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ADHESIVE PERFORMANCE, FLAMMABILITY EVALUATION AND BIODEGRADATION STUDY OF PLANT POLYMER BLENDS

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Abstract—A renewable polymer, collected as gum from a local plant (*Moringa oleifera*), was dry blended with various rubbers, e.g. natural rubber (NR), nitrile rubber (NBR), chloroprene rubber (CR) and also with different commodity polymers, viz. polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC). The plant polymer (PP) was also solution blended with NR and NBR. The adhesive performance of NR, NBR, NR/PP and NBR/PP blends was studied by the 180° peel test. The results were compared with a commercial adhesive (Dhole's rubber solution, India) used as a sealant. Flame retardancy of the plant polymer blends with commodity polymers and rubbers was monitored by limiting oxygen index (LOI) study. Structure-flammability correlations for CR/PP and PVC/PP blends were also reported. Biodegradability of the NR/PP blend was studied by the standard soil burial test and evaluated by scanning electron microscopy (SEM) as well as optical microscopy. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Evaluation of chemical, physical and other special properties such as adhesiveness and flammability helps in predicting the performance and reliability of materials under service conditions. Polymers, both natural and synthetic, have poor fire resistance due to their organic nature. Since polymeric products have been extensively used in building and construction, transport and consumer goods markets, imparting fire retardancy to polymers has, of late, become an important concern. Especially evaluation of flammability of polymers has immense importance to the practical as well as laboratory scientists to certify the material under the flammability–smoke evolution and toxicity (FST) standard. A study on the biodegradability of polymers also offers useful informations [1–4] about preventing or retarding the attack of polymers by bacteria, insects, fungi and other microorganisms as well as in waste disposal problems.

One of the traditional ways of imparting fire resistance to polymers is the addition of fire retardant additives. Conventional flame retardant (FR) additives in polymer compounds generally suffer from their migration and leaching from the bulk of the polymer products due to noncompatibility of these FR additives with the macromolecules. This in turn decreases the durability and affects the performance characteristics of the product. Besides, these FR additives usually contain a higher percentage of halogens, and therefore, on burning, emit a lot of toxic chemicals like hydrohalides, as gases or vapors, which are highly health hazardous and environmental pollutants. Polymeric FR additives, on the other hand, can offer better compatibility, migration and/or leaching stability, thereby enhancing the service life of the polymer product. Moreover, if such polymeric FR additives are developed from renewable nonpetroleum resources, it would be doubly beneficial.

In this paper we report the results of our investigation on the performance of a plant polymer (PP), collected as a gum from a local plant, as a flame retardant to some of the synthetic polymers e.g. low-density polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) and a few rubbers, viz, natural rubber (NR), nitrile rubber (NBR) and neoprene rubber (CR). An attempt has also been made to study the adhesive strength of the NR/PP and NBR/PP blends, taking a commercially available sealant as a reference material. Since PP is of plant origin, its biodegradability behavior in the NR/PP blends was also studied.

EXPERIMENTAL PROCEDURES

Materials

NR (RMA1), SBR 1502 (Synthetics & Chemicals), PBR (IPCL Cisamer 1220), NBR (Paracryl CZLT, 40% AN content) and CR (Neoprene WRT), polyethylene (FS 300, IPCL), polystyrene (Synthetics & Chemicals) and plasticized PVC (rigid PVC + 20% dibutyl phthalate) were used as received. All other chemicals used in the study were of analytical reagent grade.

Preparation of blends with rubbers

Appropriate amounts of rubber and the plant polymer were mixed in a laboratory two-roll rubber mixing mill of size 6″ × 13″ with a friction ratio of 1.2 following the standard method of ASTM D15-54T [5]. At first the rubber

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was masticated without the addition of peptizer to form a band on the front roll, then other additives were added for compounding in the sequence ZnO, stearic acid, accelerator, sulfur for gum vulcanizates. For filled vulcanizates, after the formation of a smooth band on the front roll, carbon black (N 330) was incorporated with or without spindle oil as a processing aid. Then the other additives were added in the same sequence as in gum vulcanizates. The friction ratio of 1.2 was maintained throughout the compounding cycle. The mixed stocks were finally shuted off by passing through a small nip of the rolls at even speed. The whole cycle of the operation was of 15 min duration at 50 + 5°C for gum vulcanizates and of 20 min for filled vulcanizates at 60 + 5°C.

