Polymer Bulletin (2023) 80:5623–5639
https://doi.org/10.1007/s00289-022-04319-7

ORIGINAL PAPER

Enhancement and investigation of biodegradability of poly (methyl methacrylate) and poly (vinyl chloride) by blending with biodegradable polymer

Yethadka Narahari Sudhakar[1] · Muthu Selvakumar[1] · Denthaje Krishna Bhat[2]

Received: 26 June 2021 / Revised: 15 December 2021 / Accepted: 9 June 2022 /
Published online: 1 July 2022

Abstract

Presently, society needs an eco-friendlier alternative for non-biodegradable polymers, nonetheless, synthetic polymers have established the market because of cost and easy to manufacture. To address the challenge of reducing the lifetime of degradation of these polymers, the scope of blending natural biopolymers is effective. This paper focuses on confirming the effectiveness of biodegradation in the molecular level of polymer blends between synthetic polymers and biopolymers. The synthetic polymers such as poly (methyl methacrylate) (PMMA) and poly (vinyl chloride) (PVC) were blended with varying compositions of biodegradable cellulose acetate butyrate (CAB). Using dimethylformamide (DMF) the films of PMMA/CAB, PVC/CAB blends were prepared by the solution casting method. Four different methods for studying biodegradability of these blends, namely soil burial test, enzymatic degradation, activated sludge degradation followed by microbial degradation were performed. The confirmation of degradation was done by NMR, FTIR, and Gel Permeation Chromatography (GPC) studies. Moreover, degradation analyses were determined by the weight loss method. Sufficient biodegradability was shown with an increase in CAB content in the blend. This work provides an approach for bringing about the degradation of synthetic polymers without much compromise on their properties. Also, the type of microorganisms that effectively degrades these polymer bends can be known.

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

✉ Muthu Selvakumar
chemselva78@gmail.com

[1] Department of Chemistry, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

[2] Department of Chemistry, National Institute of Technology, Surathkal, Srinivasnagar-57, Mangalore, Karnataka, India

Introduction

Common polymers like polypropylene, PMMA, PVC, polyethylene are extensively used, and reusing or recycling them is a serious task. Even their composites add on to the non-biodegradable wastes throughout the world. The alternative is the use of biodegradable polymers which mainly originates from renewable sources. However, their properties of brittleness, low thermal stability, water vapor permeability, and uncontrolled molecular weight are the main challenges that are yet to be overcome when compared to synthetic polymers. Moreover, there are no single biodegradable polymers that can be used as such in applications such as carry bags, biomedical, and food packages. Therefore, it is desirable to modify existing synthetic polymers by blending with a wide range of biopolymers, fillers and bring about enhanced degradation [1]. Some researchers have attempted for preparing these kinds of composite polymers by blending biopolymers with synthetic polymers [2–4]. Optimum balancing of physical and biodegradation properties of biopolymer/synthetic polymer blends will minimize the waste disposal problems. Biopolymer nanocomposites have a scope in industrial sectors as it is easy to process and have slightly greater biodegradation property [1]. Cellulose is a biopolymer that is found in abundance in wood and bacterial origin. Untreated cellulose behaves as a thermosetting polymer and has less solubility. On the other hand, cellulose derivatives are thermoplastics in nature and easy to process which makes them blend with synthetic polymers. Most of the cellulose derivatives are readily biodegradable by microorganisms that utilize cellulose enzymes, but due to the additional acetyl groups cellulose requires the presence of esterases. Thereby, the blending of the CAB may induce biodegradation in the synthetic polymer. PMMA a versatile synthetic polymer has enormous useful properties required in industrial and pharmaceutical applications. The literature survey on PMMA/Cellulose shows that a higher concentration of cellulose improves the bonding within them. PMMA/Cellulose blends [5] were subjected to dynamic mechanical analysis showed greater interaction at a high concentration of cellulose with PMMA. The nanocomposites with PMMA molecules covalently grafted to cellulose exhibited much higher optical transparency, thermal stability, and hygro-mechanical properties than the control samples [6]. PMMA/2,2,6,6-tetramethylpiperidyl-1-oxyl oxidized CNFs (PMMA/TOCN) nanocomposites with high transparency, controllable birefringence, and enhanced mechanical properties exhibit great potential for applications in the optical devices and engineering field [7]. Porosity and stability can be seen in membranes based on CA/PMMA which was used for the separation of proteins and toxic heavy metals [8]. To effectively modify the synthetic polymer, a few grafted copolymers based on cellulose-g-PMMA were found to be more moisture resistant and also exhibited better chemical and thermal resistance [9]. Carboxymethyl cellulose-g-PMMA showed thermal stability better than that of PMMA [10]. Nevertheless, none of the literature discussed the biodegradation of these fibers/films. Hence, this paper focuses on the aspects of PMMA/CAB degradation. One more synthetic polymer PVC which is dominated in pipe and automobile industries is of major concern

as this polymer is non-degradable. The preparation of PVC and biopolymer composites is challenging and requires more study. Cellulose acetate (CA) and PVC nanofiber mats were electrospun into nanofibers which showed smooth fibers at 14% CA and solution concentration had a significant influence on the tensile strength of the nanofiber mats [11]. It was found that there are no biodegradable studies on PVC/cellulose derivative films. CAB as one of the biodegradable and biocompatible cellulose materials has attracted much attention in both academic and industrial fields ranging from a food packages, biomedical products, clothing to automotive materials [12]. Hence, this paper reports the preparation and degradation of PVC/CAB film in various standard conditions. Different ratios of films PMMA/CAB, PVC/CAB blends were prepared and characterized using chemical, spectroscopic, and chromatographic techniques. A comparison of the mode of degradation was made to understand the microbial degradation as well as the physical degradation of the polymer. This paper has been split into two parts, the first part shows biodegradation studies such as soil-burial, activated sludge, and enzyme-based methods using ASTM D6954, D5988, D5209-92, D5247-92 [13, 14]. In the second part, the degradation of polymer to smaller elements was monitored by microbial degradation method and verified using FTIR, NMR, GPC techniques [15, 16].

Materials and methods

PMMA, PVC, and CAB were obtained from commercial sources. The viscosity average molecular weight of PMMA, PVC, and CAB were 75,000, 101,000, 70,000 g mol^{-1}, respectively. Bushnell-Hass broth and Bushnell-Hass agar (BH, Hi-Media) were used as the medium. All other chemicals used were of analytical reagent grade.

