Controlled Release of 2-Methyl-4-chlorophenoxy Acetic Acid Herbicide from Waste Gelatin–Based Blends and Composites

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ABSTRACT: The volume of plastic waste is becoming a serious problem for waste management. Waste management is based on four hierarchical approaches: reduction, reuse, recycling, and energy recovery. We now report on recycling of gelatin scraps that are derived during the production of pharmaceutical capsules, by using the gelatin scraps in the production of controlled-release systems. This may help to minimize the side effects that often accompany the conventional application of pesticides. More important, the gelatins themselves, when degraded, might be useful to soil solarization and crop growth. Using and recycling these waste materials in the proposed application would save natural resources and consequently would be economically useful. The synthesis of gelatin films, and composites incorporating 2-methyl-4-chlorophenoxy acetic acid (MCPA) as herbicide, will be described. Morphology and mechanical properties of the films were investigated by scanning electron microscopy and tensile tests, respectively. The release of the MCPA herbicide from the prepared blends and composites was investigated. The prepared formulation proved to be useful for agricultural applications. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1420–1427, 2004

Key words: waste; herbicides; gelation; recycling; controlled release

INTRODUCTION

The increase in the use of plastic materials in all sectors of industry, coupled with the reduction in the lifetime of plastic products, has been responsible for the continuous increase in the generation of plastic wastes.[1] The volumes of the resultant plastic waste are becoming one of the most serious problems for waste management.[2] Plastics can be recycled using two different approaches: mechanical and feedstock recycling. The plastics are recycled as polymers in the first case, whereas in the second, plastic wastes are transformed into chemicals and fuels.[1]

Polymers supporting agricultural chemicals have recently been developed to overcome the serious environmental problems of conventional agrochemicals.[3–7] The delivery of herbicides by controlled-release formulations offers ecological and economic advantages.[8] Success of these formulations is based on a suitable choice of polymer support. Degradable polymeric materials and hydrogels are of special interest because of their dual functions in this use.[9] Gelatin, a naturally occurring polymer, is currently in use in various industrial applications. Gelatin scraps, generated in different manufacturing processes, may constitute a concern for the environment because of their strong swellability in water medium and high carbon and nitrogen content, which lead to high oxygen demand once they reach the sewage drainage system and waste-treatment plants.[10] The use of mulching film, in particular, has led to a very substantial increase in the yield of soft fruits and vegetables because plastic film not only aids in increasing the temperature of the soil, but also reduces the usage of irrigation water and fertilizers, with consequential beneficial economic and environmental returns.[11]

However, the use of conventional nonbiodegradable mulching films results in inherited problems to the next crop as a result of the residues of the mulching films, which interfere with the roots of the crops and consequently cause drastic reduction to the crop yield. Herein, we report on the solution of two problems: the first is use of the huge amounts of gelatin scraps produced by the pharmaceutical companies; the second is the problem accompanying the administration of agricultural chemicals by conventional methods by using controlled-release systems. Blends and composites, based on waste gelatin and other

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natural or synthetic waste materials, can be used in agricultural applications for the fabrication of environmentally sustainable mulching films, and soil conditioners, and at the same time be helpful in solving problems with the correct management of gelatin scraps.

EXPERIMENTAL

Materials and methods

Materials used in this study were either waste or commercially available. Waste gelatin (WG), consisting of net shape rubbery scraps, as derived from the punching process applied in pharmaceutical soft capsules manufacturing, was kindly supplied by Rp Scherer Co. (Alexandria, Egypt). The elemental microanalysis of waste gelatin found: carbon (42.43%), nitrogen (14.77%), and hydrogen (6.32%). Poly(vinyl alcohol) (PVA) was a product of Hoechst AG (Frankfurt am Main, Germany); it is recognized as one of the few synthetic polymers that is truly biodegradable under both aerobic and anaerobic conditions.[12,13] The PVA, with an average molecular weight of 67 kDa and 88% hydrolysis degree, was used without further purification. Sugar cane bagasse (B) was dried in an oven at 50°C for 24 h before its use, and then ground with a blade grinder. The ground bagasse (B) was sieved and the fraction passing through a 300-μm mesh sieve was collected. Sawdust (S), sieved through a 300-μm mesh sieve, was collected and used. Glutaraldehyde (X) was a product of Adwic (Cairo, Egypt), commercialized as a 50% aqueous solution, and was used as a crosslinking agent in various weight proportions without any further purification treatment. 2-Methyl-4-chlorophenoxy acetic acid (MCPA) was purchased from Aldrich (Milwaukee, WI) and used as received.

