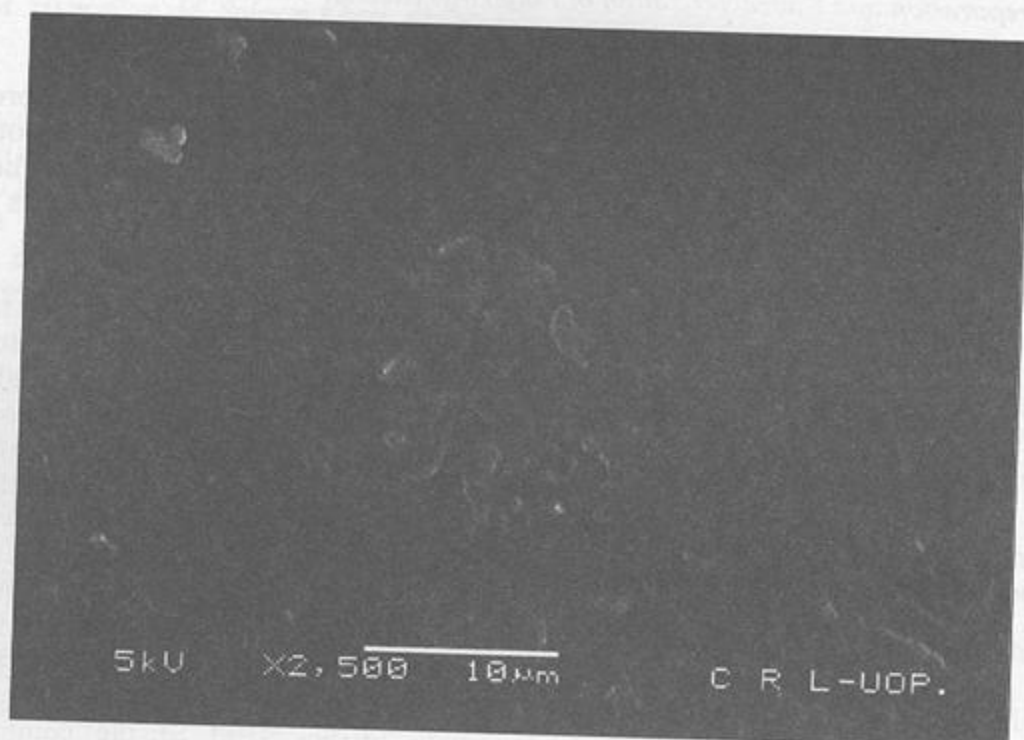


Fig. 1. SEM Micrograph of representative PVA thin film.