Preparation of blends with plastics

Appropriate amounts of polymers and the plant polymer were blended separately by melt mixing in a Brabender Plasticorder, Model 810603 at about 150°C for 30 min at 15 rpm.

Solution blending procedure

Appropriate amounts of the plant polymer and rubber (NR and NBR) were dissolved separately in a mixed solvent of dimethyl acetamide: toluene (30:70, v/v) and added together carefully so that no precipitate was obtained. The total solid content of the solution was 5.5%.

Flame retardancy test

The flame retardancy test of the polymer blends was carried out with a Stanton Redcroft FTA-Flammability Tester under controlled nitrogen–oxygen mixed environments with test samples having 15 cm length, 0.8–1.0 cm width and 0.2 cm thickness following the standard procedure of limiting oxygen index (LOI) test ASTM D2863-77 [6]. A mixture of nitrogen and oxygen was allowed to pass through the sample burning in a carefully controlled rate. The amount of oxygen in the particular gas mixture just sufficient to keep the sample burning was taken as the basis for calculating the LOI value according to the relation:

$$\mathrm{LOI} = \frac{\mathrm{O}_2}{\mathrm{N}_2 + \mathrm{O}_2} \times 100$$

where O_2 and N_2 are the volume concentration of O_2 and N_2, respectively.

Test for adhesive strength

The adhesion strength was measured by the T-peel test in an Instron 4204 and is expressed as the peel fracture energy G. G is related to the average force F required to separate the joint and the specimen width W by the equation:

$$G = \frac{2F}{W}$$

The peel fracture energy is the sum of the intrinsic work of adhesion the bulk energy dissipitated in the stripping member.

The test specimens were cut from the cycle tube rubber according to ASTM specifications. Surface preparation of the adherents was done by different mesh-size metal brushes before applying adhesive solutions. The contact area of the adhesive zone was 40 mm × 25 mm [7]. All the specimens were cured at 150°C for 30 min by a Carvar laboratory hydraulic press. Commercial sealant (Dhole's rubber solution) for cycle tube repair was taken as the reference material. Peel tests were performed at two elongation rates of 25 mm/min and 50 mm/min.

Test procedure for biodegradability

Soil burial is the most widely used testing method for the biodegradability of polymers. The samples having size of 50 cm length, 25 cm width and 0.2 cm thickness were buried in the soil under compost conditions at a depth of 60–75 cm under ambient (30 ± 2°C) temperature for 1 month. The samples were then recovered carefully from the soil, washed with water, dried under ambient conditions after blotting out adhering water, and finally examined under a Cam Scan II Scanning Electron Microscope or Versamet-2, Union 7221 optical microscope for evidence of degradation.

RESULTS AND DISCUSSION

Adhesive strength of blends of plant polymer with rubbers

The adhesive strength of the solution of rubbers (NR, NBR and CR) as well as their respective blends with PP has been compared with that of a commercial adhesive. The results are summarized in Table 1. The reproducibility may be expressed as the difference of the test values from the average of 95% confidence level.

The adhesive strength of the blend of PP with NBR is higher than that of a commercial adhesive and virgin CR solution in both higher and lower peel rates. But the adhesive strength of the NR/PP blend is higher than that of the virgin NR solution but lower than that of the commercial adhesive, Dhole's rubber solution. These can be explained on the basis of initial breakage of the longer molecular chains of the plant polymer during melt mixing, generating highly polar groups which chemically interact with NBR to exhibit better adhesive performance. At a higher peel rate the peel fracture energy is more in some cases because of stress concentration at the edge of overlap [8]. Since NR is nonpolar, its interaction with polar PP, unlike NBR, a polar rubber, is marginal. Thus the adhesive strength of the NBR/PP combination is higher than that of NR/PP.