Preparation of PMMA/CAB and PVC/CAB films

Dimethylformamide (DMF) was used as a common solvent for preparing polymer solutions of CAB and PMMA and the preparation of PVC/CAB polyblends. We have previously prepared synthetic/natural polymer blends and studied their biodegradability. The procedure is the same as Krishna et al. [14]. Briefly, 1 g of polymers was dissolved in 50 mL of DMF at ambient temperature and used as stock solutions. Composites were prepared by mixing different ratios of stock solutions. Mainly, CAB content were 0%, 30%, 50%, 70%, and 100% in PMMA/CAB and PVC/CAB blends. The solutions were stirred well for an hour and the solution was cast on the Petri dish. Films thicknesses ranging from 0.2–0.4 mm were obtained. Polarizing microscope (SDTECHS make) was used for analyzing the pure polymers and their interaction in blends.

Soil burial degradation study [17, 18]

As reported in the literature about the soil nature [14] the blend films were subjected to soil burial tests by maintaining 25% moisture weight. The films were taken out, washed with water, dried, and weighed in the intervals of 5, 10, and 15 days. In the case of soil adhering to the blend films after the tenth day, the films were washed and extracted with DMF. Using filtration, the soil was separated after evaporating the solvent residue. The experiment was repeated thrice and results were reproducible with ± 2% error.

Activated sludge degradation study

Activated sludge was provided by BASF Company. The characteristics of the sludge have been reported in [14]. Aeration was provided for jars containing fixed volumes of activated sludge and blend films. The degraded films were tested after 5, 10, 15 days after washing with distilled water and drying at 60 °C. The experiment was repeated thrice and results were within ± 3% error.

Enzymatic degradation study

The films were tested as reported in [14] using enzyme lipase from the porcine pancreas in buffer solution. The test was reproduced thrice with ± 3% error. Briefly, Bushnell-Hass agar (BH, Hi-Media) and Bushnell-Hass broth were used for detecting the biodegradation process. The pH of the medium was set to 7. The mixture of bacteria culture containing *Pseudomonas*, *Escherichia coli*, *Bacillus*, and *Klebsiella* was used in this study. Commercially available enzyme lipase was obtained from Hi-Media. As the sole carbon source about 10 mL of CAB, PMMA/CAB (30:70), PMMA/CAB (50:50), and PVC/CAB (30:70), solutions with control was taken in Erlenmeyer flasks and dissolved in dichloromethane (DCM). 50 ppm of mixed culture (*Pseudomonas*, *Escherichia coli*, *Bacillus*, *Klebsiella*) was inoculated. The test was carried as reported in [14]. After 30 days of the incubation period, the residual blend films were extracted with an equal volume of DCM. The resultant solute of polymer blends (about 1 µL) after evaporating the solvent was analyzed by using FTIR, (PerkinElmer, Paragon 500 model), NMR (Bruker 300 MHz, deuterated chloroform as solvent, and 20 µL of samples) and Gel Permeation Chromatography (GPC). Tetrahydrofuran (THF) was used as an eluent with a flow rate of 1 ml min^{-1} at 60 °C for GPC studies. The column was 3 × p1 gel 10 µm MIXED-B 300 × 7.5 mm with differential refractometer as detector and PI caliber GPC software. The preparation of samples was done by dissolving 1–2 mg ml^{-1} of blends and taking in a different aliquot of the eluent. 0.45 mm membrane was used to filter these solutions and 100 µL was injected for analysis.

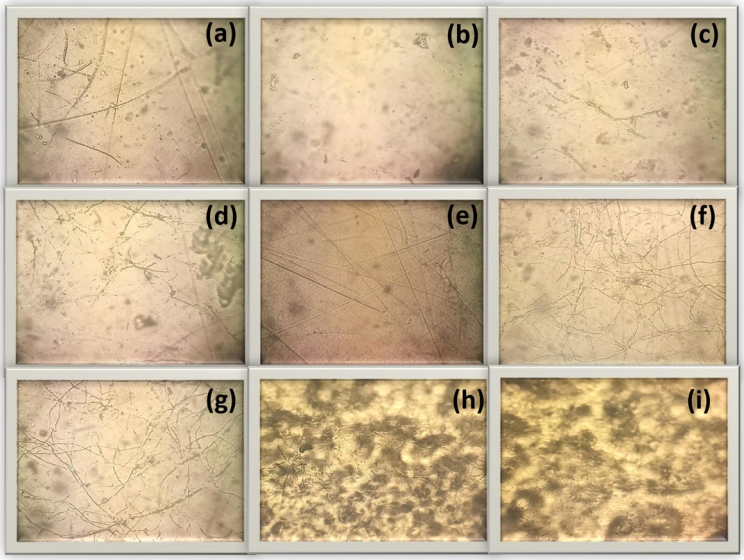


Fig. 1 Polarized optical micrograph of **a** PMMA, b PMMA/CAB (70:30), **b** (50:50), **c** (30:70), **e** PVC, **f** PVC/CAB (70:30), **g** (50:50), **h** (30:70), and CAB

Result and discussions

CAB was found to be miscible in both PVC and PMMA solutions [14] indicating CAB chains have specific interaction with PVC and PMMA. Figure 1 shows polarized optical micrograph of (a) PMMA, (b) PMMA/CAB (70:30), (b) (50:50), and (c) (30:70). With an increase in CAB content in the blend homogenous morphology was intact in all the blends wherein pure PMMA had a plane morphology while PMMA/CAB showed wrinkles at higher CAB content. In (e) PVC, (f) PVC/CAB (70:30), (g) (50:50), (h) (30:70), and CAB, the pure PVC had a clear morphology and with increasing CAB content more wrinkles were observed without losing the homogenous characteristics. The wrinkles may be caused due to miscible interaction between synthetic polymer and CAB. In CAB (i) the image shows wavy morphology wherein the film formed is not as smooth as its blends. So, due to the presence of miscibility between synthetic polymers and CAB, the films formed were uniform, had less crystalline region, and no spherulites regions.