Scanning electron microscopy (SEM)

SEM inspection was carried out on a JSM-820 scanning electron microscope (JEOL, Tokyo, Japan) at the Medical College of Virginia, Virginia Commonwealth University (Richmond, VA). The film samples were prepared by critical-point drying, followed by sputtering with gold and observation at 15 kV. Fractured surfaces were prepared under liquid nitrogen by breaking the strips, and specimens were examined under by SEM.

Elemental analysis

Elemental microanalyses of carbon, hydrogen, and nitrogen content were performed for each film. They were recorded on Heraeus (Hanau, Germany) micro and semi-micro analyzers (type Standard) at the Microanalytical Centre in Cairo University.

Tensile testing

The tensile properties of the prepared films were determined by using a Zwick-a (Stuttgart, Germany) modular testing system for loads up to 2.5 kN. The specimens were cut and then maintained in air at 25°C for 10 days before testing. Values were averaged on at least five specimens. The test was based on the ASTM D 882-75b standard.

Preparation of buffer solutions

The buffer solution, pH 7, was prepared as follows: to 100 mL of 0.4*M* boric acid (H_3BO_3) was added 100 mL of 0.4*M* acetic acid and 100 mL of 0.4*M* phosphoric acid (H_3PO_4), followed by addition of a few drops of sodium hydroxide solution (10%) to achieve the required pH. The mixture was diluted with distilled water to 1 L.[14]

High-performance liquid chromatography (HPLC)

The release of the bioactive agent MPCA was monitored by a Shimadzu (Kyoto, Japan) HPLC. The injection parameters were as follows: 25°C; volume injected, 10–100 μL; mobile phase, A: 5 mm KH_2PO_4, 0.001% v/v CH_3COOH; B: 50% acetonitrile, 50% methanol, 0.001% CH_3COOH; gradient, 15% B to 50% B (at 16 min), to 55% B (at 20 min), then to 15% B (at 21 min); detector parameter: flow rate 1 mL/min; column Hypersil, ODS 5 μm.

Film preparations

Films were prepared by casting a water dispersion of all the ingredients in Teflon-coated aluminum trays followed by water evaporation at room temperature. Table I details compositions of the prepared films.

Measurement of the releasing bioactive agent MCPA

The hydrolysis of the bioactive agent MCPA, from gelatin films containing the herbicide, was carried out by charging 500 mg of the active film to a flask containing 100 mL of an aqueous buffer solution at 25°C for a prescribed period of time. At intervals, the amount of MCPA released was determined by a Shimadzu HPLC (SPD-6AV UV–vis detector) spectrophotometer, two LC-6AV pumps, and an ODS reversed-phase column (CTO-6A column oven; Shimadzu). After the first few days, fresh buffer was added to the flask after each analysis. The measurements of releasing bioactive agent were carried out in neutral media.

RESULTS AND DISCUSSION

The objectives of this work were to produce a controlled-release system, based on waste gelatin, and at the same time solve the scrap problem of a pharmaceutical company. Waste gelatin (WG) cast films, which appeared orange because of the color in the gelatin, were cohesive and flexible. Blending with sugar cane bagasse (B) and sawdust (S) conferred a dark color to the films. WG/B and WG/S composites resulted in harder films than the flexible WG films. Increasing bagasse and sawdust content produced more fragile films. When blends were prepared by mixing a WG water suspension and PVA, a homogeneous water suspension was produced, thus showing compatibility of the two components in the solvent, whereas cast films appeared homogeneous for only a limited amount (20%) of PVA. MCPA was selected as the active species because it was known to be a selective herbicide, translocatable with the properties of growth substances, and used for the postemergence control of annual and perennial broad-leaf weeds, cereals, and sugarcane. It is also effective for the protection of many other crops.[15] Moreover, MCPA is commercially available at prices that make it suitable for large-scale use. Also, it is nontoxic to fish and bees and its degradation and metabolism pathways are known.[16] The elemental microanalysis data of the prepared formulations are shown in Table II. These results show that waste gelatin samples have high nitrogen content (up to 11.5%), which indicates the value of the prepared materials as a fertilizer if it is mixed with the soil.