Table 1. Peel strength of commercial adhesive and plant polymer blends with NR and NBR

	Elongation rate (25 mm/min)		Elongation rate (50 mm/min)	
Adhesive material	Peel strength[a] (N/m^2) × 10^3	Peel fracture energy (kJ/m^2)	Peel strength (N/m^2) × 10^3	Peel fracture energy (kJ/m^2)
NR (virgin)	10	0.8	10	0.8
NR + PP (10 phr)	12	0.9	12	0.9
NBR (virgin)	12	0.9	12	0.9
NBR + PP (10 phr)	14	1.1	17	1.4
CR (virgin)	14	1.1	16	1.3
Commercial adhesive	13	1.0	13	1.1

[a] Each result is an average of three replicate experiments

Flame retardancy behavior of polyblends with commodity polymers

It has been reported earlier [6] that the plant polymer contains phosphorus (4.34%, w/w). This has prompted us to investigate its flame retardancy behavior in its blends with other commercial plastics and rubbers. Table 2 presents data of LOI values of various polyblends containing a small amount of the plant polymer (5–25 phr). It is observed that the presence of the plant polymer at the 10 phr level in both PE and PS enhances the LOI value of virgin polymers by 12–15%. But in the case of PVC this increment is slightly better, upto about 23% at the 25 phr level of the plant polymer. This could have been still better if the PVC/PP blends did not contain dibutyl phthalate. This is perhaps due to the synergistic effect of the chlorine from PVC with the phosphorus of PP [9, 10].

Flame retardancy of various rubber compounds

The results of the LOI test of various rubber compounds are presented in Tables 3–6. The flame retardancy (FR) of all the rubbers is enhanced due to the fire retardancy effect of the plant polymer; the modified LOI designated as the $(\mathrm{OI})_m$ value [11] of PP is very high (42.0). The FR effect of PP is excellent in the case of neoprene rubber. This may be due to the synergistic effect [10] of chlorine from CR rubber with phosphorus present in the plant polymer. To compare the flame retardancy of the plant polymer in these rubber blends with the most commonly used FR additive Sb_2O_3, some studies have been made with rubber containing 5 phr Sb_2O_3 (Tables 5 and 6).

To compare the flame retardant efficiency of commercial FR additives with the plant polymer, the LOI values of the rubber compounds containing 0.4 wt% phosphorus of the plant polymer (10 phr), 0.4 wt% phosphorus of Na_3PO_4 and 0.4 wt% Sb in Sb_2O_3 (0.5 phr) have been determined. The results are presented in Table 6 and Fig. 1. The LOI values of the plant polymer used as the FR additive in these rubbers are higher than all other cases. It is surprising that the LOI value of neoprene rubber containing the same wt% of Sb_2O_3 is lower than that containing the PP. The reason for this cannot be ascertained by this limited study. But it may be said that PP as a fire-retardant additive for plastics and rubbers is highly efficient and promising. However, further study is required to pinpoint the mechanism and/or cause for this unusual behavior.

Structure flammability relationship of the plant polymer used in PVC

Limiting oxygen indices of the PVC blends with the plant polymer are plotted against the plant polymer content (phr) in Fig. 2. From regression analysis a linear curve is obtained, which follows the empirical equation:

$$y = 0.22x + 23.66 \tag{1}$$

where y = LOI value of PVC, and x = parts per hundred of the plant polymer in the PVC blend as a fire-retardant additive.

Table 2. Results of LOI values for commodity polymer blends with the plant polymer

Blend composition	LOI value
PE/PP (10 phr)	20.5
PS/PP (10 phr)	20.6
PVC	23.6
PVC/PP (5 phr)	24.5
PVC/PP (10 phr)	25.8
PVC/PP (12 phr)	27.0
PVC/PP (25 phr)	29.0

Table 3. LOI values of various rubber gum vulcanizates with plant polymer

Blend no. and composition of rubber compounds[a]	LOI value
1 (NR)	18.0
2 (NR/PP)[b]	19.5
3 (PBR)	18.0
4 (PBR/PP)[b]	18.9
5 (NBR)	18.5
6 (NBR/PP)[b]	19.2
7 (CR)	25.0
8 (CR/PP)[b]	33.5

[a] Base formulations (phr): ZnO:5, Stearic acid:2, CBS:2 (except blend nos. 7 and 8 where no CBS is used but MgO:4 and Na-22:0.5 are used), and sulfur:1.

[b] Rubber/PP = 100 phr/10 phr.