Soil burial degradation

Soil degradation test of PMMA/CAB blend films showed 0.3 to 2.95% of degradation order, while the PVC/CAB blend films comparative less as 2.4% as seen in Fig. 2a and b. It is visible that 100% CAB had shown more degradation than other blends. The polymers exposed to soil might have initially experienced

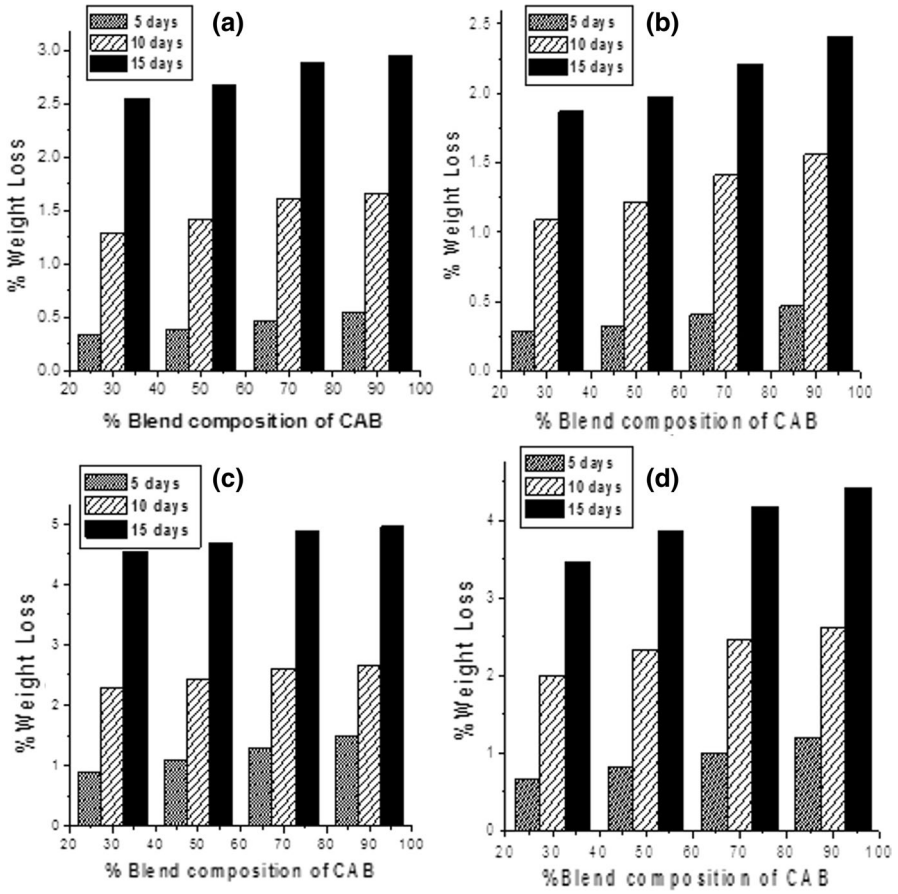


Fig. 2 Soil-burial degradation **a** PMMA/CAB, **b** PVC/CAB; Enzyme degradation **c** PMMA/CAB, **d** PVC/CAB

biodegradation, where microorganisms consume the natural cellulose component. Consequently, the oxygen can attack the newly generated surface with the formation of peroxides, hydroperoxides, oxides, etc., which promote the scission of PMMA and PVC polymeric chains into small fragments. These chains are further susceptible to microorganism attacks [17, 18]. Soil bacteria and fungi might be responsible for biodegradation [19]. Moreover, introducing CAB (30%, 50%, 70%, and 100%) into PMMA and PVC showed an increase of almost 0.8% in the overall degradation of the blends. This suggests that CAB had a major role in initiating the biodegradation in the blend. Nevertheless, PVC/CAB weight loss is less as compared to pure CAB which suggests that the breakdown of PVC is quite difficult. It is noticeable that with an increase in days of the test, the biodegradation of each blend ratio increased up to 1% every 5^{th} day. This biodegradation might be due to bacteria and fungi present in the soil [19].

Enzymatic degradation

In the presence of phosphate buffer, the blends are initially hydrolyzed and then followed by enzymatic degradation. Lipase from porcine pancreas under a controlled environment was able to degrade about 0.9–4.95% for PMMA/CAB blend and 0.6–4.42% for PVC/CAB blends (Fig. 2c and d). Within fifteen days, the blends showed biodegradation to an extent similar to 100% CAB. Therefore, enzymes have a major contribution to the biodegradation of the blends. However, the pure PMMA lost 0.4 mg and PVC lost 0.03 mg of weight after fifteen days of estimation period.

Degradation in activated sludge

The blends subjected to activated sludge for 15 days showed degradation of about 1.1 to 5.21% for PMMA/CAB blends and 0.9 to 4.87% for PVC/CAB blends.

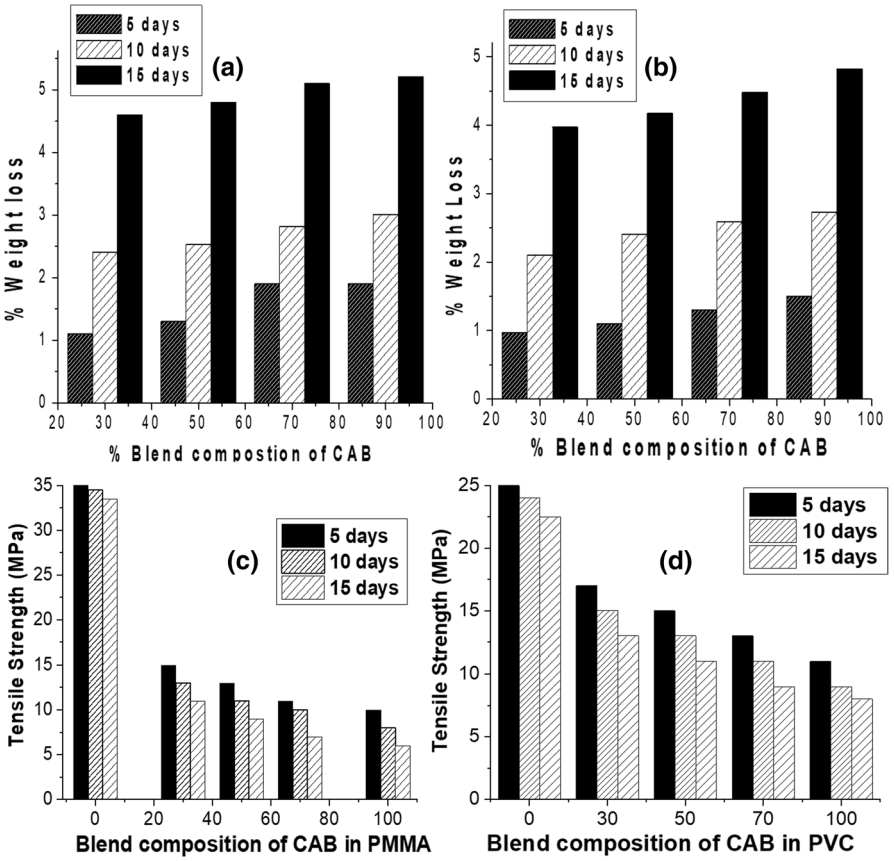


Fig. 3 Activated sludge degradation **a** PMMA/CAB, **b** PVC/CAB; tensile properties **c** PMMA/CAB, **d** PVC/CAB