TABLE I
Composition (wt %) of the Blends and Composites Based on Waste Gelatin (WG) Containing 10% 2-Methyl-4-chlorophenoxy Acetic Acid (MCPA)[a]

Sample	WG	PVA	X	B	S
WGM	90	0	0	0	0
WGMa	85	0	0	0	0
WGMP20	70	20	0	0	0
WGMP35	55	35	0	0	0
WGMP50	40	50	0	0	0
WGMX2P20	68	20	2	0	0
WGMX5P20	65	20	5	0	0
WGMB10	80	0	0	10	0
WGMB20	70	0	0	20	0
WGMX2B20	68	0	2	20	0
WGMX5B20	65	0	5	20	0
WGMS10	80	0	0	0	10
WGMS20	70	0	0	0	20
WGMS50	40	0	0	0	50
WGMX2S10	78	0	2	0	10
WGMX5S10	75	0	5	0	10

[a] WG, waste gelatin; P, poly(vinyl alcohol); X, glutaraldehyde; B, sugar cane bagasse; S, sawdust; M, MCPA; a, containing 5% adipic acid.

TABLE II
Elemental Analysis of the Prepared Waste Gelatin (WG) Formulations Containing 2-Methyl-4-chlorophenoxy Acetic Acid

Formulation code	Composition (%)		
	C	H	N
WGM	43.8	7.4	*11.5*
WGMa	43.6	5.1	9.2
WGMP20	44.8	4.9	7.3
WGMP35	47.8	5.0	5.8
WGMP50	46.3	6.2	3.9
WGMX2P20	47.7	4.6	7.8
WGMX5P20	45.1	6.3	7.7
WGMB10	42.8	4.2	9.0
WGMB20	42.5	5.1	6.3
WGMX2B20	45.4	5.0	7.1
WGMX5B20	46.5	4.6	6.7
WGMS10	42.7	3.5	8.5
WGMS20	44.7	4.5	7.5
WGMS50	46.6	3.7	3.4
WGMX2S20	46.3	3.6	6.9
WGMX5S20	43.8	3.6	6.5

Scanning electron microscopy (SEM)

Figure 1 shows microphotographs of a characteristic WG/B (WGMB20) composite film obtained from solution casting of waste gelatin (WG) (70%), bagasse (B) (20%), and 10% MCPA (M). Microphotographs of the film's surfaces were recorded and the result shows that the top surfaces of the film were generally smooth [Fig. 1(a)]. However, SEM for the bottom layer showed random distribution of bagasse fibers that were tightly embedded within the continuous gelatin matrix [Fig. 1(b)], indicating that good adhesion between the two components had occurred. The freeze-fractured transversal section of the composite WGMB20 (Fig. 2) showed empty tubes in the composite, which revealed possible sites for trapping the bioactive ingredient within the composite.

The composite films obtained from WG/B or WG/S, having coarse surfaces of either bagasse or sawdust fibers, were cemented and covered by gelatin. The freeze-fractured transverse section of the composite films showed similar tubes as described for film WGMB20. The empty tubes, seen in the microphotographs of the composite films [Fig. 2(a), (b)], revealed the possibility of trapping the bioactive ingredient inside. This could be used as another barrier or rate controller for the release of the active agent.

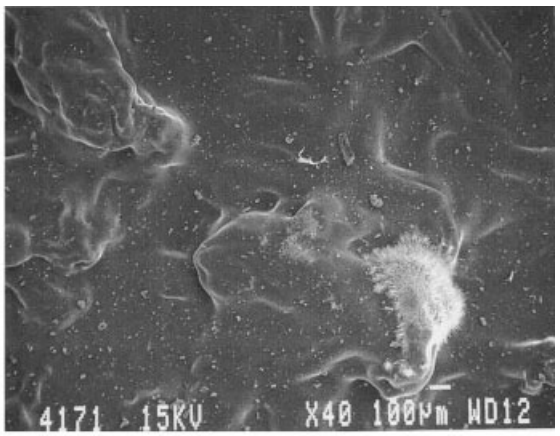
Figure 3 shows SEM micrographs of a composite based on waste gelatin (70%), sawdust (20%), and MCPA (10%). This composite shows a coarse surface [Fig. 3(a)] with S fibers cemented and covered by gelatin. The bottom layer of the film [Fig. 3(b)] showed a less-smooth structure than that of the upper surface.