Table 4. LOI values of various filled rubber vulcanizates with plant polymer

Blend no. and composition of rubber compounds[a]	LOI value
1 (NR)	18.0
2 (NR/PP, 10 phr)	19.8
3 (NBR)	18.5
4 (NBR/PP, 10 phr)	18.9
5 (CR)	25.0
6 (CR/PP, 10 phr)	33.6
7 (CR/PP, 7.5 phr)	31.0
8 (CR/PP, 6.5 phr)	30.8
9 (CR/PP, 5 phr)	29.2

[a] Base formulations (phr): ZnO:5, Stearic acid:2, CBS:2 (except blend nos. 7 and 8 where no CBS is used but MgO:4 and Na-22:0.5 are used), and sulfur:1.

CBS, *N*-cyclohexyl-2-benzothiazole sulfenamide

Table 5. LOI values of various filled rubber vulcanizates with plant polymer and Sb_2O_3

Blend no. and composition of rubber compounds[a]	LOI value
1 (NR)	18.0
2 (NR/Sb_2O_3, 5 phr)	19.6
3 (NR/PP, 10 phr)	20.5
4 (NBR)	18.5
5 (NBR/Sb_2O_3, 5 phr)	19.2
6 (NBR/PP, 10 phr)	20.5
7 (CR)	25.0
8 (CR/Sb_2O_3, 5 phr)	30.5
9 (CR/PP, 10 phr)	31.5

[a] Base formulations (phr): ZnO:5, Stearic acid:2, CBS:2 (except blend nos. 7 and 8 where no CBS is used but MgO:4 and Na-22:0.5 are used), and sulfur:1.

CBS, *N*-cyclohexyl-2-benzothiazole sulfenamide

Table 6. Comparative LOI values of the plant polymer, Na_3PO_4 and Sb_2O_3 fire retardants with various rubber filled vulcanizates[a]

Name of rubber	LOI values			
	Virgin state	With Sb_2O_3 (0.5 phr)	With Na_3PO_4 (0.5 phr)	With plant polymer (10 phr)
NR (RMA1)	18.0	19.6	19.1	20.5
PBR (Cisamer 1220)	18.0	19.2	19.0	18.9
NBR (Paracryl CZIT 40% AN content)	18.5	19.2	19.8	20.5
Neoprene WRT	25.0	30.5	26.5	31.5

[a] Base formulation (phr): ZnO:5, Sulfur:1.5, Spindle Oil:5, C-black:40, Stearic acid:2, CBS:2 (except Neoprene WRT where Na-22:0.5 and MgO:4 were used)