The activated sludge method involves the use of rich inoculated biodegrading microbes and constant stirring with sufficient aeration. The polymer blend with higher CAB content showed maximum degradation (Fig. 3a and b). The results comparatively showed higher degradation than any other methods under study. Moreover, there is a notable increase of 2% in weight loss percentage compared to the soil degradation method. This strongly suggests that the combined effect of microbes and hydrolysis enhanced the biodegradation of PMMA/CAB and PVC/CAB blends. The pure PMMA lost 0.8 mg while PVC lost 0.2 mg of weight in this analysis. Nonetheless, the sign of the impact of hydrolysis on blend shows that the CAB is bleaching out of the intramolecular network, thereby exposing synthetic polymer strands vulnerable to microbes and other means of degradation [20, 21].

Tensile properties

Figures 3c and 3d show the tensile properties of PMMA/CAB, PVC/CAB blend films along with pure PMMA, PVC, and CAB as examined for different days. The tensile strength of the blend films decreased with increasing days of biodegradation. This result aids the concept of biodegradation of the synthetic polymers in the presence of CAB. Additionally, the presence of CAB was not able to show a major setback as there was a marginal decrease by 2 MPa in tensile strength within the blend systems. However, pure PMMA being elastic in nature showed around 20 MPa difference from its blends. Whilst, pure PVC showed tensile strength increase of 8 Mpa than its blend (30:70). This indicates that PVC/CAB have almost retained their property as similar as pure synthetic polymers. This can certainly find its application in the packaging industry.

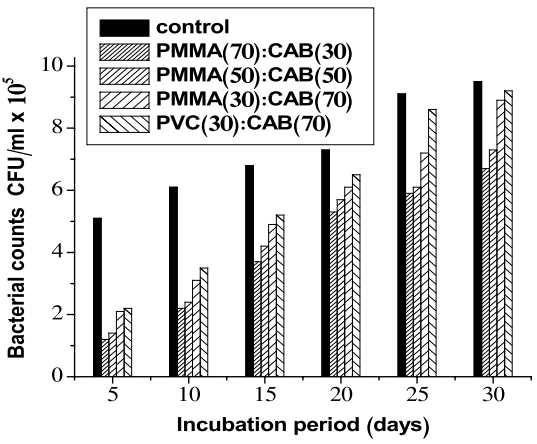
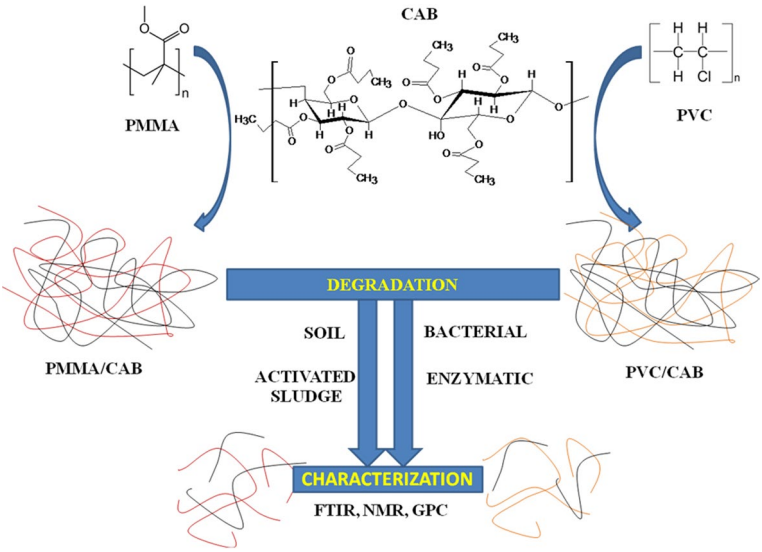


Fig. 4 Bacterial growth chart, Control: without polymer blend film, PMMA/CAB (70:30), PMMA/CAB (50:50), PMMA/CAB (30:70), PVC/CAB (30:70)



Scheme 1. Preparation and biodegradation investigation of polymer blends

Enumeration of bacteria during degradation

The control and test samples containing polymer blends were examined at intervals of five days for 30 days (Fig. 4). The bacteria recovery in control showed exponential growth than test samples. The bacterial count was about 5.1×10^5 CFU/mL for control on the fifth day while test samples remained below $2.1 \times 10.^5$ CFU/mL. A gradual increase in bacterial count in test samples was noticed with an increase in the number of days. Killing efficiency between the test sample and control showed no significant difference. This indicates that the blend polymer is comparatively stable up to fifteen days, thereafter the bacterial count increased due to the regeneration capability of bacteria. Even significant changes in the pH of the test solutions were observed. The initial pH value of 7.0 ± 0.2 was reduced to 6.8 in 30:70 (PMMA/CAB) systems. Similar results were obtained for PVC/CAB blends. *Pseudomonas* and *Bacillus* would be the main reason for the biodegradation of PVC [22]

Enumeration of the enzyme during degradation

The BH medium was taken in five sets of Erlenmeyer flasks and commercially available enzyme lipase was used for the efficiency studies. 250 mL of BH medium + 250 units per 10 mL of lipase was dissolved in phosphate buffer. The bacterial count was done at a regular interval of five days. While comparing the enumeration of bacterial studies with the enumeration of the enzyme studies

both showed a similar increase in the bacterial count with an increase in exposed days. Nevertheless, the lipase enzyme attacks the ester bonds of CAB wherein the products formed to interact with PVC/PMMA chains to either liberate chlorine from PVC or peroxides from PMMA. This breakdown of long chains into smaller chains exposes the vulnerable function group in polymers and hence, boosting the bacteria growth. Moreover, the presence of hydrophobic regions in synthetic polymer provides a surface to effectively catalyze the ester bond linkage. The overall process pathway of enzyme and bacteria degradation of polymer blends is shown in scheme 1.