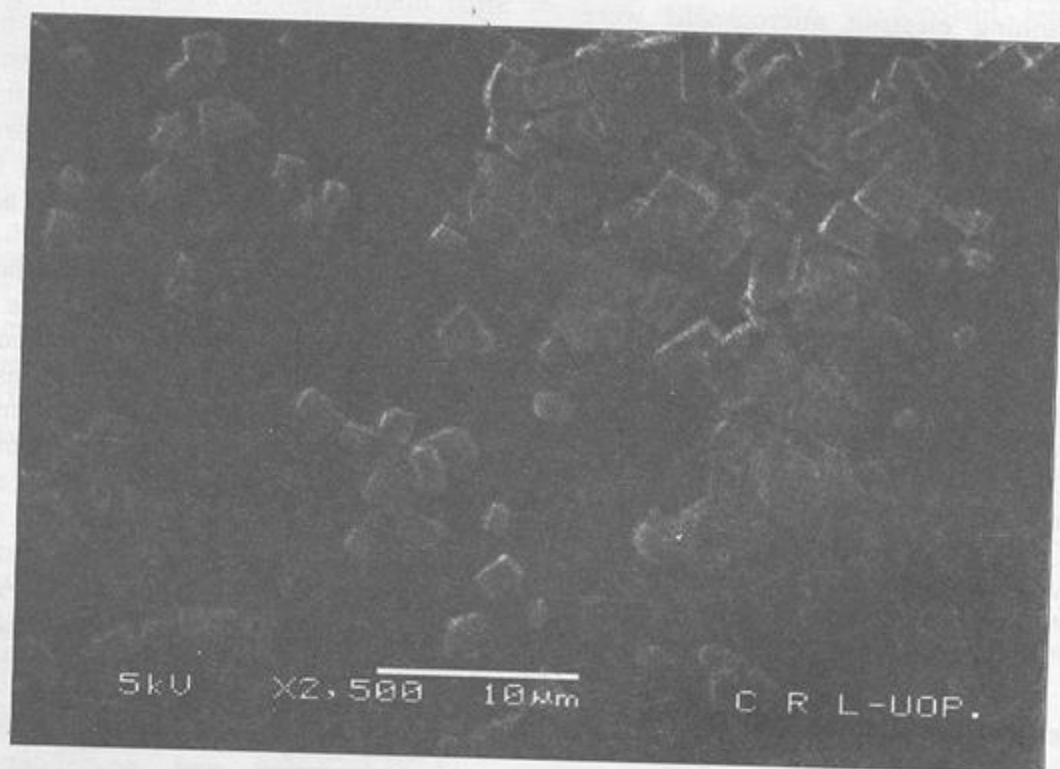


Fig. 2. SEM Micrograph of representative PVA-alumina thin film.

### Energy Dispersive X-Ray (EDX) Mapping

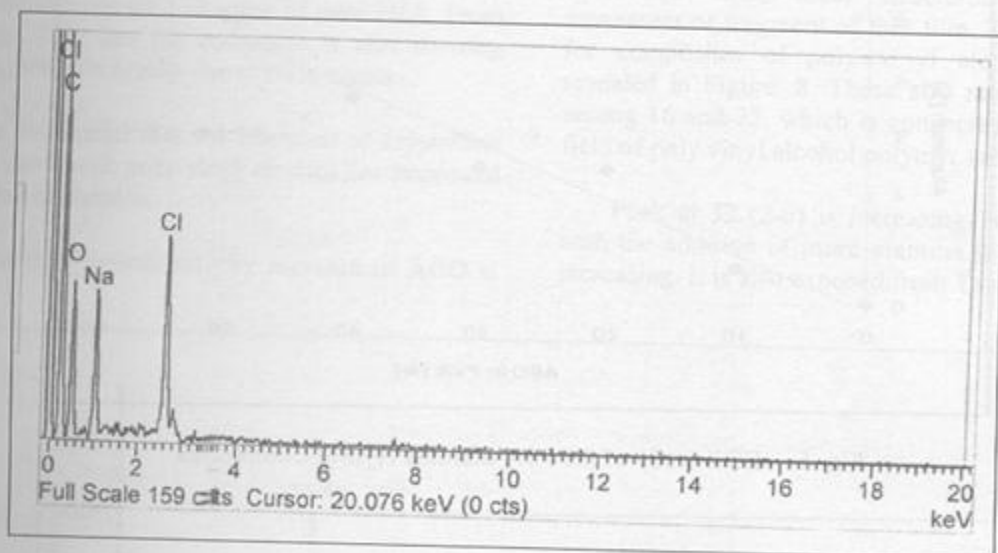


Fig. 3. EDX spectrum of PVA.

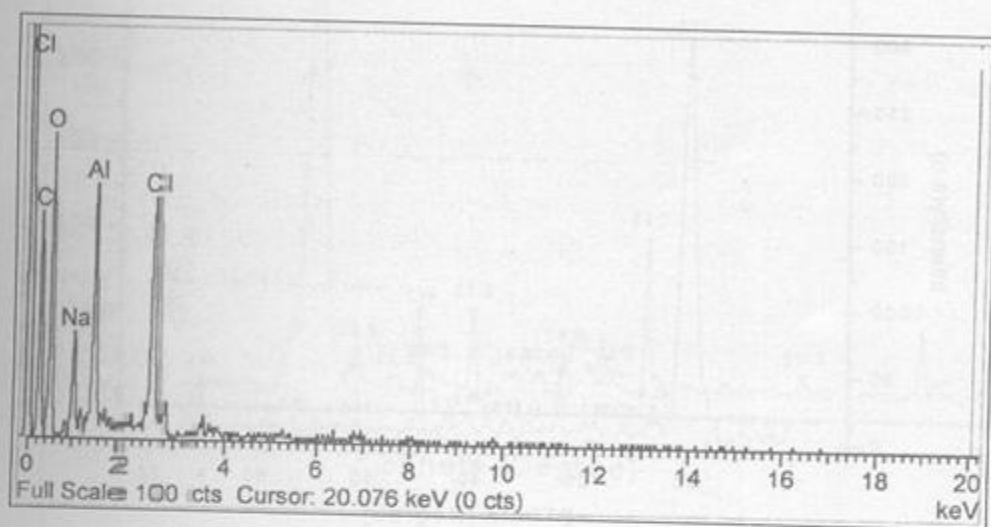


Fig. 4. EDX spectrum of PVA-alumina.

The consequences of Energy Dispersive X-ray studies of PVA and aluminum in element form in the PVA-alumina composites are shown in Fig. 3 and 4 (Fig.4 is representative EDX of all the composites studied). The Figure demonstrates homogeneous dispersion of elemental aluminum in the PVA matrix.