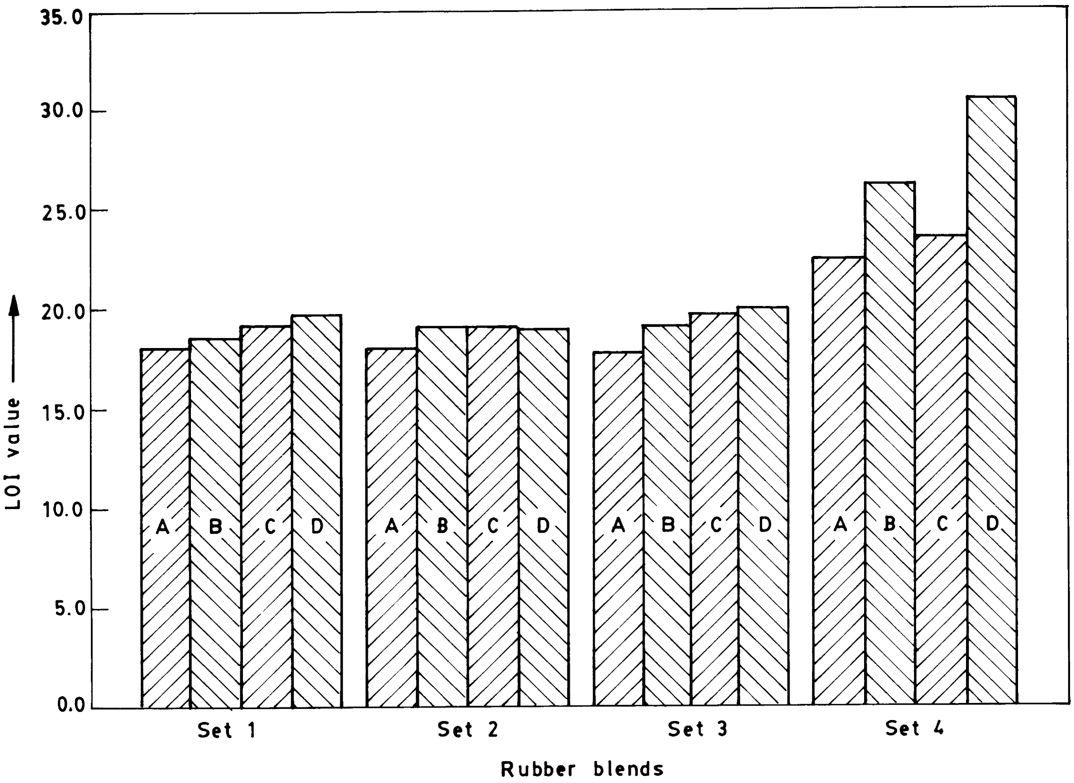

Fig. 1. LOI histogram of various rubber blends: Set 1; NR, Set 2; PBR, Set 3; NBR, Set 4; CR (A: virgin rubber, B: with Na_3PO_4, C: with Sb_2O_3, D: with plant polymer).

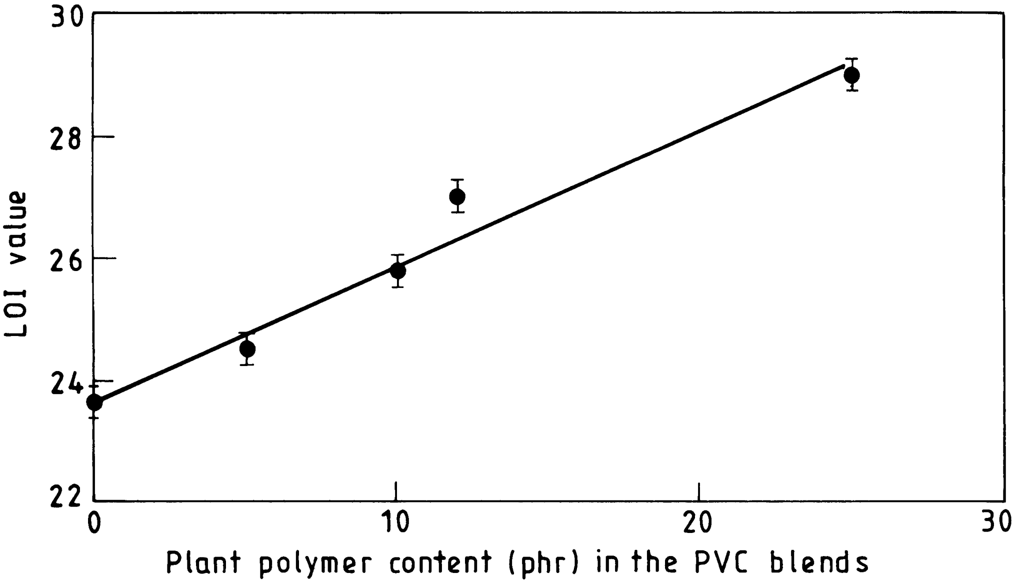

Fig. 2. LOI value against plant polymer content in PVC–plant polymer blend.

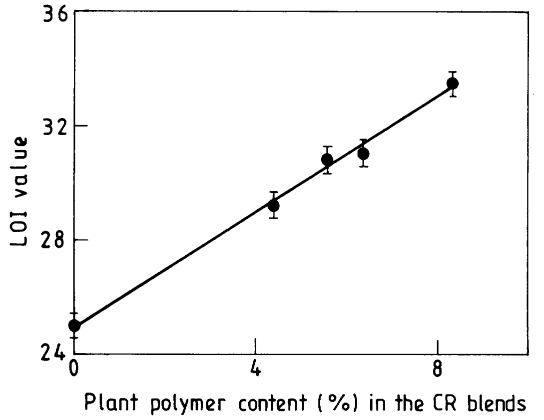

Fig. 3. LOI value vs plant polymer content (phr) in CR–plant polymer blends.