FTIR analysis of blend polymer degradation

FTIR spectra of pure CAB at different stages of degradation are shown in Fig. 5a. Before biodegradation the spectrum (a) shows the cellulose characteristic bands at 3484 cm^{-1}, 2984 cm^{-1} (C-H aliphatic stretch); 1743 cm^{-1} (C=O carbonyl group), 1092 cm^{-1} (C=O stretch for C–O–C alicyclic anhydride group); 911 cm^{-1} (C-H stretch for substituted benzene). Spectrum (b) for bacteria degradation, the characteristic bands at 3607 cm^{-1} (OH stretch); 2924 (C-H aliphatic stretch); 2111 (C-H aliphatic stretch); 1282 (C-O stretch for alicylic anhydride group), 787 (mono substituted benzene) diminished. Spectrum (c) for enzyme degradation, all

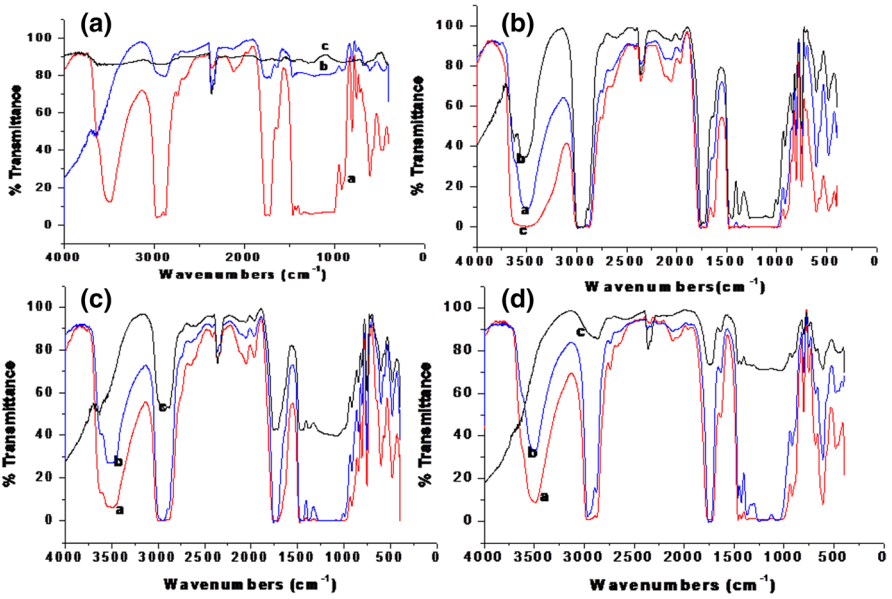


Fig. 5 FTIR spectra of **a** CAB (**a**) Before degradation (**b**) After 30 days of bacteria degradation (c) after 30 days of enzyme degradation; **b** PMMA/CAB (30:70) **a** Before degradation (**b**) After 30 days of bacteria degradation (**c**) After 30 days of enzyme degradation; **c** PMMA/CAB (50:50) (**a**) Before degradation (**b**) After 30 days of bacteria degradation (**c**) after 30 days of enzyme degradation; **d** PVC/CAB (30:70) (**a**) Before degradation (**b**) After 30 days of bacteria degradation (c) After 30 days enzyme of degradation

the characteristic stretching frequency showed less intensity indicating polymer has reduced to simpler elements [23, 24]. FTIR spectra of PMMA/CAB (30:70) at different stages of degradation are shown in Fig. 5b. Before biodegradation the spectrum (a) shows the characteristic bands at 3446 cm^{-1} (OH), 2936 (C-H aliphatic stretch), 1743 cm^{-1} (C=O carbonyl group), 1365 cm^{-1} (C-H for methyl group), 576 cm^{-1}, (C-H stretch for monosubstituted benzene). Spectrum (b) shows signs of degradation having the characteristic bands at 3421 cm^{-1} (OH), 2931 (C-H aliphatic stretch), 1743 cm^{-1} (C=O carbonyl group) reduced. The same diminishing of characterization stretching frequency in the spectrum (c) for enzyme degradation is observed. FTIR spectra of PMMA/CAB (50:50) at different stages of degradation are shown in Fig. 5c. Spectrum (a) shows the characteristic bands at 3471 cm^{-1} (OH), 2832 (C-H aliphatic stretch); 2017 cm^{-1} (C=O carbonyl group) 1741 cm^{-1} (C=O carbonyl group), 1446 cm^{-1} (C=C stretch in aromatic nuclei) 887 cm^{-1} (C-H stretch for substituted benzene). In spectrum (b) characteristic stretching frequency is diminished in 400 to 600 cm^{-1}. In enzymatic degradation spectrum (c), stretching frequency is observed but the intensity of the peak is less. This implies that the degradation has occurred in the blend film. FTIR spectra of PVC/CAB (30:70) at different stages of degradation are shown in Fig. 5d. Spectrum (a) shows the characteristic bands at 3495 cm^{-1} (OH), 2974 (C-H aliphatic stretch); 2104 cm^{-1} (C=O carbonyl group), 1756 cm^{-1} (C=O carbonyl group), 1408 cm^{-1} (C\=C stretch in aromatic nuclei) 887 $cm.^{-1}$ (C-H stretch for substituted benzene). Spectrum (b) shows the bacteria degradation wherein all the stretching frequency is in less intensity, whereas in enzyme degradation all the frequency is diminished [25]. Similar structural molecular changes have been observed by several researchers in polystyrene-starch blends [26]

^{1}H NMR analysis of blend polymer degradation

Table 1 shows the functional groups of the before and after biodegradable polymers, respectively. The ^{1}HNMR spectra of before and after degradation samples are shown in Fig. 6a for pure CAB, Fig. 6b for 30:70 PMMA/CAB, Fig. 6c for 50:50 PMMA/CAB, Fig. 6d for 30:70 PVC/CAB. PMMA is a proton acceptor polymer and CAB is a proton donor polymer and they are found to be miscible due to hydrogen bonding. Before degradation, as per the CAB structure point of view, four ester groups are present in the 6, 3, 2, and 7 positions. One more ester group is formed due to blending with PMMA. These ester groups show multiple peaks between 0.10 to 2.5 ppm. The CH_2 aliphatic protons can be observed between 2.19 and 2.29 ppm. Another acetylenic proton peak is observed between 2.19 and 2.29 ppm. The aliphatic methylene (CH_2) peaks are noticed at 1.1 and 1.6 ppm and the methyl protons peaks are observed at 0.86 ppm. The peak at 3.5 ppm is due to vinyl compounds [13, 16, 24, 25]. After 15 days of biodegradation, plenty of small peaks is observed in the region of 1.5 to 5, because of the breakage of long-chain polymers and hydrolytic degradation of esters into CO_2 and H_2O.

