

# Biodegradability of PMMA Blends with Some Cellulose Derivatives

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**Abstract** High polymer blends of Polymethyl methacrylate (PMMA) with cellulose acetate (CA) and Cellulose acetate phthalate (CAP) of varying blend compositions have been prepared to study their biodegradation behavior and blend miscibility. Films of PMMA–CA, and PMMA–CAP blends have been prepared by solution casting using Acetone and Dimethyl formamide(DMF) as solvents respectively. Biodegradability of these blends has been studied by four different methods namely, soil burial test, enzymatic degradation, and degradation in phosphate buffer and activated sludge degradation followed by water absorption tests to support the degradation studies. Degradation analysis was done by weight loss method. The results of all the tests showed sufficient biodegradability of these blends. Degradability increased with the increase in CA and CAP content in the blend compositions. The miscibility of PMMA–CA and PMMA–CAP blends have been studied by solution viscometric and ultrasonic methods. The results obtained reveal that PMMA forms miscible blends with either CA or CAP in the entire composition range. Miscibility of the blends may be due to the formation of hydrogen bond between the carbonyl group of PMMA and the free hydroxyl group of CA and CAP.

**Keywords** Polymers · Blending · Biodegradation · Degradation tests · Miscibility

## Introduction

Biodegradable polymers are a newly emerging field. They are eco-friendly materials so that their disposal to the environment does not cause any pollution hazards. This class of polymers give significant contribution to waste management technologies and composting of organic materials. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have also been identified. Biodegradable polymers featuring ecological advantages for sustainable development have attracted great commercial interest because of growing environmental concerns [1]. In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions. As a result, attempts have been made to solve these problems by including biodegradability into these polymers in everyday use through slight modifications of their structures or blending them with biodegradable materials [2, 3].

The development of biodegradable polymer blend with an optimum balance of physical properties and biodegradable properties is of importance to relieve environmental problems like waste disposal. With this in view, as a part of our ongoing programme of studies of conducting and biodegradable polymers, several polymer blends based on Polymethylmethacrylate (PMMA) and Cellulose derivatives such as Cellulose Acetate (CA) and Cellulose Acetate Phthalate (CAP) have been prepared. The miscibility of these blends and their biodegradation behavior under different conditions has been investigated. The choice of blends of PMMA with CA and CAP in the present study is because of their pharmaceutical applications [4, 5]. PMMA is a versatile

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synthetic polymer with many user desired properties and hence finds enormous use in industrial applications and also in the pharmaceutical field as base material. CA and CAP being derivatives of natural polymer, cellulose, are expected to have good biodegradability. Therefore blends of these two materials are expected to exhibit both novel physical properties as well as biodegradability and can be used for various purposes like water repellent materials and a host of biomedical applications. Miscibility of the constituent polymers ensures that blend properties will compare favorably with those of the components. Polymers containing proton donor groups are found to miscible with those containing proton acceptor groups, due to specific interaction like hydrogen bonding [6]. The ester group or carbonyl group in PMMA can function as proton acceptor and the free hydroxyl group available in CAP or CA can act as a proton donor and therefore hydrogen bonding would contribute to specific interaction and hence miscibility in the final mixture.

## Experimental

The polymers used for the present study, namely PMMA, CA and CAP were obtained from commercial sources. The viscosity average molecular weight of PMMA, CA and CAP were 101,000, 75,000 70,000 grams per mole respectively. All other chemicals used were of analytical reagent grade. Double distilled water was used wherever required throughout the experiment.

### Miscibility Studies

The experimental techniques used in this work for characterizing blend miscibility were solution viscosity and ultrasonic velocity measurements of solutions [7–10].

### Viscosity Studies

2%(w/v) stock solutions of pure CAP and PMMA were prepared in DMF. Acetone is used as a common solvent for CA and PMMA blend preparation. Using these stock solutions, CAP/CA–PMMA polyblend solutions of varying compositions were prepared. Solutions of varying blend compositions in CAP/CA–PMMA were prepared using solvent DMF/Acetone. Viscosity measurements were made using Ubbelohde viscometer at 30°C with an accuracy of  $\pm 0.2\%$ . Temperature maintenance was done by using a thermostat. (Raaga Industries, Chennai.)

