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A More Biodegradable Alternative to Flex Banners

Anala R

Plant Biotechnology Laboratory, Department of Biotechnology,
Cochin University of Science and Technology, Kochi, Kerala, India-682022

Abstract - Flex is the most common material used for advertisement displays, banners and labels. However, flex is chemically a mixture of completely synthetic polymers like polyvinyl chloride and polyester, which are non-biodegradable in nature. In the circumstance of growing public concern on the massive use of non-biodegradable materials, semi biodegradable alternatives are being tried for the purpose. While paper and cotton cloth have been proposed as alternatives for flex, both are unsuitable – paper is fragile and easily torn, cloth is absorbent resulting in spread of printing ink. The study presents the results of tests of degradability of cotton cloth coated on one side with acrylic emulsion to reduce absorption of ink compared with flex and uncoated cotton cloth. The effect of shake culture of the three materials for fifteen days with a consortium of bacterial strains known to secrete extracellular catabolic enzymes – ligninases, lipases, alkane hydroxylases, aromatic hydrocarbon ring cleaving oxygenases- was assessed by means of changes in average weight and tensile strength before and after biological treatment and FTIR to gauge the overall impact of the treatment. Decrease in weight as well as tensile strength was observed in all the three materials after biological treatment; the decrease in both due to bacterial enzymes was however the most significant in acrylic coated cotton cloth compared to the other two materials. A few new absorption peaks representing new bonds were identified in the IR absorption spectra in all of the three materials after treatment, besides deepening of the existing peaks. The study indicates that coating cotton cloth on one side with acrylic emulsion to improve printability renders it significantly more biodegradable than flex polymer in the presence of a suitable mixture of microbial enzymes.

Keywords: Flex, cotton cloth, acrylic emulsion, biodegradation, alternative.

I. INTRODUCTION

There has been considerable public concern on the use of non-biodegradable materials as components in signages, labels, graphic displays used for commercial as well as house hold purposes, as a result of which, actions have been taken to reduce synthetic flex boards by imposing ban on unauthorized flex boards, ban on synthetic flexes and encouragement of use of cotton banners.

The flexes are usually made of polyester and poly vinyl chloride with small amount of additives like plasticizers, which being non-biodegradable are burnt after its use in display. PVC, the major component, is an agent suspected to cause cancer [1] and its decomposition on burning releases, besides carbon dioxide, hydrogen chloride, benzene, phosgene and carbon monoxide which are toxic and/or carcinogenic gases [2, 3, 4]. PVC burns at around 350^0C which raises the temperature of the surroundings [4].

Use of natural materials like cotton is emphasized over synthetic materials but, the tendency of printing ink to spread on natural materials is considered a disadvantage. As an alternative, cotton cloth coated on one side with acrylic emulsion is suggested; the material should be more biodegradable compared to the currently used non-biodegradable flex. The work presented here involves testing of degradability of the proposed material and comparison with flex and the natural material, cotton cloth. The relative impact of biological treatment on a material determined by comparison with the same material not subjected to the treatment reveals the degree of biodegradability.

Degradation of a polymer owing to changes in its chemical structure like decrease in chain length, breakage of bonds and formation of new bonds is reflected in its physical properties such as tensile strength, elasticity, colour, etc. The chemical changes in any material can be detected by Fourier Transform Infrared Spectroscopy [5, 6] which gives information on the type of chemical bonds present in a material from the IR frequencies absorbed and the number of a particular bond from the intensity of the absorption [7]. The ultimate tensile strength is the maximum applied stress a material withstands before undergoing physical deformation and is an intrinsic property dependent the strength of the chemical bonds and the degree of cross linking between chains. Hence, any reduction in tensile strength of a polymeric material is due to failure of chemical bonds in it.[8] As any substance is degraded by physical, chemical or biological factors, bond cleavages occur resulting in subsequent removal of low molecular weight chains from the bulk of the material. If this loss is large enough, it can be detected weighing the bulk material. Weight loss and tensile strength have been used as criteria of biodegradation [9, 10].