Table 1 NMR Chemical shift values of before and after degradation of polymer blends

Compound	Position	δ (ppm) Before degradation	δ (ppm) After degradation	Remarks
A	7	3.7	2.3	Due to the splitting of carbonyl compounds, CH_3, CH_2, C=C the 3–5 small peaks are observed. + +
Pure CAB	6	2.0	2.2	
	2	1.9	1.2	
	3	1.9	1.7	
	$-CH_3$	0.9–1.2	0.9–1.2	
B	7	3.7	2.3	Due to the splitting of carbonyl compounds, CH_3, CH_2, C=C the 3–5 small peaks are observed
PMMA/CAB (30:70)	6	2.0	2.2	
	2	1.9	1.2	
	3	1.9	1.7	
	$-CH_3$	0.9 – 1.2	0.9 – 1.2	
C	7	3.7	2.3	Due to the splitting of carbonyl compounds, CH_3, CH_2, C=C the 3–5 small peaks are observed
PMMA/CAB (50:50)				
D	7	3.7	2.3	Due to the splitting of carbonyl compounds, CH_3, CH_2, C=C the 3–5 small peaks are observed
PVC/CAB (30:70)	6	2.0	2.2	
	2	1.0	1.2	
	3	1.4	1.7	
	$-CH_3$	0.9 – 1.2	0.9 – 1.2	
E	7	3.7	5.0	Due to the splitting of carbonyl compounds, CH_3, CH_2, C=C the 3–5 small peaks are observed
PVC/CAB (50:50)	6	2.0	3.7	
	2	1.0	2.0	
	3	1.4	1.0	
	$-CH_3$	0.9 – 1.2	1.4	
			0.9–1.2	

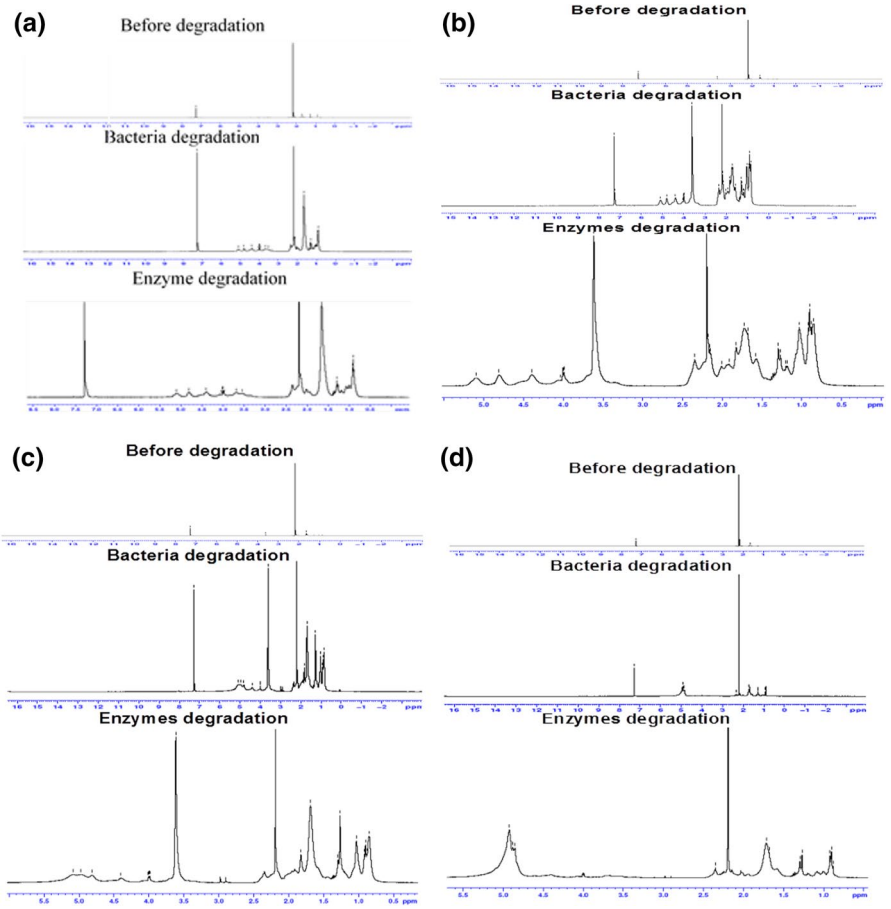


Fig. 6 NMR spectra of **a** CAB (**a**) Before degradation (**b**) After 30 days of bacteria degradation (**c**) after 30 days of enzyme degradation; **b** PMMA/CAB (30:70) (**a**) Before degradation (**b**) After 30 days of bacteria degradation (**c**) After 30 days of enzyme degradation; (5) PMMA/CAB (50:50) **a** Before degradation (**b**) After 30 days of bacteria degradation (**c**) after 30 days of enzyme degradation; **d** PVC/CAB (30:70) **a** Before degradation (**b**) After 30 days of bacteria degradation (**c**) After 30 days enzyme of degradation

GPC characterization

PEO/PEG standards were used to calibrate GPC [12] and molecular weights were calculated before and after bacterial degradation are shown in Table 2. The blend film containing high CAB showed greater degradation as observed in molecular weight. Figure 7a–d shows GPC response of PMMA/CAB (30:70), PVC/CAB (30:70), PMMA/CAB (50:50), and PVC/CAB (30:70), respectively. The decrease in molecular weight shown in spectral data matched with NMR and FTIR studies. Thus, it implies that biodegradability increases when synthetic polymers are modified using natural polymers like CAB. In the enzymatic degradation study,

Table 2 GPC characterization and molecular weight values of before and after degradation of polymer blends

