

Aluminosilicate-Filled Composites of PVA–PVP—An Improved Biodegradable Polymeric Material

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ABSTRACT: Poly(vinyl alcohol)–poly(vinyl pyrrolidone) biodegradable polymer blend was modified with aluminosilicate. Sample films containing 5, 10, 15, and 20 wt % filler were prepared by conventional solvent casting technique using glass plates as casting surfaces. The newly developed biodegradable composites are bright red, with magnetic properties due to the presence of iron compounds. Physical, chemical, and biodegradable properties

of the films were studied with the conclusion that the presence of aluminosilicate affects the properties of the matrix and enhances biodegradability of the polymer composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4963–4970, 2006

Key words: aluminosilicate; biocomposites; biodegradable polymer; PVA–PVP blend

INTRODUCTION

The history of green polymers as biodegradable materials goes back to 15,000 B.C. Use of tree leaves, natural resins (including natural rubber) found the way into the heart of civilization. As most of them lacked durability, these natural polymers started to be modified to prolong their lives and also improve their properties. However, the increased production of these and manufacturing of synthetic polymers has lately caused huge problems with waste, as they survive in nature for a long time. These contradictory requirements, i.e., good properties during the lifetime and decomposition when they are disposed, caused a growing interest in the use of biodegradable polymers, which should ensure cleaner environment.^{1–3} The advantages of such materials include not only easier end-of-life disposal but also use of renewable raw materials, industrial waste materials, and reduced requirements on fossil reservoirs.

One of the ways to modify polymeric materials' properties is to prepare blends, a mixture of two or more homopolymers, or to combine a polymer with filler, in other words, to prepare composites.⁴ A composite comprises two parts: the matrix (continu-

ous phase), and the reinforcing material (dispersed phase in the case of powders). The properties of the composite are a function of the properties of the individual phases, their relative amounts, and the geometry of the dispersed phase, i.e., shape, size, and orientation of the particles. At the selection of fillers, those of inorganic origin are preferred by industrial people, as they are cheap and do not lower the hardness of the composites. Keeping this in mind, we modified poly(vinyl alcohol) (PVA)–poly(vinyl pyrrolidone) (PVP) blends with aluminosilicate, a multi-component natural clay material, to improve the biodegradability of composites and thus contribute to the preparation of environment-friendly materials. The matrix system of (PVA)–(PVP) blend has been chosen because it provided a better polymer matrix with excellent physical properties such as electrical insulation properties;⁵ moreover, PVA and PVP are both important biodegradable polymer and has application in biomedical engineering; micro devices such as implantable drug delivery systems are currently being developed.⁶ It is advantageous to design and fabricate such micro devices using biodegradable and biocompatible polymers because they would naturally degrade and disappear in the tissue or in the environment over a period of time. Biodegradable systems on the other hand, should be thoroughly checked from the toxicological point of view with regard to their effect on tissue/cell and the mode of metabolism. Some of the biodegradable drug delivery systems find application in fertility control, treatment of narcotic addicts antimalarials,⁶ and cryoprotectant, specially PVP, to maintain islet

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TABLE I
Characteristics of Aluminosilicate with Respect to Structure and Properties of Mineral Components^{5,17}

Mineral name	Chemical structure	wt %	Admixture	Type
Gibbsite	Al(OH) ₃	92.1	Fe, Ga, Be	Hydrate
Hematite	α-Fe ₂ O ₃	63.8	Ti, Al, H ₂ O	Oxide
Ilmenite	FeTiO ₃	36.2 {52.65% of TiO ₂ }	Mg ²⁺ , Mn ²⁺ , Fe ³⁺ , Cr ³⁺ , V ⁵⁺ , Nb ⁵⁺	Compound oxides
Kaolinite	Al ₂ [Si ₂ O ₅](OH) ₄	67	Fe	Hydrate
Quartz	SiO ₂	33	–	Oxide
Anatase	TiO ₂	66.7	–	Oxide
Rutile	TiO ₂	34.3	–	Oxide