Tensile testing

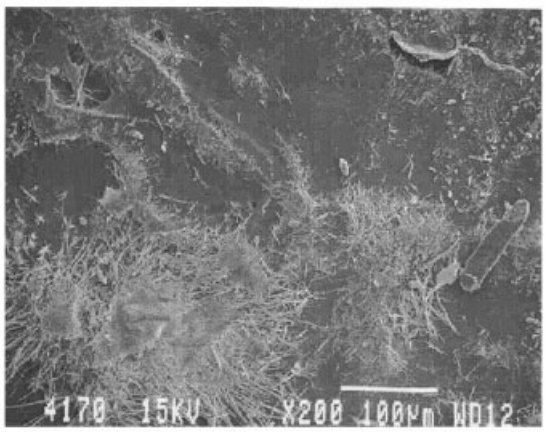
WGMP20 and WGMP35 cast films had elongations at break of 30.91 and 149.11%, and maximum loads of 53.67 and 117.45 kg/cm^2, respectively. WG/PVA blends showed a sharp increase in both the strain % and the break load. It appeared to be more flexible than blends with higher amounts of WG whose films became harder and started to turn opaque. Introducing bagasse in waste gelatin sharply reduced both the strain and break load. WGMB10 composites showed elongation at break of 10.25% that was about three times lower than that of WGM. The presence of sawdust fibers decreased the elongation, but not sharply like bagasse, and also decreased the break load at the same time. Introducing glutaraldehyde (X) increased the elongation and decreased the break load, whereas increasing the amount of X decreased both the strain and the break load. The tensile data are shown in Table III.

As mentioned earlier, this work was inspired by the goal of solving the accumulation problem of gelatin scraps by developing a long-term delivery system for MCPA. To control the release of MCPA and reuse of gelatin scraps, cast-film formulations were prepared with different synthetic and natural additives. These waste gelatin–based formulations have dual applications because they contain a combination of herbicide MCPA and water-preservation medium (waste gelatin). These formulations, containing herbicide and the gelatin gel, could be used to control a fairly large amount of water.[17–19] In addition to the water-preservation property, the films based on the waste gelatin would function as an herbicide to control undesirable weeds and, because of the high nitrogen content of the films, would be useful as a source for nitrogen to enrich the soil.

The release of MCPA herbicide from cast formulations was carried out at 25°C in water-buffered solutions at pH 7. The amount of herbicide released over time was monitored by HPLC and the release profiles are shown in Figures 4–7. In general the rates of

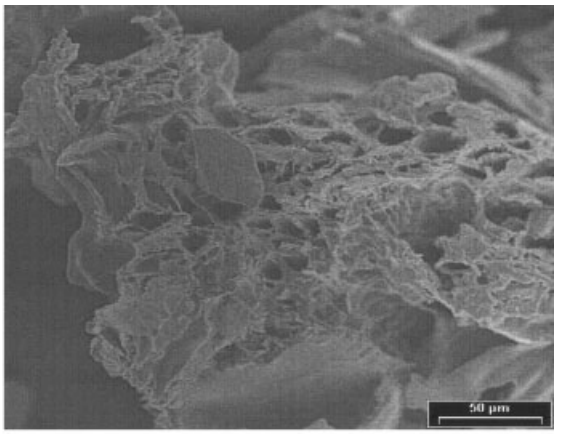


(a) Top surface

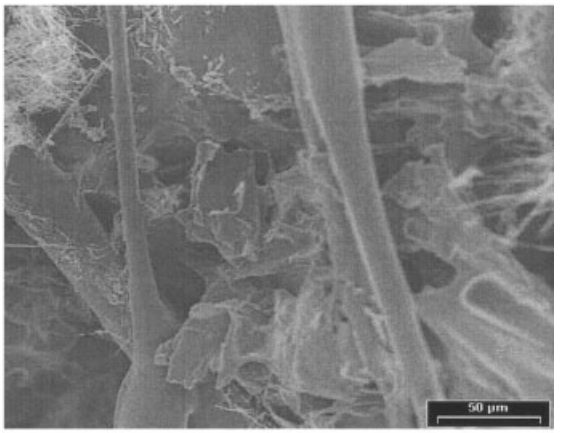


(b) Bottom surface

Figure 1 SEM microphotographs of WG/B/M composite film containing 20% B and 10% M (MCPA).