Sample	Molecular weight before degradation	Molecular weight after degradation	Difference
A (CAB)			
Peak 1	92,186	77,993	14,193
Peak 2	6421	5238	1065
B PMMA/CAB (50:50)			
Peak 1	92,462	84,791	7491
Peak 2	6473	5900	573
C PMMA/CAB (30:70)			
Peak 1	92,186	80,910	11,276
Peak 2	6421	5477	944
D PVC/CAB (50:50)			
Peak 1	85,878	79,176	6702
Peak 2	6475	5574	905
E PVC/CAB (30:70)			
Peak 1	99,440	78,348	21,092
Peak 2	6271	5639	632

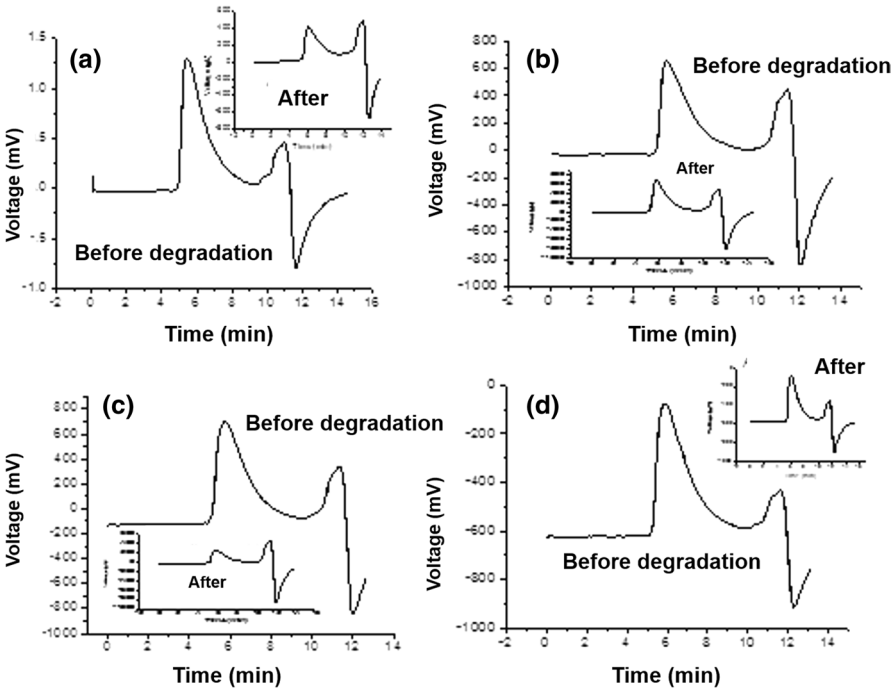
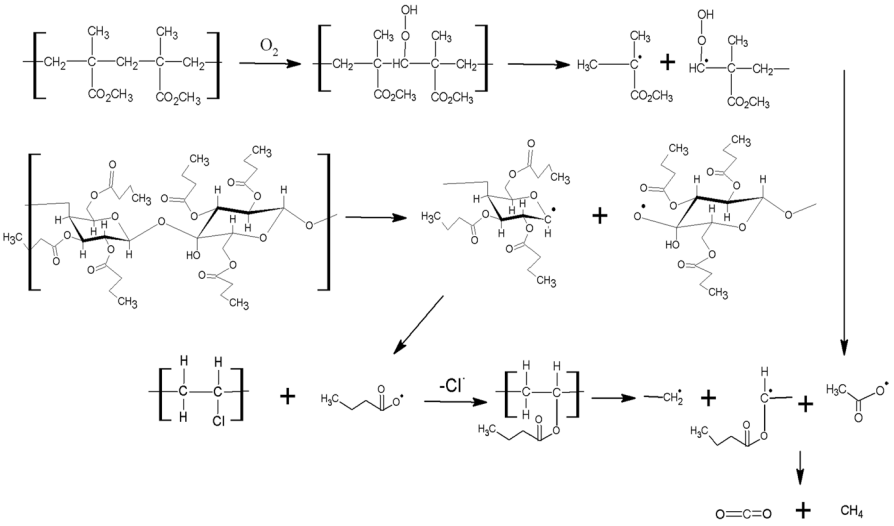


Fig. 7 GPC spectrum of **a** CAB **a** Before degradation **b** After 30 days of bacteria degradation; **b** PMMA/CAB (30:70) (**a**) Before degradation (**b**) After 30 days of bacteria degradation; **c** PMMA/CAB (50:50) (**a**) Before degradation (**b**) After 30 days of bacteria degradation; **d** PVC/CAB (30:70) (**a**) Before degradation (**b**) After 30 days of bacteria degradation



Scheme 2. Probable mechanism of degradation pathway of PMMA/CAB and PVC/CAB blends in bacterial and enzymatic conditions

the presence of CAB polymer chains as intermolecular network with PMMA and PVC demonstrated enhanced polymer degradation as enzymes were not only able to hydrolyze surface but also able to penetrate the matrix. Microplastics are yet another problem polluting coastal and marine habitats [27, 28]. Because of enhanced degradation in these synthetic polymers in our blend polymers, the generation of microplastics is minimized. As performed as per ASTM methods [29–33], we propose a probable mechanism of degradation of PMMA and PVC in the presence of CAB in Scheme 2. The CAB being vulnerable to microbial attack starts degrading first which generates peroxides and hydroperoxides groups on PMMA and PVC. These peroxides groups cleave the carbon backbone of the synthetic polymers. These smaller fragments further undergo depolymerization to give carboxylic end groups and finally carbon dioxide and water. The extent of 4–5% weight loss in a matter of 15 days is remarkable as pure synthetic polymer takes 100 years for the same. In PVC/CAB blends, the major degradation may be due to CAB rather than PVC, as observed in FTIR and NMR studies. But the formation of ester groups in NMR studies suggests that the dechlorination is promoted to some extent in the presence of CAB. Nonetheless, these synthetic polymers need organic solvents for extraction and analysis at the starting analysis stages, which later were soluble in water indicating the breakdown of long chains into smaller fragments.

Conclusion

The problem of the least understood biodegradation of synthetic polymer when blended with natural polymer is addressed in this paper. The weight loss, bacterial, enzymatic methods were used to study biodegradation of blend polymers. The

results obtained from FTIR, NMR, and GPC indicated a positive response for biodegradation of blend films in which the content of CAB is more. Moreover, pure CAB partially degraded probably because the reduced number of free hydroxyls enhanced the interaction with water and inhibited enzymatic hydrolysis. While, in a less water-containing solid culture medium, synthetic polymer blended CAB showed biodegradation.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal.