cell integrity and function during cryopreservation.⁷ Nevertheless, they are commercially available, water soluble, and easy to mix with natural inorganic filler (aluminosilicate). Polymeric materials prepared in combination with organic and inorganic compound at a nanoscale^{8–11} have additional advantages, such as the possibility of obtaining a new material that has the advantages of both organic materials (e.g., light weight, flexibility, and good moldability) and inorganic materials (e.g., high strength, heat stability, and chemical resistance).¹² The development of novel polymer composites, including biodegradable polymers filled with multicomponent fillers and the investigation of their properties are the subject of much research interest due to the increasing application of these materials in microelectronics area, such as radioelectronic devices to infill the space between electrical circuits, antennas for engineering of radomes, etc. The application of such multicomponent composites with biodegradable properties in radomes is important in terms of protection of the environment and the ability to pass electromagnetic waves.⁵ In the present work, we attempted to understand the effect of filler (aluminosilicate, a multicomponent inorganic natural clay material) on microstructure of polymer composites, physical and chemical behavior, mechanical properties, hardness, and biodegradability.

EXPERIMENTAL

Materials

Poly(vinyl alcohol), (PVA), is a creamy white, fully biodegradable polymer available in powder form, mainly used for biomedical application and membrane application.^{13–16} In this study, PVA from Loba, India, in the form of powder and granules was used.

Poly(vinyl pyrrolidone), (PVP), is a fully biodegradable polymer. It is a white powder readily soluble in water. Because of this unique solubility, complexing ability, and physiological inertness it is widely used in pharmaceuticals, cosmetics, foodstuff manufacturing, drinks, adhesives, synthetic resins, textile dye printing, detergents, pigments, coatings, electronic and bioengineering materials, and medical

instruments.¹⁶ In our research, PVP from SRL, India, was employed.

Aluminosilicate, an industrial waste material of an aluminum company from India, was used as inorganic filler for the preparation of PVA–PVP biodegradable polymer composites. It is bright-red in color, multicomponents (Table I) system, powdery in nature, and is readily distributed in water.

Preparation of polymer blend and composites

The composition and content of biodegradable material are shown in Table II. PVA film was prepared by dissolving PVA granules in distilled water at the temperature of 100°C and then cooled to room temperature. The solution was spread on a glass mold and the water evaporated at room temperature.

For the blend of PVA/PVP, the polymer solutions were prepared at a concentration of 5 wt % by dissolving dried powdered PVA and PVP at 100°C and at room temperature, respectively, under continuous stirring. The two solutions were mixed and then stirred for 10 min at room conditions. The blend of PVA and PVP was cast from aqueous solution on a glass mold, and the water was evaporated at room temperature (~ 30°C). The blend sample is designated as APC.

Biodegradable composites were made using aluminosilicate and the blend of PVA/PVP, as shown in Figure 1. First, PVA/PVP blend solution was made, then the (aluminosilicate) was mixed into it and finally the material was cast onto glass. The samples were designated as APC 5, APC 10, APC 15, APC 20 and their properties were measured.

TABLE II
Composition and Content in Polymer Films

Sample index	Distilled water (mL)	PVA (g)	PVP (g)	Aluminosilicate (g)
PVA	100	10	0	0.0
APC	100	5	5	0.0
APC 5	100	5	5	0.5
APC 10	100	5	5	1.0
APC 15	100	5	5	1.5
APC 20	100	5	5	2.0