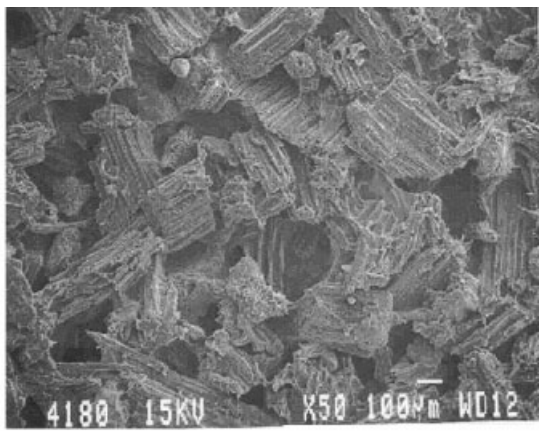


(a) (300X)

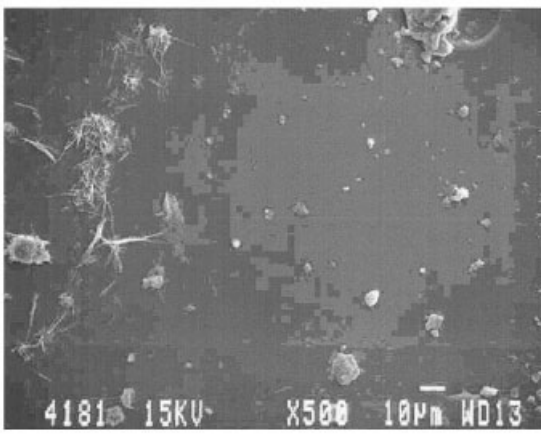


(b) (300x)

Figure 2 SEM microphotographs of freeze-fractured transverse section of waste gelatin–based composite containing MCPA: (a) film containing bagasse 20%; (b) film containing sawdust 20%.



(a) Top surface



(b) Bottom surface

Figure 3 SEM microphotographs of WG/S/M composite film containing 20% sawdust and 10% MCPA.

release from these formulations showed no initial fast release. The crosslinked waste gelatin, which showed slow release compared with the release rate of uncrosslinked films, suggested that crosslinking slows the release by inhibiting the penetration of water and hydrolysis of the scraps.

Figure 4 shows the effect of incorporation of adipic acid as crosslinker. The film containing 10% MCPA, embedded in the waste gelatin films (WGM), showed a relatively faster release than that of the crosslinked film (WGMa). In Figure 5, film WGMP50, containing 40% WG, 50% PVA, and 10% MCPA, showed a faster release: it released 115 mg MCPA in 60 days. Decreasing the PVA content to 35% decreased the rate of release. For example, formulation WGMP35 released 105 mg in 60 days. A greater reduction in the amount of PVA to 20 resulted in a slower release rate. This may be attributable to the water solubility and the hydrophilic nature of the PVA, which facilitated the transfer of MCPA to the release medium. Introducing glutaraldehyde as crosslinker in the formulation reduced the rate of release; for example, introducing 5% glutaraldehyde decreased the released MCPA from 100 to 75 mg/60 days (Fig. 5).

Figure 6 shows the effect of adding bagasse to the formulation, where 10% bagasse showed a relatively faster release rate for MCPA: it released 105 mg/60 days. Increasing the bagasse content to 20% decreased the amount released to 82 mg/60 days. Also, the effect of the crosslinking with glutaraldehyde clearly decreased the rate of release of MCPA to 70 and 40 mg/60 days when using 2 and 5% glutaraldehyde, respectively. A formulation containing 40% WG and 50% sawdust (WGMS50) showed a relatively faster release than that of the formulation containing only 20% S (WGMS20) (Fig. 7). Crosslinking of the formulation containing sawdust with glutaraldehyde decreased the rate of release from 70 to 45 mg/60 days.