Aluminum content in the matrix varies regularly by varying amount of aluminum butoxide (ABO). Pure

PVA thin film contains none of the aluminum contents and ABO 10 thin films reveals the smallest aluminum in the medium. The aluminum increases in ABO 30 in comparison to that in the ABO 10 film. Larger is the amount of the alumina particles in the ABO 50 thin film having 50 % of aluminum butoxide (ABO). The EDX study shows uniform dispersal of alumina particles, whose amount is increasing with the increase in ABO content (Fig. 5).

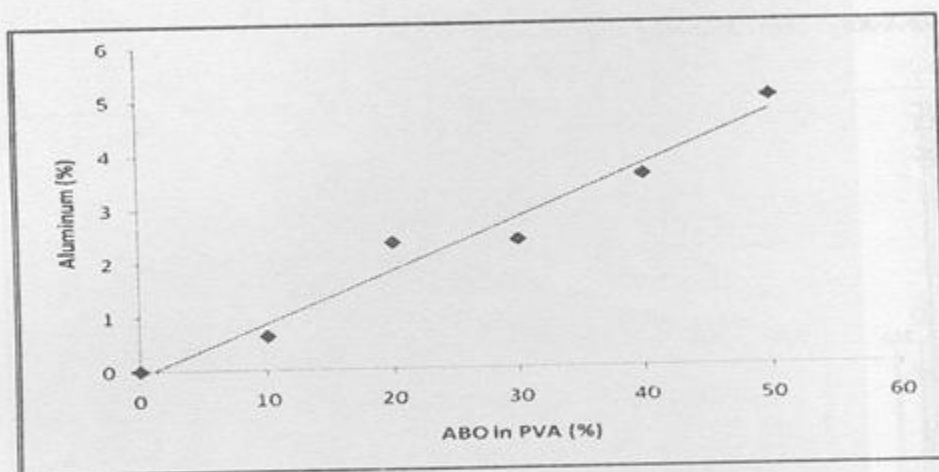


Fig. 5. EDX study of the PVA-alumina Hybrid Composites.

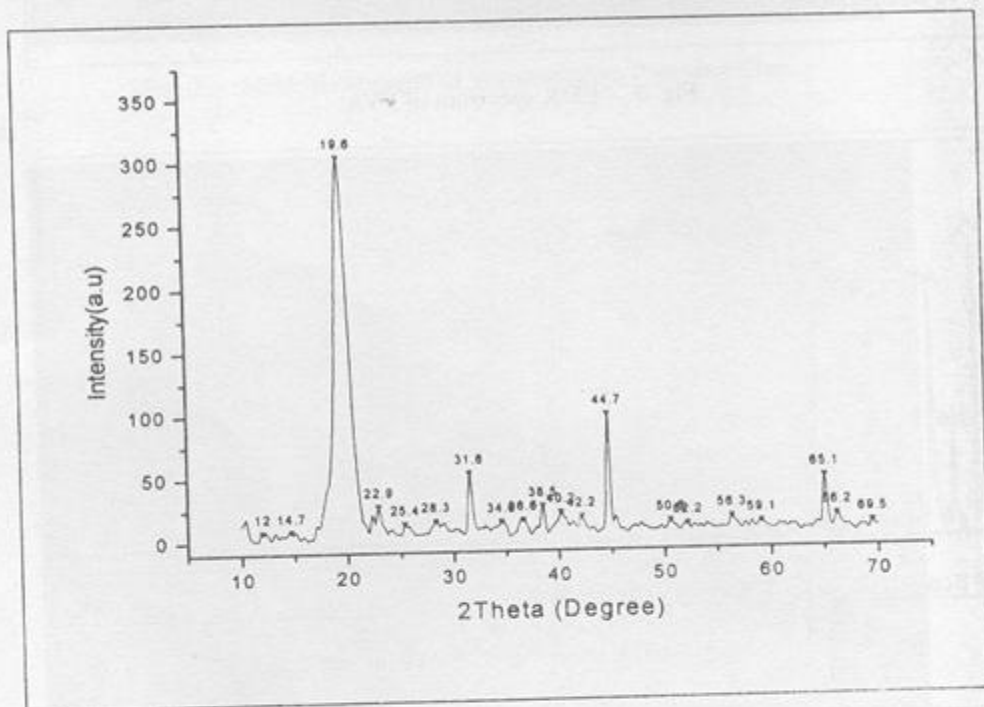


Fig. 6. XRD Pattern of PVA.