### Ultrasonic Studies

Poly blend solutions of different compositions were prepared as in the case of viscometric studies. Ultrasonic velocity of solutions were measured at 30°C using an ultrasonic interferometer. (Model M-81, Mittal Enterprises, Delhi) at a measuring frequency of 2 MHz. The accuracy of measurement was  $\pm 0.1\%$ .

FTIR Spectra of pure CA, CAP, 50:50 blends of PMMA–CA and PMMA–CAP were taken in a Thermo Nicolet Avatar 330 model FTIR spectrometer.

### Preparation of PMMA–CAP and PMMA–CA Polyblend films

Dimethyl formamide (DMF) was used as a common solvent for preparing polymer solutions of CAP and PMMA. Acetone was used as a common solvent for the preparation PMMA–CA polyblends. One gram each of the polymers was dissolved in 50 ml of DMF/Acetone each by magnetic stirring for one hour. The mixture was kept at room temperature. This gives 2%(w/v) stock solutions of PMMA and CAP/CA in DMF/Acetone. Calculated amounts of PMMA and CAP/CA stock solution were mixed in different ratio in a beaker to get varied PMMA, CAP/CA blend compositions. These solutions of blend compositions were stirred well by magnetic stirrer and allowed to stand for 30 min and then poured on to Petri dishes. The solvent was evaporated to dryness in hot air oven for 48 h at 75°C. The films were transparent and their thickness was about 0.2–0.4 mm and radii were in the order of about 1.5–2.5 cm. The films of blend compositions were then accurately weighed and subjected to different degradation tests. The degradation analysis was done by weight loss method.

### Biodegradation Studies [11–13] : Soil Burial Degradation

The soil used was obtained from N.I.T.K. garden. The soil was slightly acidic with a pH value of 6.7. The characteristics of the soil used were as follows; Class: Ultisol(loamy type), Electrical conductivity: 0.08 dS/m, Organic Carbon: 33 g/kg, CEC: 16.2 cmol/kg, Average Nitrogen: 151.4 mg/kg, Average Phosphorus: 5 mg/kg, Ex. K: 0.15 cmol/kg, Ex. Ca: 4.6 cmol/kg, Ex. Mg: 1.4 cmol/kg, Ex. Na: 0.2 cmol/kg. The polyblend films were buried in soil in desiccators. The soil was maintained at approximately 20% moisture weight. The desiccators were kept at room temperature and the average temperature during the study period was 30°C.

The films were taken out, washed with water, dried and weighed again accurately to know the degradation in the intervals of 10, 20 and 30 days. In the case of soil adhering to the blend films, the films were washed and extracted with DMF. The soil was then separated by filtration. The solvent from the filtrate was evaporated and the residue was dried to get a constant weight. A minimum of three separate tests per blend composition were made and the average value was considered. The test was reproducible within  $\pm 2\%$  error.

#### Degradation in Activated Sludge

Activated sludge in the form of slurry was obtained from nearby BASF plant. The sludge had the following characteristics; Mixed liquor suspended solids: 4000 mg/L, Liquid content: 45%, pH: 8.1, COD without biomass: 235 ppm, Color: 348 Hazen units, C: 52%, H: 07%, O: 22%, N: 16%, P: 1.2%, S: 1.7%. Fixed volumes of activated sludge solutions were taken in glass jars. The blend films were kept immersed in the solution and the solution was aerated intermittently by air bubbling using a pump, to keep aerobic condition. The films were removed from the sludge solution after 5, 10, 15 days, washed well with double distilled water and dried in a hot air oven at  $75^\circ\text{C}$  to perfect dryness and then weighed to obtain the degree of degradation. The test was reproducible within  $\pm 3\%$  error.

#### Enzymatic Degradation

In this test blend films were allowed to undergo degradation in buffer solution in the presence of an enzyme lipase from porcine pancreas. Phosphate buffer solutions of  $\text{pH} = 7.5$  were prepared by mixing known amounts of  $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  solutions in a fixed ratio. Buffered enzyme solution was prepared by adding a fixed amount of enzyme to these buffer solutions. Enzyme concentration used was 250 units per 10 ml. The weighed blend films were kept immersed in enzyme solution at room temperature ( $30^\circ\text{C}$ ) and were intermittently aerated. The films were removed after 1, 3, 5 days, washed well with water and dried in hot air oven to complete dryness and weighed. The error involved in this test was about  $\pm 3\%$ .