Structure flammability relationship of the polyblends with rubbers

To investigate the structure–property relation of the CR blends, limiting oxygen indices of the CR blends and the plant polymer content are graphically represented in Fig. 3. From regression analysis it is evident that these two parameters, the LOI value and the plant polymer content in the CR blends, also follow a linear relation:

$$y = 1.01x + 24.94 \qquad (2)$$

where y = LOI value of the CR blends and x = percentage of the plant polymer in the sample.

The validity of this equation has not been tested. However, this sort of empirical equation is useful to working scientists to fabricate various grades of flame retardant chloroprene rubber compounds. Comparing the intercept with the x-axis and slope of two Equations (1) and (2), it is found that the flame retardancy of the plant polymer in CR is higher than that in PVC. Again, the reason for this observed effect is not known.

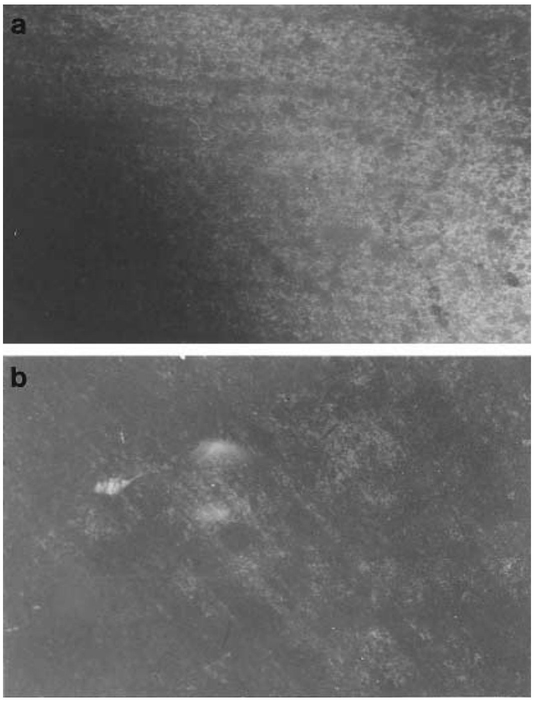

Fig. 4. Optical micrographs of NR/PP blend (a) virgin blend; (b) kept under compost soil.

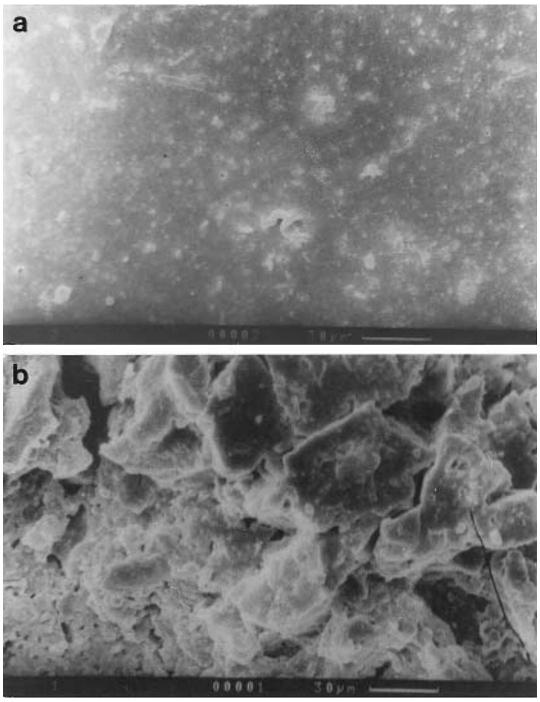

Fig. 5. SEM photomicrographs of NR/PP blend (a) virgin blend; (b) kept under compost soil.

Biodegradability of NR/PP blend

Optical and SEM micrographs and SEM of the NR/PP blends kept under compost soil are shown in Figs 4 and 5. The fractured surface is observed from both the SEM and optical micrographs of the blends kept under compost soil. The fractured surface is more prominent in SEM micrographs than in optical micrographs. However, the rubber samples in absence of the plant polymer do not exhibit any sort of degradation. This is expected due to the vegetative origin of the PP. Thus, rubber and/or commercial polymers may be made biodegradable by blending them with this plant polymer. Use of the plant polymer may be promising for initiating biodegradability in synthetic polymer products.

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