II. MATERIALS AND METHODS

1. The three materials – the plastic flex, the degradable alternative cotton cloth and cotton cloth coated on one side with acrylic emulsion (called AEC from here on) were provided by Ellora Picture Products, Perumbavoor, Ernakulam, Kerala. Sheets of the materials were cut in to rectangular pieces of 10 cm X 1.5 cm to be used as samples in the study.
2. Fifteen samples of each material were weighed and the average weight was recorded (‘Untreated control’ (UC) for weight loss). 5 pieces of each were kept aside for tensile strength testing before biological treatment (UC for tensile strength changes).
3. Five samples of each were put in to 100 ml Bushnell and Haas minimal salt medium (BHM) in a 250 ml conical flask to be used as the ‘treated control without bacterial consortium’ (TC). Another five pieces of each were put in to 100 ml BHM in a 250 ml conical flask and inoculated with 4 ml of bacterial consortium (‘treated sample with bacterial consortium’ (BTS)) known to produce extracellular enzymes *viz.* ligninases, alkane hydroxylases, lipases and aromatic hydrocarbon cleaving oxygenases. The mixed culture was prepared by mixing together 1 ml of 24 hour Nutrient broth cultures (37^0 C, 120 rpm) of each of the 22 bacterial strains used.
4. The minimal salt medium with the materials to be tested as the sole carbon source for the bacterial consortium (BTS) and the treated control without bacterial consortium (TC) were shaken at 37^0C, 120 rpm for 15 days.
5. On the 16th day the samples were taken from the flasks, washed in 70 % ethanol and water to remove the bacterial biomass adhering to the samples and dried at room temperature.
6. After the treatment, the samples were weighed and the average weight (of TC and BTS) calculated for each material.
7. The ultimate tensile strength (UTS) of each of the materials was determined according to ‘Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension’ [11] with extensometer gauge length 60.00mm, width 14.00 mm and thickness 2.02 mm. Tensile tests were performed until failure and stress-strain curves were generated. The UTS was determined as the maximum stress reached during a test.
8. The average tensile strength and average weight of each of the materials (Untreated and treated controls and the biologically treated sample) were compared, graphs plotted with the average mean values and standard deviation (represented as error bars) and significance values calculated statistically by Welch corrected Unpaired t-test using SigmaPlot software.
9. To detect any qualitative evidence of degradation by the impact of all physical, chemical and biological factors in the experiment (the overall effect of agitation in aqueous medium of mineral salts and treatment with the bacterial consortium), FTIR spectra of the UC and the BTS samples of all the three materials were analyzed in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1} using Fourier Transform Infrared Spectrometer Model Thermo Nicolet, Avatar 370.

Note: All the bacterial strains used in the study have been isolated from various soil sources for their ability to grow on low density polyethylene powder as the sole source of carbon. The enzyme profile of each of the isolates has been obtained after replica plating on BHM medium containing either lignin (test for ligninolytic activity), tributyrin (test for lipolytic activity), hexadecane (activity of alkane hydroxylases) or xylene (test for aromatic hydrocarbon degradation) as the sole source of carbon, compared to their growth on BHM agar plate with no other carbon source. The strains were chosen as these enzymes could be expected to degrade the constituent polymers in the three materials. All the strains have been checked for cross inhibition by cross-streak method prior to use as consortium.

III. EXPERIMENTAL RESULTS

The average weight and average tensile strength of the untreated and treated controls and biologically treated samples of all the three materials were measured and the values are compared graphically in Figure 1 and 2 respectively.

***Cotton cloth**: Difference between UC and TC – extremely significant (p<0.0001), TC and BTS- not significant (p-0.2223); **AEC**: Difference between UC and TC – extremely significant (p<0.0001), TC and BTS- very significant (p-0.0014); **Flex**: Difference between UC and TC –not quite significant (p-0.0865), TC and BTS- not significant (p-0.4506).*

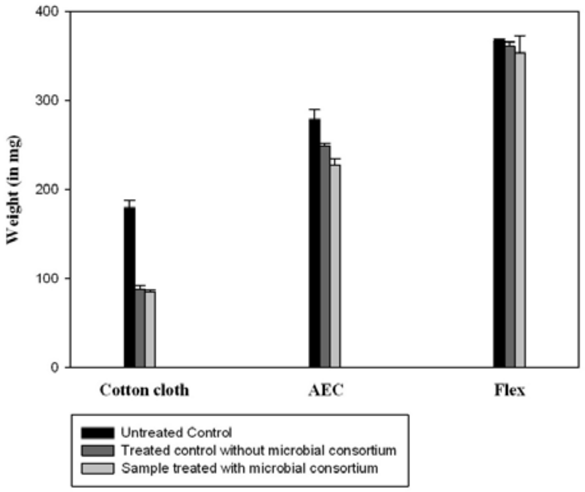


Fig. 1: Graph showing average weight of untreated, treated controls and biologically treated sample.