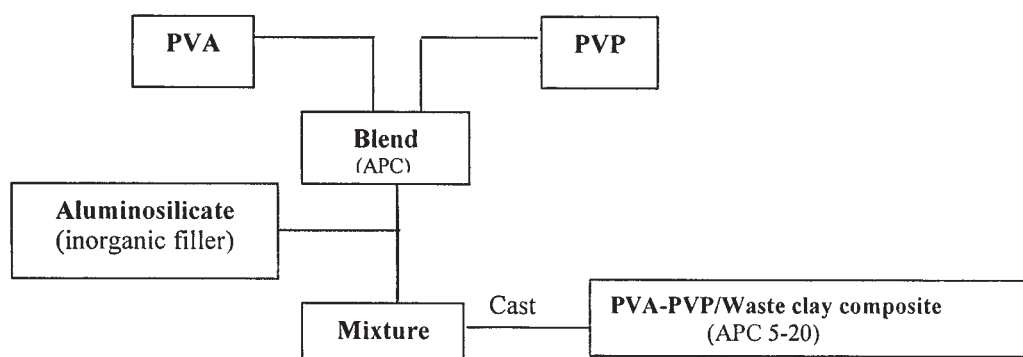


Figure 1 Preparation of polymer blend and composites.

Scanning electron microscopy

A scanning electron microscope (SEM; JEOL, JSM-5800) was used to analyze the aluminum silicate filled biodegradable composite material. A thin section of the sample was mounted on an aluminum stub using a conductive (silver paint) and was sputter coated with gold prior to fractographic examination. The SEM micrographs were obtained under conventional secondary electron imaging condition with an acceleration voltage of 20 kV.

Fourier transform infrared spectroscopy

To identify the physicochemical structure of the samples (PVA, aluminosilicate, PVA-PVP blend, and its

composite with aluminosilicate) FTIR spectroscopic analysis was carried out. ATR-FTIR spectroscopic analysis was conducted on thin film by using NICOLET 320 FTIR spectrophotometer with "Omnic" software package over the range of $4000\text{--}600\text{ cm}^{-1}$ at room temperature. A uniform resolution of 2 cm^{-1} was maintained in all cases.

Measurements of XRD

A sample for the XRD measurement is prepared by using a glass-slide with a groove in it as the sample holder. The aluminosilicate was placed in the groove and then compressed gently with the help of another glass slide to create a plane surface of the powder in

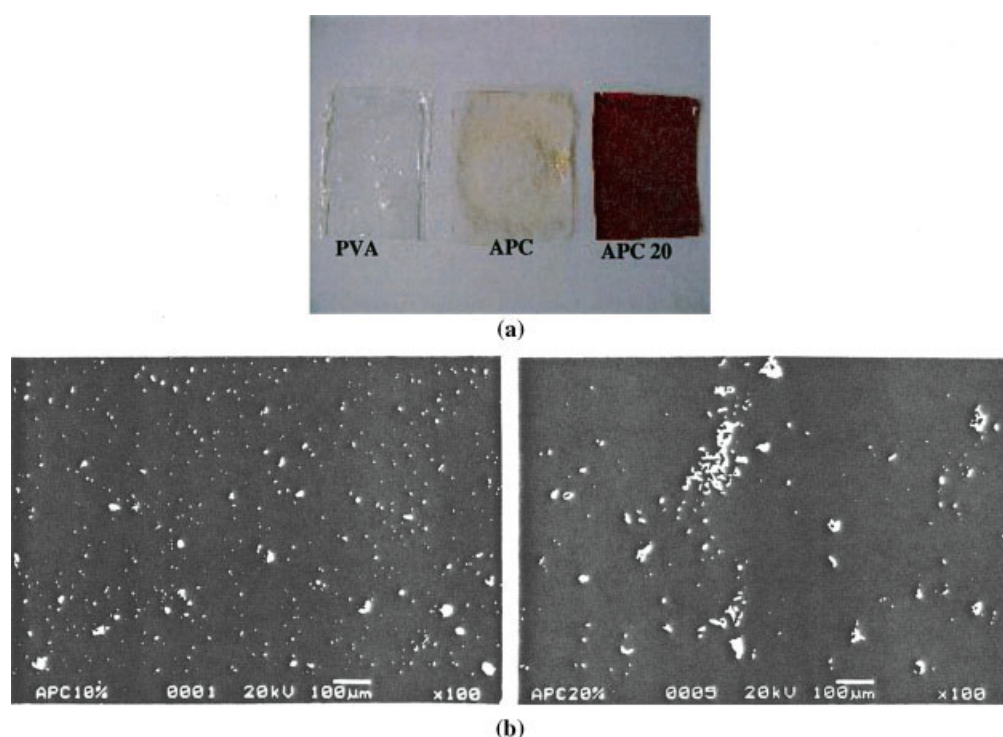


Figure 2 (a) View of polymer films. (b) SEM view of aluminosilicate-filled biodegradable composite material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