References

1. Bari SS, Chatterjee A, Mishra S (2016) Biodegradable polymer nanocomposites: An overview. Polym Rev 56(2):287–328
2. Kweon DK, Cha DS, Park HJ, Lim ST (2000) Starch-g-polycaprolactone copolymerization using diisocyanate intermediates and thermal characteristics of the copolymers. J Appl Polym Sci 78:986
3. Albertsson CA, Ljungquist O (1998) Degradable polyesters as biomaterials. Acta Polym 39:95
4. Tudorachi N, Cascaval NC, Rusu M (2000) Biodegradable polymer blends based on polyethylene and natural polymers degradation in soil. J Polym Eng 20:287
5. Merenga AS, Katana GA (2010) Dynamic mechanical analysis of PMMA-cellulose blends. Int J Polym Mater 60(2):115–123
6. Boujemaoui A, Ansari F, Berglund LA (2019) Nanostructural effects in high cellulose content thermoplastic nanocomposites with a covalently grafted cellulose-poly (methyl methacrylate) interface. Biomacromol 20:598–607
7. Huang T, Kuboyama K, Fukuzumi H, Toshiaki O (2018) PMMA/TEMPO-oxidized cellulose nanofiber nanocomposite with improved mechanical properties, high transparency and tunable birefringence. Cellulose 25:2393–2403
8. Vidya S, Mohan D (2010) Application Studies of Cellulose Acetate and polymethylmethacrylate blend ultrafiltration membranes. Sep Sci Technolo 45(6):740–750
9. Thakur VK, Singha AS (2011) Rapid synthesis, characterization, and physicochemical analysis of biopolymer-based graft copolymers. Int J Polym Anal Ch 16(3):153–164
10. Fuqin H, Desheng X, Qingwen W, Bo S, Mo C (2013) Thermal properties of carboxymethylcellulose and methyl methacrylate graft copolymers. J Macromol Sci B 52(9):1242–1249
11. Tarus B, Fadel N (2016) Affaf Al-Oufy; magdi el-messiry, effect of polymer concentration on the morphology and mechanical characteristics of electrospun cellulose acetate and poly (vinyl chloride) nanofiber mats. Alex Eng J 55:2975–2984
12. Ye H, Owh C, Jiang S, Ng C, Wirawan D, Loh XJ (2016) A thixotropic polyglycerol sebacate-based supramolecular hydrogel as an injectable drug delivery matrix. Polymers 8:130
13. Marek K, Jacques L, Anne MD (2006) Biodegradation of polyethylene films with prooxidant additives. Chemoshpere 64:1243
14. Krishna BD, Selvakumar M (2006) Biodegradability of PMMA blends with some cellulose derivatives. J Polym Environ 14:385

15. Samion E, Dart KR, Dawkins CJ (1997) Preparation, characterization and biodegradation studies on cellulose acetates with varying degrees of substitution. Polymer 38:3045
16. Muthukumar N, Maruthamuthu S, Palaniswamy N (2007) Role of cationic and nonionic surfactants on biocidal efficiency in diesel-water interface. Colloids Surf B: Biointerfaces 57:152
17. Zhang L, Deng X, Zhao S, Huang Z (1997) Biodegradable polymer blends of poly (3-hydroxybutyrate) and hydroxyethyl cellulose acetate. Polymer 38:6001
18. Okada M, Yamada M, Yokoe M, Aoi K (2001) Biodegradable polymers based on renewable resources. V. Synthesis and biodegradation behavior of poly(ester amide)s composed of 1,4:3,6-dianhydro-D-glucitol, α-amino acid, and aliphatic dicarboxylic acid units. J Appl Polym Sci 81:2721
19. Chandra R, Rustgi R (1997) Biodegradation of maleated linear low-density polyethylene and starch blends. Polym Degrad Stab 56:185
20. Peanasky JS, Long JM, Wool RF (1991) Percolation effects in degradable polyethylene-starch blends. J Polym Sci Polym Phys Ed 18:565
21. Seidenstucker T, Fritz GH (1998) Innovative biodegradable materials based upon starch and thermoplastic poly (ester-urethane)(TPU). Polym Degrad Stab 59:279
22. Giacomucci L, Raddadi N, Soccio M, Lotti N, Fava F (2019) Polyvinyl chloride biodegradation by *Pseudomonas citronellolis* and *Bacillus flexus*. New Biotechnol 52:35–41
23. Hadjiev D, Dimitrov D, Martinov M, Sire O (2007) Enhancement of the biofilm formation on polymeric supports by surface conditioning. Enzyme Microb Technol 40:840
24. Goodlett WV, Dougherty TJ, Patton HW (1971) Characterization of cellulose acetates by nuclear magnetic resonance. J Polym Sci A: Polym Chem 9:155
25. Andrea C, Roberto S, Chiellini E (2002) Biodegradation of poly (vinyl alcohol) in selected mixed microbial culture and relevant culture filtrate. Polym Degrad Stab 75:447
26. Nikolic V, Sava V, Dusan A, Aleksander P (2013) (). Biodegradation of starch-graft-polystyrene and starch-graft-poly(methacrylic acid) copolymers in model river water. J Serb Chem Soc 78:1425–1441
27. Sharma S, Chatterjee S (2017) Microplastic pollution, a threat to marine ecosystem and human health: a short review. Environ Sci Pollut Res 24:21530–21547
28. Halina K, Krzysztof B, Andrzej PR (2005) Properties of Poly(vinyl chloride) Modified by Cellulose, Properties of Poly(vinyl chloride) Modified by Cellulose. Polym J 37:340–349
29. ASTM (American Society for Testing and Materials) (1993) Annual book of ASTM standards, vol. 08.03, vols. 5209–92, Philadelphia. Pennsylvania 1993:377–380
30. ASTM (American Society for Testing and Materials) (1993) Annual book of ASTM standards, vol. 08.03, D5210–92, Philadelphia. Pennsylvania 1993:381–384
31. ASTM (American Society for Testing and Materials) (1993) Annual book of ASTM standards, vol. 08.03, D5247–92, Philadelphia. Pennsylvania 1993:401–404
32. ASTM (American Society for Testing and Materials) (1993) Annual book of ASTM standards, vol. 08.03, D5271–92, Philadelphia. Pennsylvania 1993:411–416
33. ASTM (American Society for Testing and Materials) (1993) Annual book of ASTM standards, vol. 08.03, D5338–92, Philadelphia. Pennsylvania 1993:444–449