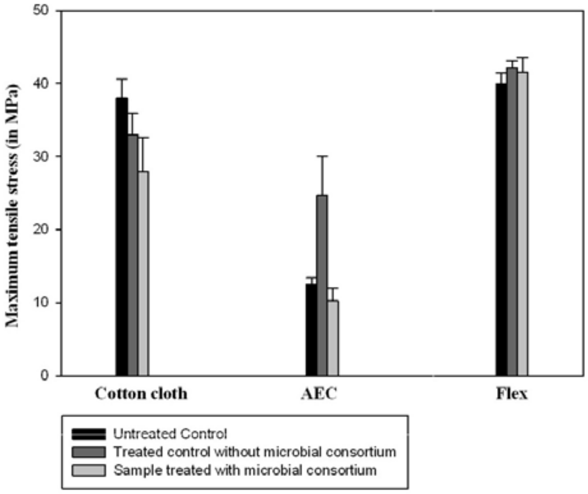


Fig. 2: Graph showing average tensile strength of untreated, treated controls and biologically treated sample.

***Cotton cloth**: Difference between UC and TC –significant (p-0.0235), TC and BTS- not quite significant (p-0.0859); **AEC**: Difference between UC and TC – very significant (p-0.0076), TC and BTS- very significant (p-0.0047); **Flex**: Difference between UC and TC –significant (p-0.0314), TC and BTS- not significant (p-0.5801).*

The difference in values of weight as well as in maximum tensile stress supported between the untreated and treated controls (UC and TC) represents the change brought about by the effect of solubility of components in the material or absorption of water by the same. On the other hand, the same differences between the TC and BTS represent the change effected as a result of bacterial action excluding that due to solubility/absorption effects of aqueous medium on the material.

Changes in weight

The TC of cotton cloth shows a significant decrease in weight from its UC (p-value<0.001) indicating that shaking the samples in the aqueous medium of salts itself renders it partially deteriorated. However, no significant reduction in weight occurred in the BTS compared to its TC (p-value=0.2223).

AEC also shows a significant decrease in weight of it TC compared to its UC (p-value<0.001) indicating that shaking the samples in the aqueous medium of salts itself renders it partially degraded owing to the solubility of the components of cotton cloth (additives like starch) and/or the acrylic emulsion coating over time under shaking conditions. The weight of the BTS shows a significant reduction from the TC (p-value=0.0014). This loss in weight is attributed to the action of the bacterial catabolic enzymes attacking the chemical bonds in the material.

The difference in weight of the TC flex and its UC is not quite significant (p-value= 0.0865); nor is the weight difference between its TC and BTS (p-value=0.4506).

Changes in maximum tensile stress supported

Except cotton cloth, the materials tested have improved in tensile strength upon shaking in aqueous medium of mineral salts. However, all materials show a decrease in the tensile strength by the effect of bacterial enzymes in addition to other conditions, the extent of which however varies.

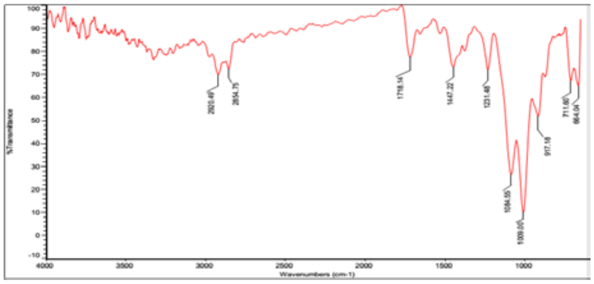
The TC of cotton cloth shows significant decrease in tensile strength from its UC (p=0.0235) probably owing to the loss of soluble components as a result of shaking in aqueous medium. However, the decrease in the same shown by BTS cotton cloth compared to its TC is not quite significant (p=0.0859) indicating that the bacterial consortium did not alter its chemical structure significantly.

The tensile strength of AEC shows a significant increase (p=0.0076) up on shaking in aqueous medium without bacteria. AEC is the only material to have decreased very significantly in terms of tensile strength upon incubation with the bacterial consortium excluding the effect of continuous shaking in mineral salt aqueous medium (p=0.0047), unlike even its parent material, cotton cloth which has failed to show a quite significant decrease by the same treatment. This indicates that the acrylic emulsion coat used in AEC is the component that is degraded as a result of incubation with the bacterial consortium.