#### Hydrolytic Degradation in Buffer Solutions

The weighed blend films were kept immersed in phosphate buffer solution of  $\text{pH} = 7.5$  in a glass jar at room temperature ( $30^\circ\text{C}$ ). The buffer solutions were prepared by making use of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$

solutions. After designated time intervals (5, 10, 15 days) the films were removed well washed with water, dried and weighed. The test was reproducible within  $\pm 3\%$  error.

#### Water Absorption Test

The weighed blend films were kept immersed in water (Deionised water,  $\text{pH} = 7.2$ ) for 24 h at room temperature. Then the films were removed and the films surfaces were dried by pressing with a tissue paper and then weighed. The error involved in this test was about  $\pm 2\%$ .

## Results and Discussion

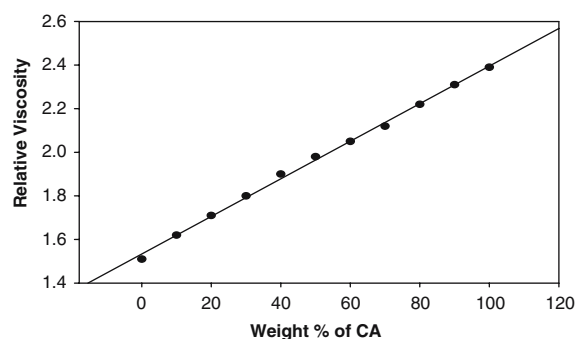
Several experimental and theoretical methods are commonly being used to characterize polymer compatibility. Several authors [7–9] have reported the use of viscometry and ultra sonic velocity measurements to characterize miscibility using solutions of various polymer blends including elastomers.

#### Viscosity Studies

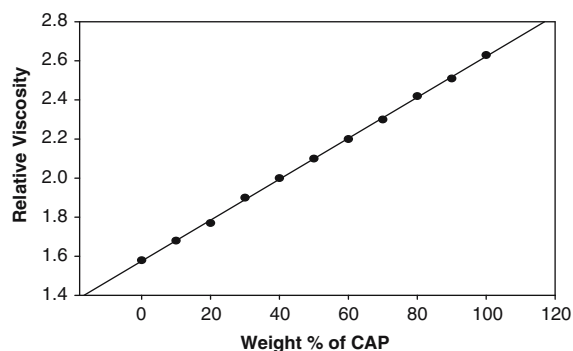
From viscometric measurements relative and reduced viscosities of homopolymers and their various blend compositions were determined. If  $\eta$  and  $\eta_0$  are the absolute viscosities of a solution and the pure solvent respectively and  $t$  and  $t_0$  are their compounding flow times, we have,

$$t/t_0 = \eta/\eta_0$$

the term  $\eta/\eta_0$  is known as relative viscosity. A plot of relative viscosity vs blend composition (Fig. 1 and 2) is found to be linear for the entire composition range, which is characteristic of a miscible blend system [14–19]. Further, Krigbaum and Wall interaction



**Fig. 1** Variation of relative viscosity with composition of PMMA –CA blends

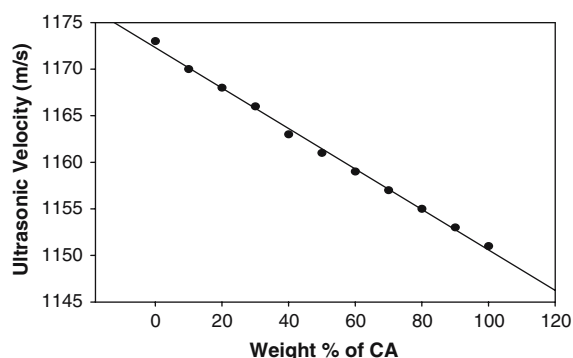


**Fig. 2** Variation of relative viscosity with composition of PMMA–CAP blends

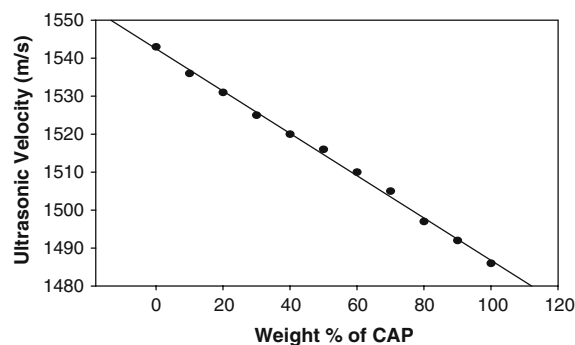
parameter ‘ $\Delta b$ ’ of the blends was determined following the literature methods [8, 15, 17]. The ‘ $\Delta b$ ’ values ranged from 0.018 to 0.03 and 0.01 to 0.028 for blend compositions of CA–PMMA and CAP–PMMA systems respectively, for decrease of CA/CAP composition in the blend from 70% to 30%. The positive value of ‘ $\Delta b$ ’ is indicative of miscibility. Miscibility of the blend system was further confirmed by calculating the heat of mixing for the blends [9, 20, 21]. The heats of mixing values ranged from 5 to 40 mJ for both the systems and are well below upper compatibility limit for all the compositions confirming the miscibility of the blends in all compositions [9].