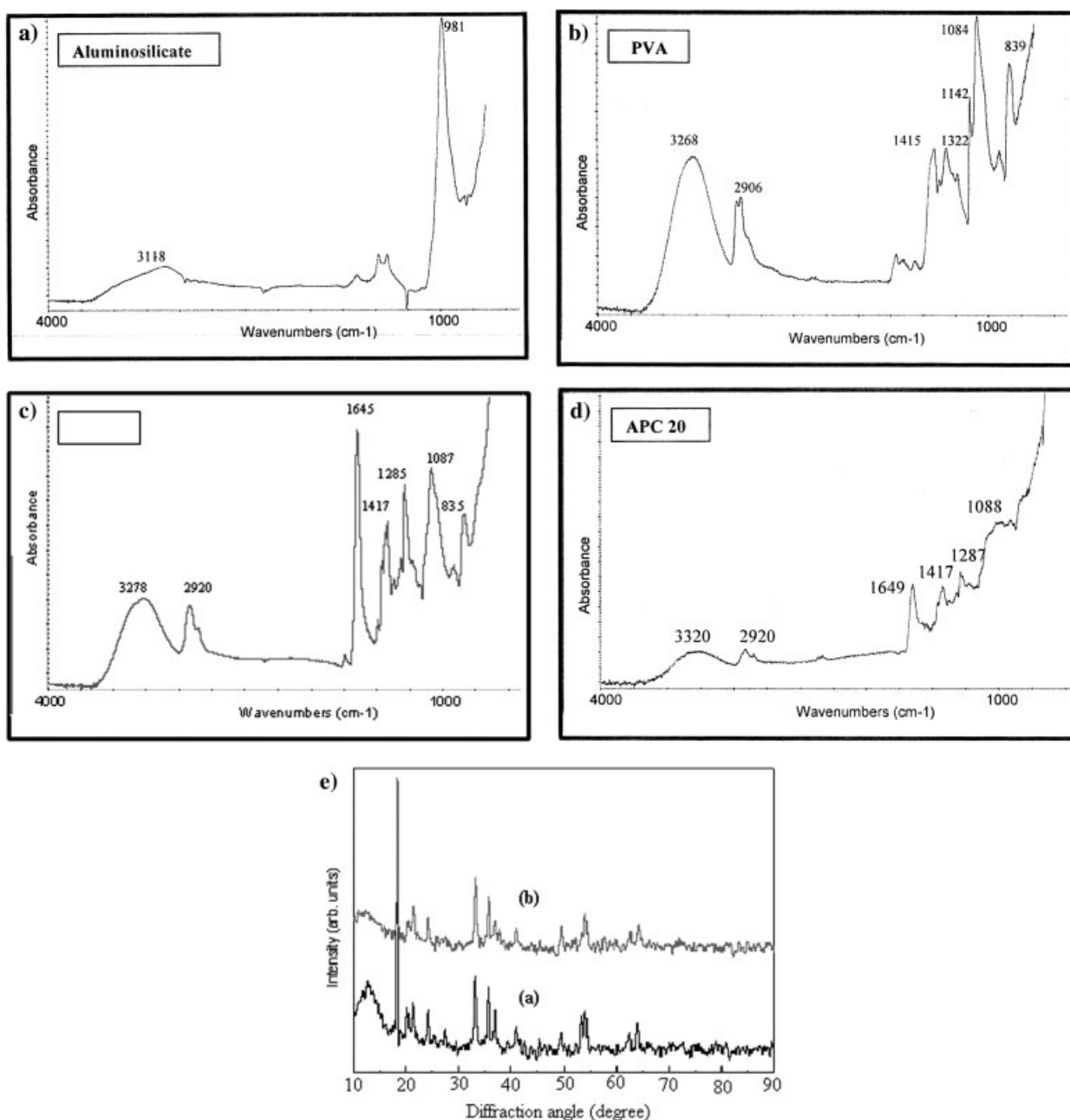


Figure 3 (a) IR spectra of aluminosilicate (used as filler); (b) IR spectra of PVA, pure polymer; (c) IR spectra of APC, polymer blend; (d) IR spectra of APC 20, polymer composites; (e) XRD patterns of inorganic aluminosilicate (a) uncoated and (b) coated with rubber.

the groove. The specimen was placed along with the glass slide in an X-ray diffractometer of PHILIPS PW-1710 to measure the X-ray diffraction pattern from its flattened surface. The diffraction data are recorded using a filtered monochromatic of $\text{CoK}\alpha$ or $\text{CuK}\alpha$ of wavelength $\lambda = 179$ or 154 nm through a Ni filter. The data were collected with a computer, interfaced through the diffractometer, at a scanning speed of 0.05 s^{-1} , unless otherwise specified, especially in the case of high resolution X-ray diffractograms in selected measurements. The range of the

diffraction angle 2θ was varied from 10° to 110° in most of the samples.

Measurement of aluminosilicate particle size

Average crystallite size (D) in the crystalline sample has been calculated from peak widths $\Delta 2\theta_{1/2}$ in the characteristic diffraction peaks using the Debye-Scherrer's formula:¹⁸

$$D = 0.89\lambda / (\Delta 2\theta_{1/2}) \cos \theta_b$$

where $2\theta_b$ is the position of a peak in the diffractogram from a specific crystallographic plane (hkl).

Static tensile measurements

The tensile tests were performed to know about the reinforcement parameters of PVA-based composite and PVA-PVP-based composites with different concentration of filler as aluminosilicate. The mechanical strength properties of such composites were determined according to ASTM standards by using an Instron tensile tester.

Measurements of hardness

Hardness of PVA and PVA-PVP based aluminosilicate composites were measured by Shore Hardness, a measuring instrument.

Biodegradability