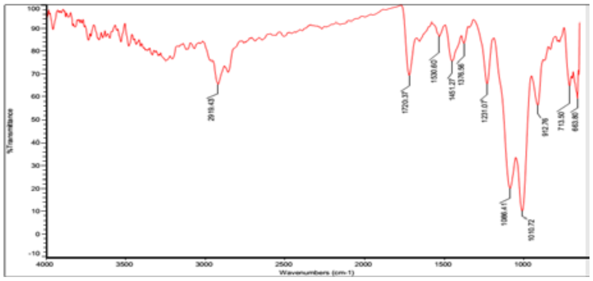
TC flex shows a significantly higher tensile strength compared to its UC (p=0.0314), whereas the decrease shown by BTS flex is not significant from its TC (p=0.5801).

FTIR spectra analysis

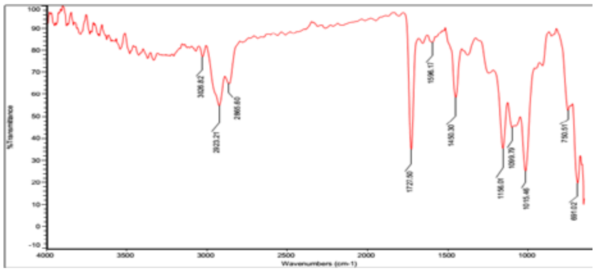
The FTIR absorption spectra of the untreated control and biologically treated samples of each of the three materials are shown in Figure 3. The major absorption bands in each of the samples are listed in tables 1-3.



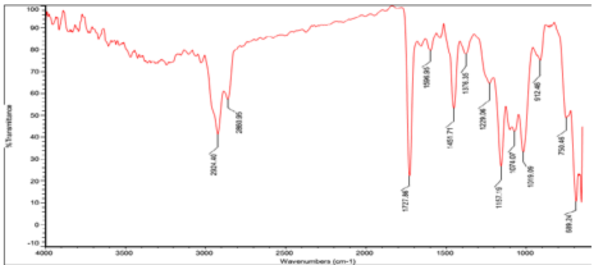
UC cotton cloth



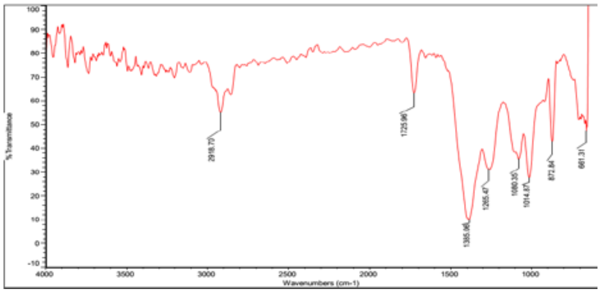
BTS cotton cloth



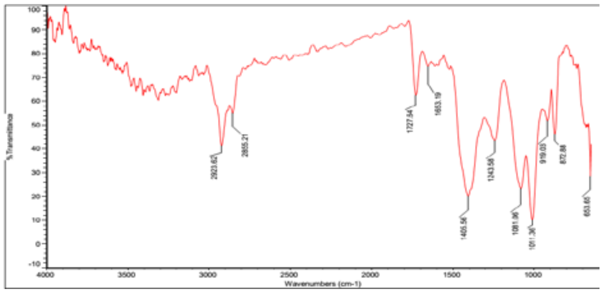
UC AEC



BTS AEC



UC flex



BTS flex

Fig. 3: FTIR spectra of untreated control and biologically treated samples

TABLE 1: MAJOR IR ABSORPTION BANDS SHOWN BY COTTON CLOTH

Control	Group if identified, interpretations	Treated	Group if identified, interpretations
2920.49	weak C-H stretch of tertiary carbon atom of aliphatic chain	2919.43	weak C-H stretch of tertiary carbon atom of aliphatic chain
2854.75	weak C-H stretch of tertiary carbon		

	atom of aliphatic chain		
1718.14	*	1720.37	*
		1530.60	*
1447.22	C-C stretch in aromatics Or CH$_2$ bend/ CH$_3$ bend	1451.27	C-C stretch in ring, aromatics Or CH2 bend/ CH3 bend
1231.48	*	1376.56	*
		1231.07	*
1084.55	C-O single bond stretch, ether	1086.41	C-O single bond stretch, ether
1009.00	C-O single bond stretch, ether	1010.72	C-O single bond stretch, ether
917.18	Methyl rock of isopropyl group	912.76	Methyl rock of isopropyl group
711.60	Out of plane C-H bending, aromatics	713.50	Out of plane C-H bending, aromatics
664.04	Out of plane C-H bending, aromatics	663.80	Out of plane C-H bending, aromatics