CONCLUSION

Controlled-release formulations, based on waste gelatin and other waste materials, were prepared with

TABLE III
Tensile Properties of Films Containing 2-Methyl-4-chlorophenoxy Acetic Acid

Sample[a]	Break load, R_b (kg/cm^2)	Maximum load, R_m (kg/cm^2)	Strain, F_{max} (%)	Elongation at break (%)
WGM	107.07	111.14	32.21	32.23
WGMX2	39.13	39.24	23.00	22.64
WGMP20	49.79	53.89	29.89	30.01
WGMP35	116.98	117.77	146.11	147.13
WGMX2P20	86.71	87.57	104.16	105.58
WGMX5P20	28.33	33.52	20.89	22.10
WGMB10	11.56	37.43	6.05	11.55
WGMB20	10.43	35.22	5.43	9.87
WGMX5B20	10.92	33.75	4.07	3.97
WGMS10	44.95	45.68	22.54	23.87
WGMX2S20	38.59	41.88	3.7	3.99
WGMX5S20	4.22	13.17	4.03	19.05

[a] WG, waste gelatin; M, 2-methyl-4-chlorophenoxy acetic acid.

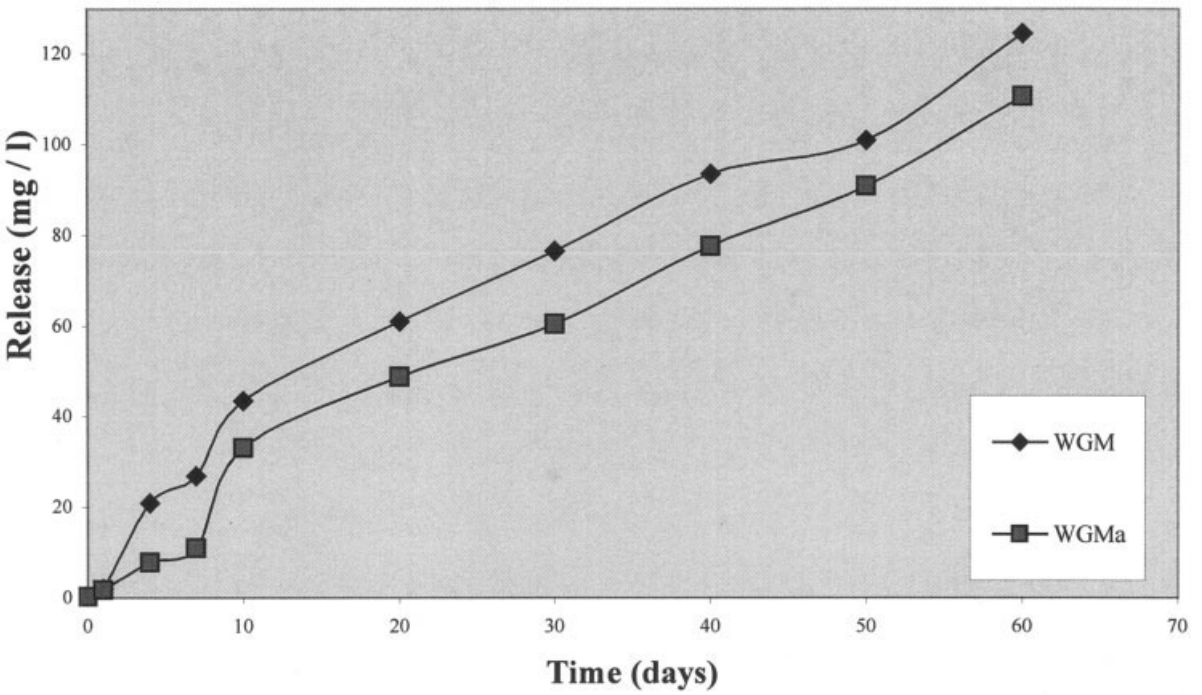


Figure 4 MCPA release from gelatin waste in the presence of adipic acid.

MCPA. The release of MCPA from these formulations was found to depend on the scrap additives. The formulations were easily crosslinked either by glutaraldehyde or adipic acid. Crosslinked films displayed a slower rate of release of MCPA. The crosslinking increased the persistence of the films in the environment for the required period because crosslinking reinforced the gelatin structure by introducing intra- and intermolecular bonds between gelatin molecules.[10] WG/B composites showed a