#### X-Ray Diffractometry (XRD) Pattern

The XRD patterns were obtained to find out crystalline morphology of the PVA, PVA-alumina composite thin films.

The XRD patterns of PVA thin film (Fig. 6) revealed that the PVA shows peak at around 31.6, 44.7 and 65.1 of 2-θ values. From this data, we can infer the

crystallinity of thin film of PVA.

In the amorphous part of PVA polymer template, the fragment movement further willingly takes place. XRD pattern points out the wide bulge among 16 and 22 and this is connected to amorphous field in poly (vinyl alcohol) thin film (Yang, 2003).



XRD patterns of poly vinyl alcohol-alumina thin film composite (Fig. 7) revealed that the large peak was at around 31.6, 44.7 and 65.1 like that of pure PVA. From this, we can infer that the composite is also showing crystallinity, which is mainly due to PVA matrix.

It was discovered that the intention of crystalline domain of composite poly vinyl alcohol has improved with addition of alumina.

The boost of crystallinity by increase of ABO is

explained as being due to a hopping mechanism among coordinate sites, local structural relaxation and movement of fragment of thin film. The XRD patterns for composites of poly vinyl alcohol-alumina are revealed in Figure. 8. These also reveal a wide lump among 16 and 22, which is connected to the shapeless field of poly vinyl alcohol polymer medium.

Peak at 32 (2- $\theta$ ) is increasing, which means that with the addition of more alumina the crystallinity, is increasing. It is also exposed from Table 2.

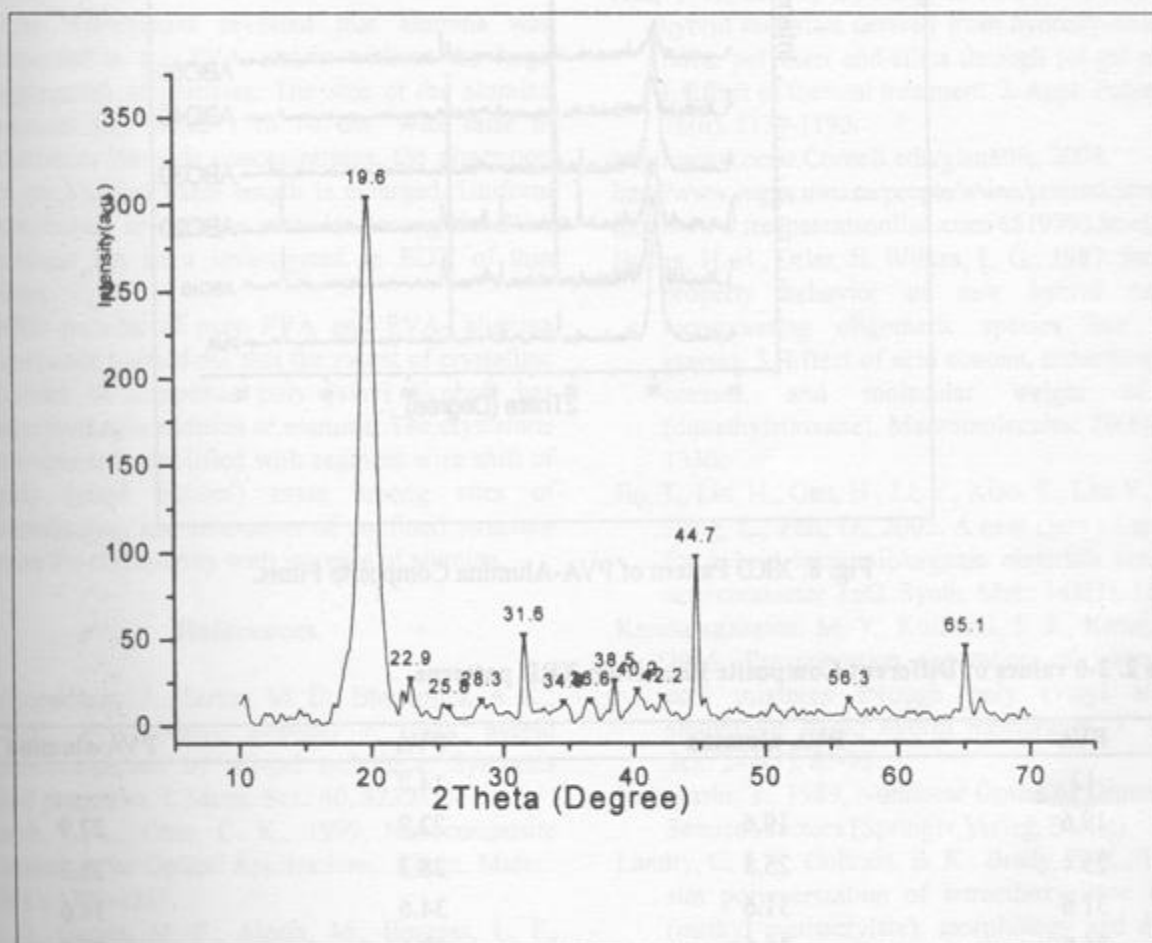


Fig. 7. Representative XRD Pattern of PVA-Alumina.