*indicates that the absorption peak has some ambiguity to interpret as either its frequency or strength does not match exactly with those in literature [12, 13, 14].

TABLE 2: MAJOR IR ABSORPTION BANDS SHOWN BY AEC

Control	**Group if identified, interpretations**	**Treated**	**Group if identified, interpretations**
3026.82	C-H stretch, alkene/aromatic	2924.40	C-H stretch, aromatic
2923.21	C-H stretch, aromatic		
2865.60	C-H stretch, aldehyde	2860.95	C-H stretch, aldehyde
1727.50	C=O stretch	1727.86	C=O stretch
1596.17	C-C partial double bond stretch, aromatic	1596.95	C-C partial double bond stretch, aromatic
1450.30	C-C stretch in ring, aromatic	1451.71	C-C stretch in ring, aromatic
		1376.35	CH$_3$ bend
		1229.06	C-O single bond stretch
1156.01	*	1157.19	*
1099.79	=C-H bend	1074.07	=C-H bend
1015.46	C-O stretch, alcohols, carboxylic acids, esters, ethers	1019.09	C-O stretch, alcohols, carboxylic acids, esters, ethers
		912.46	C-H in plane bending
750.51	C-H out of plane bends	750.46	C-H out of plane bends
691.02	C-H out of plane bends (ring bending band)	689.24	C-H out of plane bends (ring bending band)

*indicates that the absorption peak has some ambiguity to interpret as either its frequency or strength does not match exactly with those in literature [12, 13, 14].

TABLE 3: MAJOR IR ABSORPTION BANDS SHOWN BY FLEX

Control	**Group if identified, interpretations**	**Treated**	**Group if identified, interpretations**
2918.70	C-H stretch, alkanes	2923.62	C-H stretch, alkanes
		2855.21	C-H stretch, alkanes
1725.96	*	1727.64	*
		1653.19	C=C stretch, alkenes
		1405.56	C-C stretch in ring, aromatics
1385.06	*		
1265.47	*	1243.58	*
1080.35	C-O stretch	1081.06	C-O stretch
1014.87	C-O stretch	1011.36	C-O stretch
		919.03	Methyl rocking in isopropyl group
872.84	C-H out of plane bend, aromatics	872.88	C-H out of plane bend, aromatics
661.31	C-Cl stretch	653.65	C-Cl stretch

*indicates that the absorption peak has some ambiguity to interpret as either its frequency or strength does not match exactly with those in literature [12, 13, 14].

i. Cotton cloth

The IR absorption spectrum of cotton cloth shows weak C-H stretch bands after 3000 cm^{-1} and C-O single bond stretch at around 1000 cm^{-1}, other bands are ambiguous to interpret. The list of bands and their interpretations are given in table 1. Peaks at 2920, 2854, 1718, 1530, 1376, 1231, 1084, 917, 664 cm^{-1} have become more strong and sharp and peak at 1450 cm^{-1} has become less strong in the treated compared to untreated control, all with no or negligible frequency shift. The sharpening of absorption peaks in the treated reflects greater change in dipole moment of the bonds in vibration or better efficiency of each vibration probably due to the increase in the number of bonds in the treated due to the microbial attack. No new bond has been formed after the treatment with bacterial isolates on cotton cloth.

ii. AEC

The peaks shown by the untreated and treated samples of AEC are given in table 2. The presence of an ester bond, aliphatic and aromatic hydrocarbon chains are evident from the spectrum shown by AEC, obvious as acrylic emulsions are high molecular weight polymer of esters of acrylic acid and styrenated acrylic/methacrylic acid. The spectrum shows out of plane bending of aromatic C-H bonds and the ring bending C-H band at 690 cm^{-1} typical of mono substituted aromatic compounds,[12] C-O single bond stretch and carbonyl C=O stretch peak indicating ester bond. In the treated sample, peaks at 1596, 1376, 1229, 1074 and 912 cm^{-1} have become more evident compared to untreated, all the other bands have become stronger and sharper in treated, except the peak at 1019 cm^{-1} which has decreased in strength compared to the untreated spectrum. Except for the band at 1099 cm^{-1} in untreated which has shifted to 1074 cm^{-1} in the treated, all show no or negligible band shift.