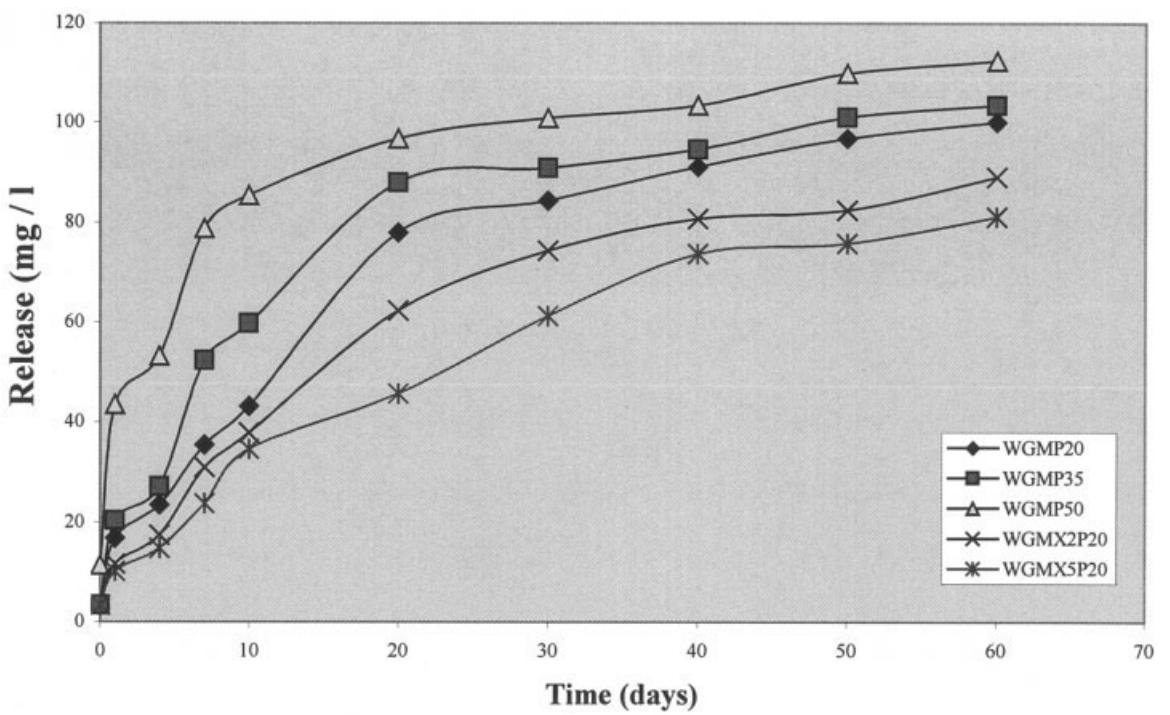


Figure 5 MCPA release from gelatin waste in the presence of PVA.