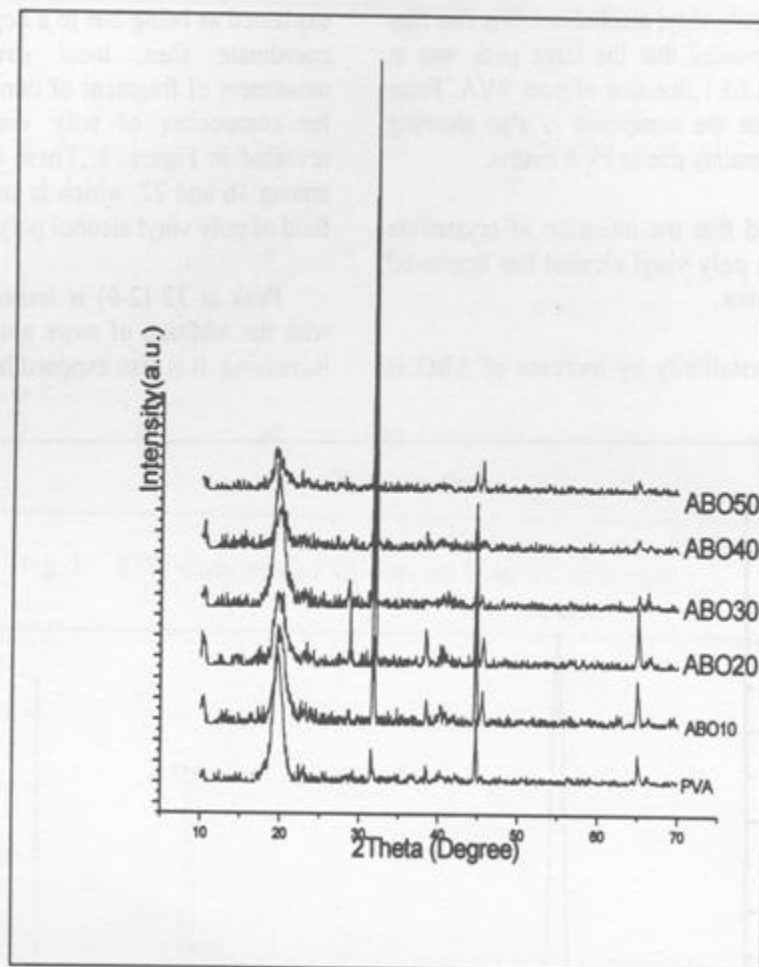


Fig. 8. XRD Pattern of PVA-Alumina Composite Films.

Table 2. 2- $\theta$  values of Different Composite films from XRD patterns.

PVA	PVA-alumina	PVA	PVA-alumina
12		14.7	
19.6	19.6	22.9	22.9
25.4	25.8	28.3	28.3
31.6	31.6	34.6	34.6
36.6	36.6	38.5	38.5
40.2	40.2	42.2	42.2
44.7	44.7	50.6	
52.2		56.3	56.3
59.1		65.1	65.1
66.2		69.5	

## Conclusion

PVA-alumina organic-inorganic composites have been prepared by means of sol-gel procedure. The precursor for alumina was aluminum butoxide. Every thin film appears translucent. The formation of colloidal stable sol assisted the formation of homogenous sol-gel mixtures and the amount of acid catalyst used played a significant role in this. The concentrations of PVA and alumina were significant factors affecting the formation of homogenous sol-gel mixtures as:

1. SEM micrographs revealed that alumina was dispersed in the PVA matrix without the large aggregation of particles. The size of the alumina particles lies inside 1 to 10  $\mu\text{m}$ . With raise in aluminum butoxide concentrations, the dimension of the alumina chain length is enlarged. Uniform distribution of alumina particles among the PVA medium has been investigated in EDX of thin films.
2. XRD patterns of pure PVA and PVA- alumina composite pointed out that the extent of crystalline domain of composite poly (vinyl alcohol) has improved with addition of alumina. The crystalline movement is amplified with segment wise shift of poly (vinyl alcohol) mass among sites of coordination and relaxation of confined structure raise the crystallinity with increase of alumina.

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