iii. Flex

Major peaks in the IR absorption spectra of the untreated and the treated samples of flex are shown in table 3. Flex has typical bonds indicative of C-O stretches, alkane C-H stretches, aromatic C-H out of plane bends and C-Cl stretch due to polyvinyl chloride and other plastics or plasticizers it may constitute. The peak at 1653 cm^{-1} has become more evident, a new peak has been formed at 919 cm^{-1} (indicative of methyl rocking in isopropyl group) which points to breaking and formation of bonds in the treated compared to the control. Peaks at 1385, 1265 cm^{-1} in the untreated spectrum have shifted to higher frequency in the treated and have decreased in intensity. The peaks at around 2920, 2855, 1725, 1080, 1014, 872 cm^{-1} have increased in intensity (stronger, sharper peaks) with no or negligible frequency shift indicating increase in the number of C=O bonds, larger number of stretchable and hence free C-H bonds reflecting existing bond breakage to form smaller alkanes. Peak at 661 cm^{-1} in the untreated spectrum has increased in intensity but has shifted to lower frequency (653 cm^{-1}) in the treated.

IV. DISCUSSION AND CONCLUSION

Degradability of cotton cloth, AEC and plastic flex were gauged in terms of changes in average weight and maximum tensile stress supported after treatment with and without bacterial consortium for 15 days. The extremely significant loss of weight upon simple shaking in aqueous medium itself proves the possibility of degradation of AEC in nature in presence of moisture. This could probably be due to the soluble additives like starch used in cotton cloth, since the acrylic emulsion coat covers only on one side of the cloth rendering the other side exposed to water. However, the weight of the sample subjected to treatment with bacterial consortium in AEC is very significantly lower than the treated control, unlike even in the parent material, cotton cloth in which the decrease in weight between TC and BTS is not at all significant. The decrease in tensile strength due to bacterial treatment was also found maximum in AEC compared to the other two materials. This indicates the selective biodegradation of the acrylic emulsion coat of AEC.

The overall impact of the treatment on the chemical structure of the materials was assessed from the FTIR absorption spectra. In terms of chemical bond alterations evident from FTIR spectra, none of the samples showed any evidence of –OH bond, the most important evidence for the presence of a hydroxyl or carboxylic acid group resulting from the oxidation of the samples. Some peaks in the spectra couldn't be assigned any bond vibration since they did not match exactly with the descriptions in literature with respect to the frequency absorbed or the intensity of absorption. However, a few evident distinctions could be made from the treated and untreated samples of all the three materials.

The treated cotton cloth showed a stronger peak due to C-H bond of a tertiary carbon atom compared to the untreated. In AEC, FTIR spectrum of the treated sample revealed elimination of C-H stretch from unsaturated or aromatic chain, a new $–CH_3$ bend indicating a terminal carbon atom probably due to the cleavage of long chains and a new C-O single bond stretch indicating ester/ether bond, relative to its untreated sample. The treated flex spectrum differed from the untreated by a stronger $–CH_3$ rocking vibration and C=C bond stretch formed probably due to cleavage of a long chain and dehydrogenation (oxidation). Besides, most of the existing peaks in all the three samples have deepened indicating the increase in the number of bonds like C-H and C=O in samples after treatment. In short, all the three materials showed evidences of chemical change as a result of physical factors like agitation and temperature, chemical -

like presence of water and mineral salts and biological- the presence of bacterial extracellular enzymes in the medium. However, with respect to physical and mechanical properties tested, AEC has impacted the most by the biological factor highlighting its biodegradability.

The bacterial consortium selectively deteriorates the acrylic emulsion in a time period as short as fifteen days leaving behind the parent material, cotton cloth which is completely natural and hence undoubtedly biodegradable in nature. Hence the application of acrylic emulsion, a synthetic polymer on cotton cloth does not highly affect its biodegradability but highly enhances its printability. With a mixture of suitable microorganisms to degrade the acrylic emulsion polymer, this material becomes a better alternative to plastic flex for advertisement purposes.

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