The biodegradation of polymeric material was carried out through the soil burial test.^{19,20} The experiment was conducted in a tray (indoor) at ambient humidity (36–92%) and temperature (25–32°C), and the incubation period was 30 days. Soil from Indian Institute of Technology campus, Kharagpur, India was used. It was moistened with water and left for 24 h to obtain uniform moisture. Polymer film of PVA, APC, APC 5, APC 10, APC 15, and APC 20 were dried under vacuum to obtain constant weight. Each film was cut into several pieces with a particular specification ($2 \times 2 \text{ cm}^2$), and buried into the wet soil. After 30 days the test samples were taken out, washed with water to remove the soil adhered on the surface of the films and dried at 50°C under vacuum to constant weight. The degradation in the polymer was then calculated using eq. (1).

$$\% \text{ Degradation of polymer} = 100(W_0 - W_d)/W_0 \quad (1)$$

where W_0 is the initial weight of the dry film and W_d is the weight of degraded film.

RESULTS AND DISCUSSION

Morphology

The film of pure PVA is transparent and soft, the same as that of PVA-PVP blend, i.e., APC sample. The film of polymer composite, however, is bright red and harder than the previous two, which is caused by the presence of aluminosilicate as natural filler. The view of polymer films is shown in Figure 2(a). The microstructures of the composites are observed by SEM. The microstructure of 10 and 20 wt % clay composites are shown in Figure 2(b). It

can be seen from the figure that the clay particles are not finely dispersed in the matrix material. The bright spots on the backscattered images correspond to clay particles. In these composites small and large agglomerates are observed. The small particle agglomerates are very important in context of mechanical properties where the microstructure control several phenomena like toughness of the composites.