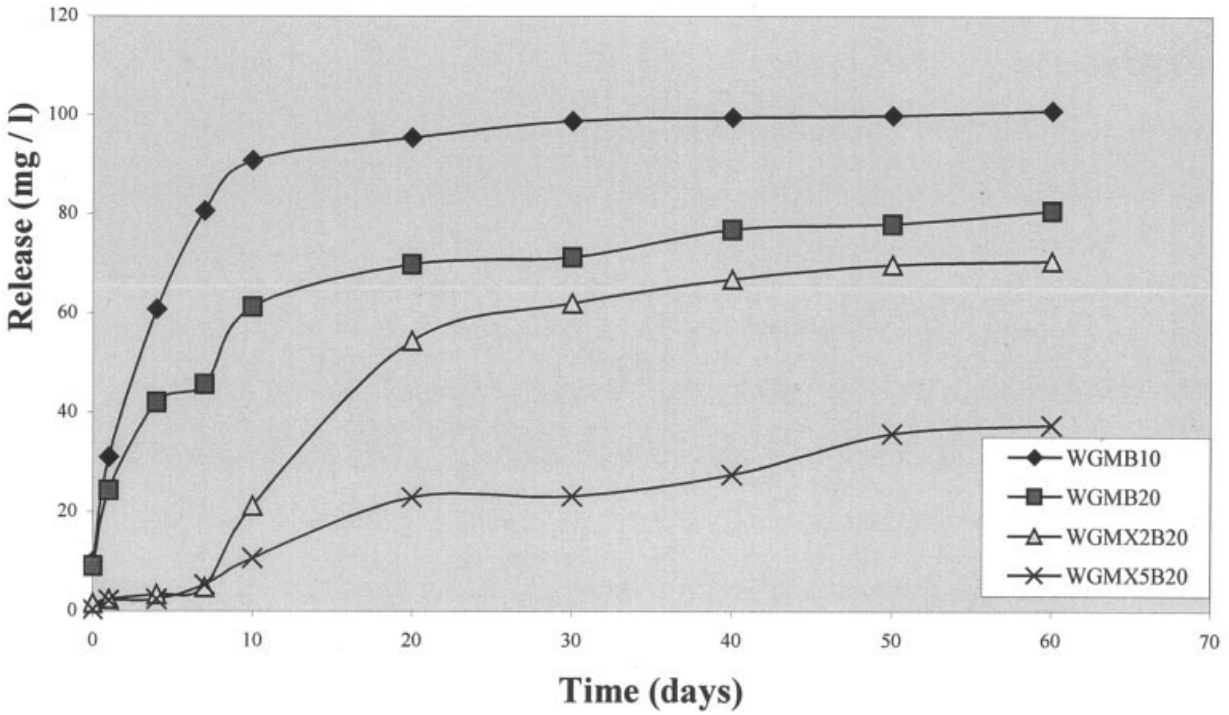


Figure 6 MCPA release from gelatin waste in the presence of bagasse.

dark color that, interestingly, might result in a good structure for the potential application of the derived films in soil enrichment and weed control. The formulations containing up to 20 wt % of B displayed mechanical properties applicable in agricultural practices. It is anticipated that these films would be useful biodegradable mulching films, with the extra advantages of enriching the soil with nitrogen. In addition they would work as controlled-release systems for herbicide MCPA.

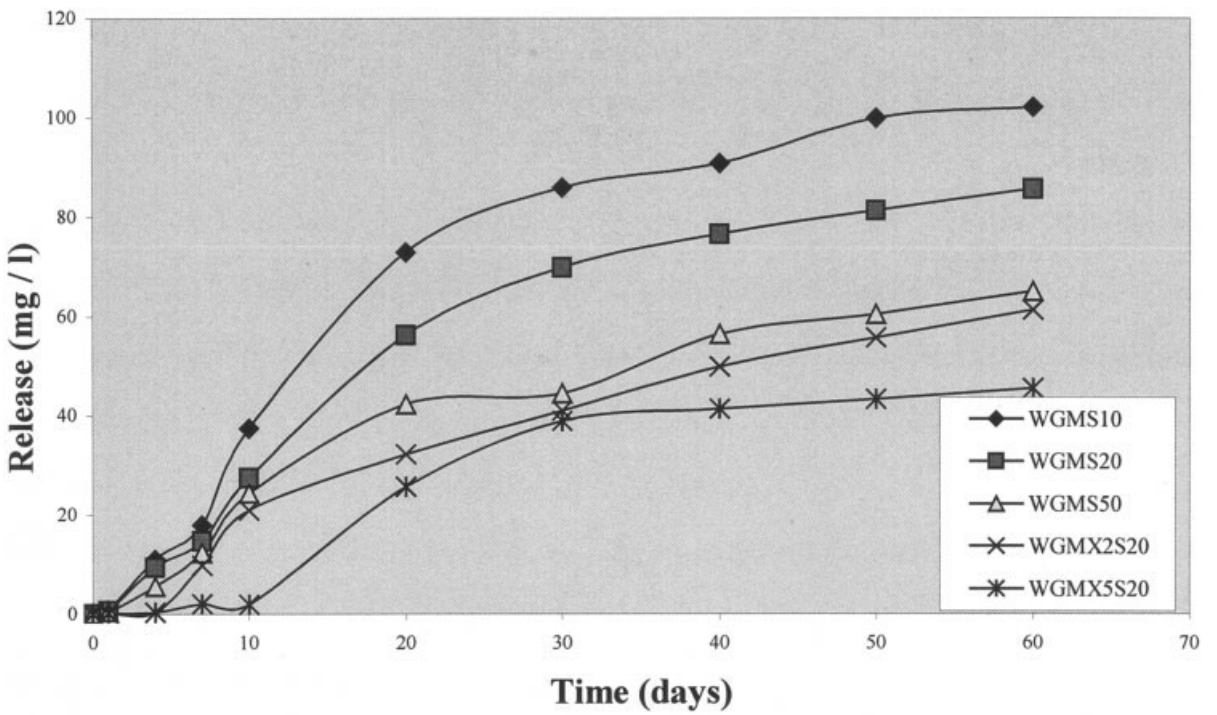


Figure 7 MCPA release from gelatin waste in the presence of sawdust.

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