#### Ultrasonic Studies

Ultrasonic velocity values of blend solutions have been determined. Ultrasonic velocities of the blend solution are plotted against blend compositions. (Fig. 3 and 4) and are found to be linear. For incompatible blend solutions ultrasonic velocity versus composition curve is non-linear showing distinct phase formation at intermediate compositions [14]. The investigations show that CAP/CA forms a miscible blend with PMMA in the entire composition range, presumably

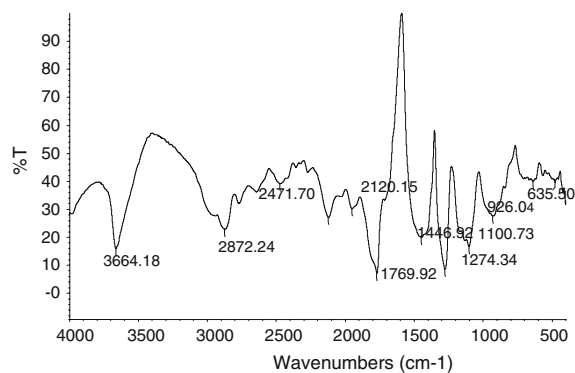


**Fig. 3** Variation of ultrasonic velocity with composition of PMMA–CA blends

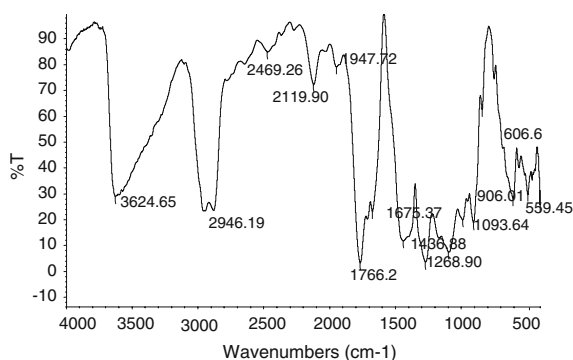


**Fig. 4** Variation of ultrasonic velocity with composition of PMMA–CAP blends

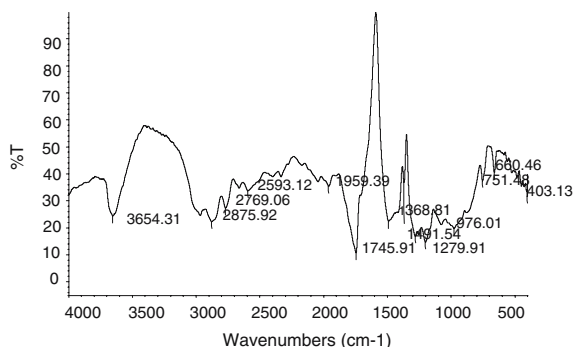
due to specific interactions between the two polymers. Compatibility in the system may be due to the formation of a hydrogen bond between the carbonyl group of PMMA and the free hydroxyl group of CAP/CA. In order to have further evidence on the existence of hydrogen bond interaction in the blends, FTIR spectra of pure CA, CAP, 50:50 blends of CA and CAP with PMMA were recorded at room temperature. The formation of aforementioned hydrogen bond between CA/CAP and PMMA is expected to weaken the strength of carbonyl bond in CA/CAP and shift its stretching vibration to lower frequencies [22, 23]. The carbonyl peak will remain unaffected in the blends of esters with no interaction [9]. The blending of CA with PMMA has shifted its carbonyl stretching vibration from  $1770\text{ cm}^{-1}$  in the pure CA to  $1766\text{ cm}^{-1}$  in the 50:50 CA–PMMA blends. Further, a second band is also observed in the blend at  $1675\text{ cm}^{-1}$ , which can be assigned to hydrogen bonded CA carbonyl groups. Similarly the free OH stretching frequency band of CA at  $3664\text{ cm}^{-1}$  is also shifted to  $3625\text{ cm}^{-1}$  in the blend, confirming the formation of a hydrogen bond (Fig. 5 and 6). Similar results have also been observed for the blends of CAP and PMMA (Fig 7 and 8).