Physical and chemical behavior

The physical properties of aluminosilicate (waste clay material), pure polymer (PVA), polymer blend of PVA-PVP (APC), and polymer composite of PVA-PVP + filler (APC 5–20) were analyzed on the basis of their IR spectra. The FTIR spectrum of aluminosilicate shows a strong 'Si—O' absorption peak at 981 cm^{-1} , as can be seen in Figure 3(a). For pure silicate this peak comes at 1000 cm^{-1} . A broad band at around wave number 3118 cm^{-1} and three small peaks of 1639, 1476, and 1402 are observed between 1800 and 1550 cm^{-1} . It indicates that beside silicate other mineral compounds are also present in aluminosilicate (as can be seen from Table I) which proves that aluminosilicate is a multicomponent filler.

The FTIR spectrums of PVA, APC, and APC 20 films are shown in Figures 3(b–d), respectively. Figure 3(b) shows a broad band at 3262 cm^{-1} . This peak is the O—H stretch peak due to intermolecular hydrogen bonding, while the split peak at 2906 is the O—H stretch peak due to intermolecular hydrogen bonding. The peaks at 1415 cm^{-1} and 1322 cm^{-1} are C—O—H bend peaks, while the sharp peak at 1084 cm^{-1} is the C—C—O stretch peak. The shoulder peak at 1142 cm^{-1} is reported to be related to the degree of crystallinity of PVA, which was proposed to be C—C stretching mode and increase with an increase in the degree of crystallinity.²¹ The IR spectra and their characteristic peaks of APC are shown in Figure 3(c), which shows the presence of both PVA and PVP in the film. The peak height of PVPs 1660 cm^{-1} peak increased with increasing PVP in the blends, while the peak height of PVAs 1085 cm^{-1} decreased, which was in agreement with the compositions in the blends. The peak at 1285 cm^{-1} was also associated with PVP composition in the blends, which was found in pure PVA spectra.

TABLE III
Evaluation of Crystallite Size [Fig. 3(e)]
of Uncoated Aluminosilicate

$2\theta_1$	$2\theta_2$	2θ	$\langle t \rangle$	Avg. $\langle t \rangle$	d
18.08	18.37	18.23	27 nm		4.86
32.90	33.30	33.10	20 nm	24 nm	2.705
35.47	35.64	35.64	25 nm		2.51

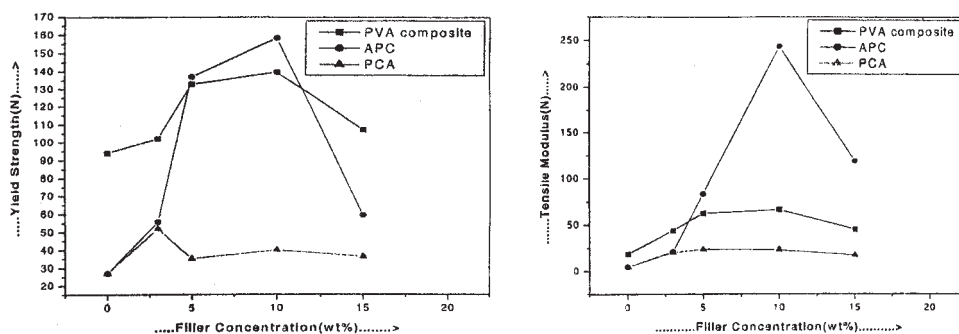


Figure 4 Variation of yield strength and tensile modulus with filler concentration.

The thermogram of APC showed a single glass transition temperature which suggested the miscibility of PVA and PVP.¹⁶ The presence of a single glass transition temperature has been widely accepted as the demonstration of miscibility of polymer blends.²² The single T_g indicates the miscibility of the blend and can be attributed to the hydrogen bonding between the C=O and OH groups.

In APC 20, the polymer composite [Fig. 3(d)], there is a broad peak of 'O—H', the same as in the spectrum of the clay material. It indicates a proper mixing of aluminosilicate with the PVA–PVP blend.