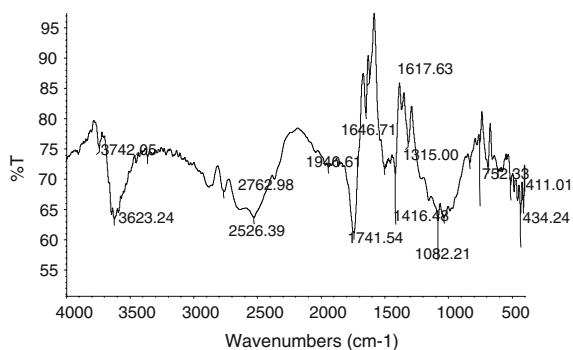
**Fig. 5** FTIR Spectra of Pure CA



**Fig. 6** FTIR Spectra of PMMA(50%):CA(50%) Blend



**Fig. 7** FTIR Spectra of Pure CAP



**Fig. 8** FTIR Spectra of 50%PMMA : 50% CAP Blend

**Biodegradation Studies**

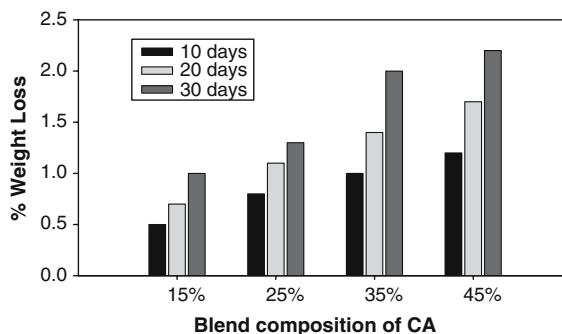
*Soil Burial Degradation*

A short-term study for a period of 30 days has been conducted on the soil degradation behavior of CAP/CA-PMMA blend films. Although long term studies are more useful in characterizing the soil degradation of matrices (e.g., for an year or two), the short term study does give an insight into the blend behavior and can be used for a rapid evaluation of biodegradability of polymers. In the present study the polyblends showed degradation of the order of about 0.5 to 2.5%.

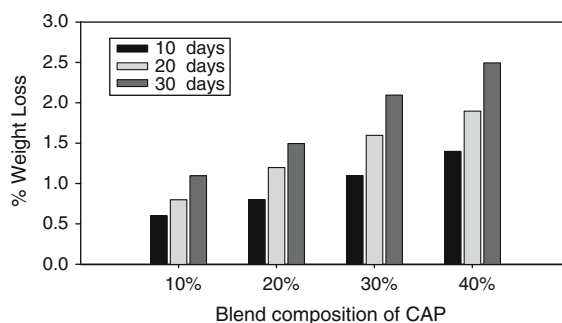
The blend with higher CA/CAP content showed maximum degradation (Fig. 9 and 10). The polymers exposed to soil might have initially undergone biodegradation, where microorganisms consume the natural cellulose component. Consequently the oxygen can attack the newly generated surface with the formation of peroxides, hydro peroxides, oxides etc., which promote the scission of polymeric chains into small fragments more susceptible to the attack of microorganisms [24, 25]. Soil bacteria and fungi might be responsible for the degradation [13].

*Enzymatic Degradation*

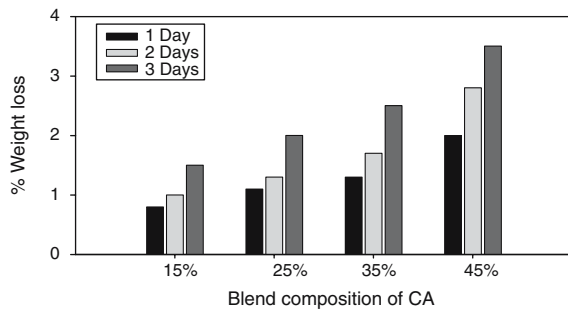
The enzymatic degradation of the polyblends films was tested by using lipase from porcine pancreas. The method is often used for rapidly evaluating the biodegradability of polymers, although it does not exactly reflect degradation under natural conditions. In the present study the degradation observed was about 0.8–4.0% for various blends (Fig.11 and 12). The extent of degradation in five days was almost comparable to that in buffer solution in fifteen days. Hence the contribution of enzymes was quite evident. As the test was conducted in phosphate buffer hydrolysis may be the initial degradation process followed by the enzymatic action.



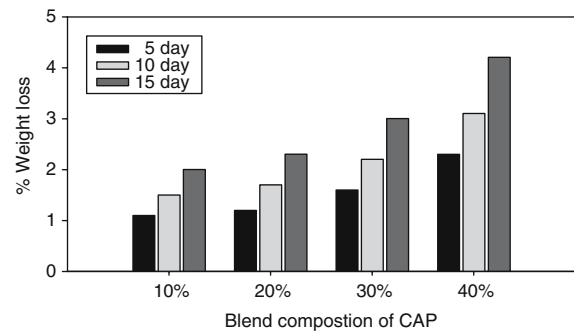
**Fig. 9** Degradation of PMMA-CA blends in soil



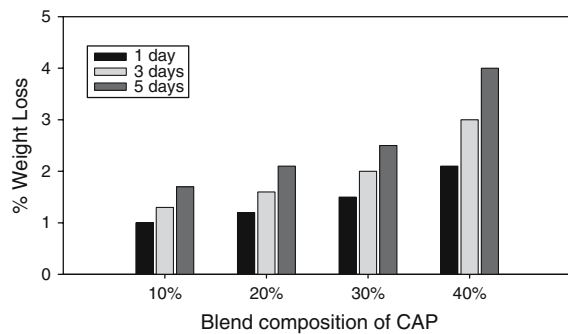
**Fig. 10** Degradation of PMMA-CAP blends in soil



**Fig. 11** Degradation of PMMA-CA blends in enzyme solutions



**Fig. 14** Degradation of PMMA-CAP blends in activated sludge



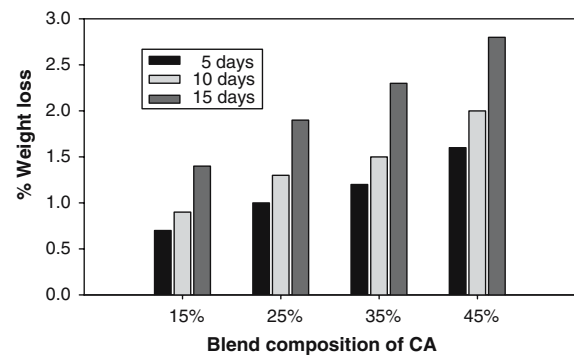
**Fig. 12** Degradation of PMMA-CAP blends in enzyme solution

### Hydrolytic Degradation in Phosphate Buffer Solutions

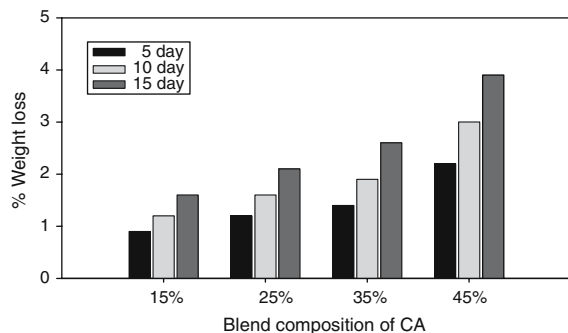
Polyblends films showed considerable degradation in phosphate buffer solutions. The degradation was found to be in the range of 0.7 to 3.2% for various blend compositions (Fig. 15 and 16). Even in this study also biodegradation was maximum in the case of blend having higher CA/CAP content. Both the constituents of blend films were esters, therefore hydrolysis could have been the major mode of degradation. The hydrolysis products of these polyesters would be, organic acids, methanol, cellulose, etc., are compounds

### Degradation in Activated Sludge

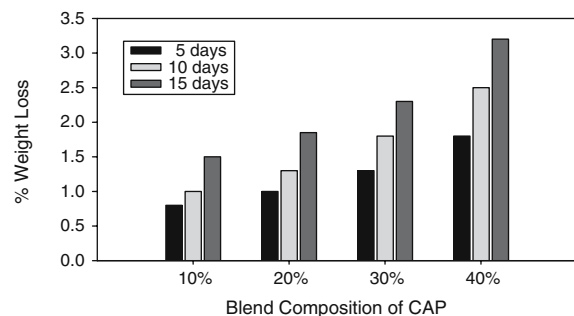
Degradation of the polyblends in the activated sludge was monitored for 15 days. The polymers showed sufficient degradation and the extent of degradation was 0.9 to 4.2%. The polymer blend with higher CA/CAP content degraded to the maximum extent (Fig. 13 and 14). Hydrolytic degradation as well as degradation by microorganisms might be responsible for the decay. The degradation of the blend films was higher in activated sludge compared to other tests. This may be due to the fact that in this test there is a combined effect of both hydrolysis and microbial attack [11, 12].