X-ray diffraction analysis of aluminosilicate

Figure 3(e) shows the X-ray diffraction patterns of inorganic aluminosilicate in the 2θ regions of 10° – 90° . It indicates that coating with rubber does not affect much on X-ray diffraction pattern of aluminosilicate. Regarding crystallite size, it is calculated from Figure 3(e) and depicted in Table III. It proves that they are nanoparticle and their size varies between 23 and 24 nm.

Mechanical properties

The tensile properties of the PVA composites, APC and PCA, are shown in Figure 4 which indicates the yield strength and toughness of PVA-based polymer composites. PVA composites are prepared with aluminosilicate, but APC and PCA contains PVA, PVP, and aluminosilicate. Though its composition is same different techniques were employed during composite preparation. In case of APC, PVA–PVP blend solution was prepared first then aluminosilicate was mixed with it, and cast the composite on glass mold whereas, in case of PCA, aluminosilicate was mixed with PVP solution first then stirred for 10 min and PVA solution was put to it, stirred for few minutes and cast the composite on glass mold (which does not show good strength properties).

It can be seen in Figure 4 that yield strength and tensile modulus both shows a highest peak at

10 wt % filler concentration with PVA composite and APC (PVA–PVP blend composite) as well. The increase of yield strength and tensile modulus properties of composite material is believed to be because of the aggregation of the filler particles. They increase with increase in filler content upto 10% filler level, then if we again increase the filler concentration, the filler particles will be stacked to each other and the matrix is found in sufficient to wet the particle equally and thus the modulus decreases.

Hardness

Hardness is one of the basic properties for characterizing polymer composites. The hardness (shore A) of the sample increases steadily with increasing filler concentration. It was found that all the composite shows steady increase of hardness with filler incorporation up to 5 wt % of filler addition, then the slope decreases steadily and again increases with higher amount of filler addition. The PVA composites always show higher hardness properties among these composites. This may be due to the incorporation of soft PVP molecules in the PVA–PVP blends. That makes some volume in between the PVA

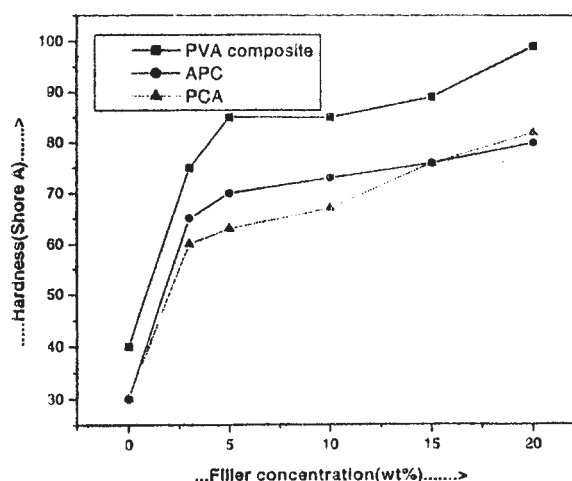


Figure 5 Variation of hardness with filler concentration.