**Fig. 15** Degradation of PMMA-CA blends in buffer solution



**Fig. 13** Degradation of PMMA-CA blends in activated sludge



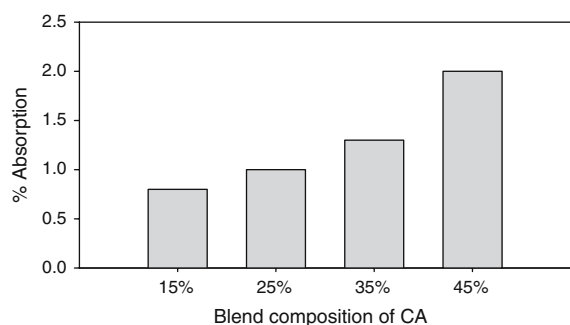
**Fig. 16** Degradation of PMMA-CAP blends in buffer solution

easily attacked by microorganisms to undergo further degradation. Hence hydrolysis followed by microbial degradation may be the path of degradation in buffer solutions [12].

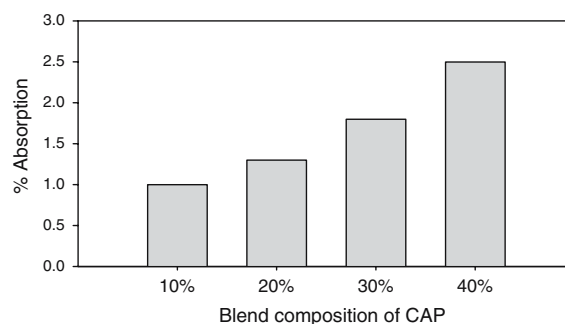
#### Water Absorption Test

Many polymers are susceptible to degradation due to the effect of water, particularly under favorable conditions. These include some naturally occurring polymers, principally condensation polymers such as polyesters and polyamides. Factors that influence the susceptibility of a given polymer to hydrolysis include water permeability and solubility which in turn are influenced by the chemical structure of polymer and its physical state. Autocatalysis of hydrolysis is possible if acidic or basic groups are produced by the polymer breakdown as in the case of polyesters which yield carboxylic acids upon hydrolysis.

The water absorption test is quite often used to indicate the tendency of polymers to undergo hydrolytic degradation [3, 13]. The polymers can absorb water, swell, undergo hydrolysis and subsequently will deteriorate in the environment. Higher tendency to absorb water may indicate higher hydrolytic degradation behavior. In the present investigation it is observed that the polymer blends have considerable hydrolytic degradation tendency. To have more evidence on this, water absorption tests have also been done on these poly blend films. The study showed that the blend with higher CA/CAP content has higher capacity of water absorption (Fig. 17 and 18). The extent of water absorption was 0.8% to 2.5% for various blends. The result is also in concordance with the observations in the previous tests, confirming the hydrolytic degradation tendency of the blend films.



**Fig. 17** Water absorption by PMMA–CA blends



**Fig. 18** Water absorption by PMMA–CAP blends

#### Conclusions

The observations in the present investigation show that CA/CAP forms miscible blends with PMMA in the entire composition range. The miscibility of the system may be due to the formation of a hydrogen bond between the carbonyl group of PMMA and the free hydroxyl group of CA/CAP.

The biodegradation tests conducted on selected polyblend films of CA/CAP–PMMA have shown that the blends are biodegradable. The results of all the tests in soil burial, enzymatic degradation, activated sludge degradation, degradation in buffer followed by water absorption tests indicated that, the polymer blends are all biodegradable and biodegradability increases with modified natural polymer CAP content, in agreement with the predictions and anticipations. A still higher CA/CAP content in the polymer blend (more than 45%) may definitely increase the biodegradability but at the same time can decrease other useful properties of PMMA.

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