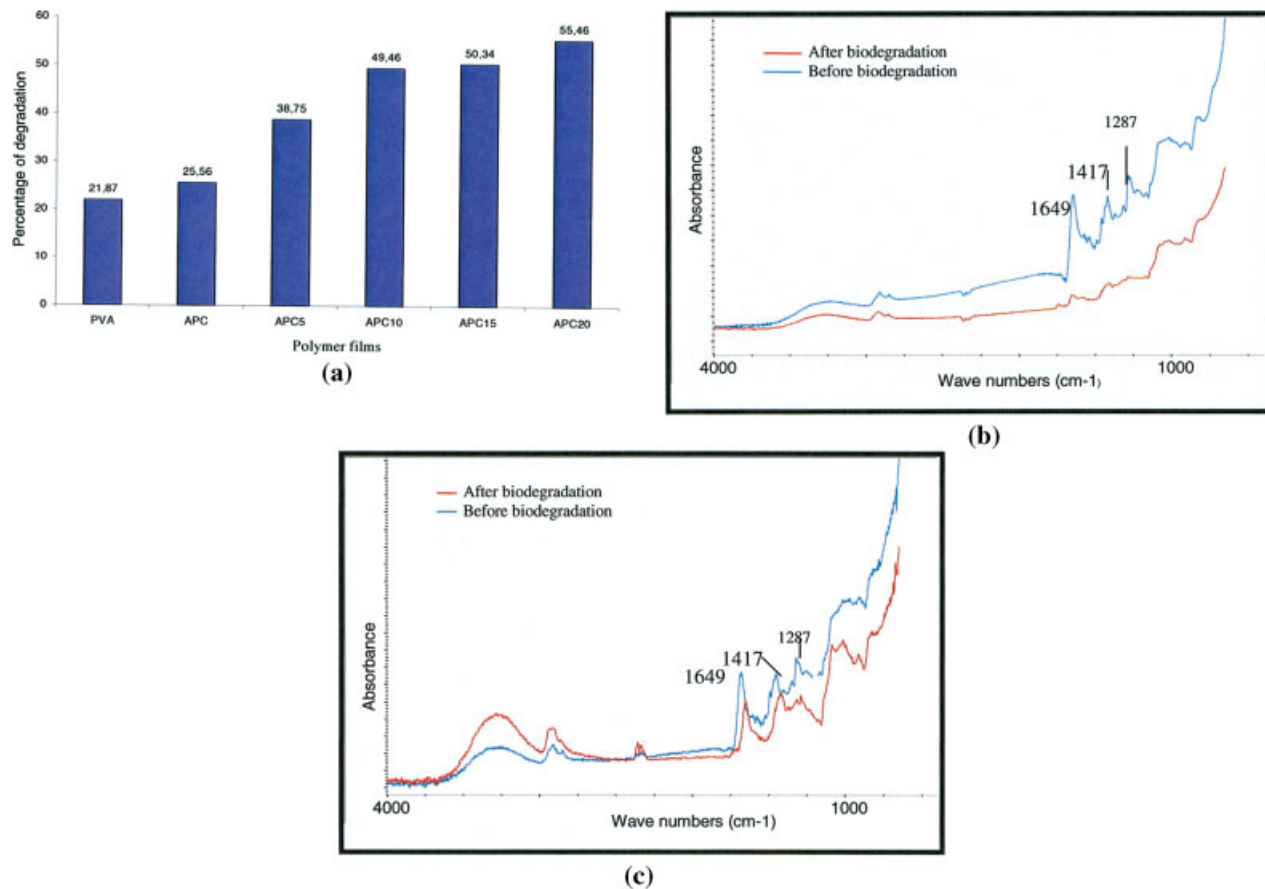


Figure 6 (a) Effect of filler on biodegradation of polymer composites; (b) IR spectra of APC 5, polymer composites; (c) IR spectra of APC 20, polymer composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chains and is then made hard. The variation of hardness with filler concentration is shown in Figure 5.

Biodegradability

As can be seen from Figure 6(a), the biodegradability of polymer film gradually increases from pure polymer (PVA), through polymer blend (APC) to polymer composites (APC 5–APC 20), i.e., the presence of clay material (aluminosilicate) enhances the biodegradability of polymer composites. The increase in percentage of biodegradation in composites indicate that the filler particles affect the properties of the matrix phase.

IR spectra of the samples with the lowest and highest concentration of the filler, APC 5 and APC 20 are shown in Figures 6(b) and 6(c). The observed changes in peak heights prove that the microorganisms present in the soil caused the samples degradation.

CONCLUSIONS

- PVA and PVP create blend easily (proved by FTIR).
- Aluminosilicate smoothly gets mixed with PVA and PVP blend (proved by FTIR).

- Aluminosilicate, an industrial waste from aluminum production, is a good source of inorganic filler for biodegradable (environment-friendly) polymer composites.
- Aluminosilicate improves the matrix quality and biodegradability of the material.
- Weight loss and IR spectra of the investigated biodegradable polymeric material prove that the microorganisms present in the soil cause degradation.

The research indicates that the aluminosilicate filled PVA–PVP composites is an improved, environment-friendly, biodegradable polymeric material.

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