

Composite Sheets with Biodegradable Polymers and Paper, the Effect of Paper Strengthening Agents on Strength Enhancement, and an Evaluation of Biodegradability

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ABSTRACT: Composite sheets composed of biodegradable polymers (BP) and paper were prepared, and their physical and biodegradable properties were investigated. The paper sheets were soaked in BP emulsions and cured at 100°C for 20 min. The wet strength of composite sheets with the same basis weight increased significantly with increasing BP content, although dry strength increased only moderately. A 0.5% addition of a common wet paper-strengthening agent, poly(amidoamine-epichlorohydrin) (PAE) resin, enhanced the wet strength, which reached 9.3 MPa, of composite sheets consisting of a BP : paper ratio of 20 : 80. Further enhancement was achieved by the addition of polyvinylamines (PVAm). The wet tensile strength of composite

sheets consisting of BP and paper (20 : 80) increased by 27% with the addition of 0.2% PVAm and 0.5% PAE, whereas it was enhanced by only 3–4% with the addition of 0.7% PAE. The biodegradability of the composite sheets was somewhat retarded by the addition of PAE and PVAm. However, a 90% weight loss was observed 60 days after placing composite sheet samples in soil. A similar weight loss was observed after 45 days for composites without additives and after 30 days for base paper alone. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 861–866, 2005

Key words: biodegradable; composites; polyvinylamine; wet strength; biomaterials

INTRODUCTION

Conventional plastics are mainly made from petroleum-based polymers and their large-scale consumption has generated serious environmental problems. Recently, therefore, much attention has been devoted to the development of biodegradable polymers (BP) with a predetermined lifetime for diverse applications such as biomedical polymers^{1,2} (e.g., wound closure,³ tissue suturing,^{4,5} controlled drug release,⁶ and bone fixation⁷) or disposable goods^{1,2,8} (e.g., packaging,^{9,10} mulching for agriculture, seeding pots, bags, and other miscellaneous applications).

We are particularly interested in the latter application, which represents a promising approach to the waste management of plastics. Aliphatic polyesters are one of the typical degradable synthetic polymers,¹¹ whereas presently available plastics are mainly composed of poly(butylene succinate), poly(L-lactide), poly(ϵ -caprolactone), and starch blended with green plastics.

Previously, the authors reported that poly(L-lactide)-laminated paper is very resistant to biodegrada-

tion.¹² This drawback is ascribed to its high glass-transition temperature (T_g , 58 to 62°C) compared to that of other biodegradable aliphatic polymers (T_g , –60 to –45°C) such as poly(ϵ -caprolactone) and poly(butylene succinate).^{13,14} It is also well recognized that biodegradability is greatly affected by crystallinity; a higher crystallinity reduces biodegradability because of the limitations imposed on hydrolytic attack by enzymes.^{15,16} In contrast, poly(L-lactide)-coated papers showed good biodegradability,¹² probably as a result of low crystallinity.

These days, there are several commercially available BP emulsions and research regarding their application is currently being undertaken to develop and expand their uses. This study attempted to prepare composite sheets of BP [mainly poly(alkylene succinate)] and papers by soaking previously prepared handmade papers in BP emulsions. The wet strengths of these composite sheets were considerably high, whereas those of genuine papers were near zero. Paper strength, especially wet strength, was substantially enhanced by the addition of a typical wet-strengthening additive, poly(amidoamine-epichlorohydrin) (PAE) resin, but reached optimal values with an approximately 0.5% addition. These results gave information on how to achieve further enhancement based on the specific effects of polyvinylamines (PVAm) on paper sizing¹⁷; PVAm also significantly contributed to enhanced

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TABLE I
Characteristic Parameters of Biodegradable Polymers

Parameter	Bionolle EM901	Bionolle EM301	Randy PL-1000
Chemical type	Aliphatic polyester	Aliphatic polyester	Poly(L-lactide)
MFT °C	60	85–95	160
T_g , °C	–60	–45	58–62

composite sheet strength. This study reports on the enhancement of tensile strength by the addition of BP, PAE and PVAm, and also the biodegradation behaviors of these composite sheets.

EXPERIMENTAL

Materials

The pulp used was a bleached hardwood kraft pulp, which was beaten to a Canadian Standard Freeness (CSF) of 345 mL by a Technical Association of Pulp and Paper Industry (TAPPI) standard beater. Bionolle EM901 and EM301, which are commercial emulsion-type poly(alkylene succinate) products, were donated by Showa Highpolymer Co. (Tokyo, Japan), whereas Randy PL-1000, which is a suspension of poly(L-lactide), was obtained from Miyoshi Oil and Fat Co., Ltd. (Tokyo, Japan). Their characteristic parameters are shown in Table I. Poly(amidoamine-epichlorohydrin) (PAE) resin (brand WS-570), which is a typical paper-strengthening agent, was supplied by Japan PMC Co., Ltd. (Tokyo, Japan). Polyethyleneimine [PEI; molecular weight (MW) $\sim 10,000$] was supplied by Sigma-Aldrich Co. (Tokyo, Japan). Low MW ($<10,000$) polyvinylamine (PVAm-L) was prepared by Hofmann degradation¹⁸ of polyacrylamide polymerized in ethanol and compared with high MW PVAm, which was prepared by hydrolyzing¹⁹ poly(*N*-vinylformamide) with a MW of 3×10^6 (Kurita Water Industries Co., Tokyo, Japan) to produce partially animated poly(*N*-vinylformamide). For convenience, the term PVAm is used to describe both the homopolymer and partially hydrolyzed copolymers. The charge densities of four PVAm (PVAm-1–PVAm-4) and other cationic polymers were estimated by polyelectrolyte titration²⁰ at pH 3 using acriflavine as a fluorescent indicator. The characteristic parameters of these cationic polymers are given in Table II.

Handmade sheets were formed using the beaten hardwood pulp described earlier according to TAPPI T205 sp-95. Previously prepared sheets with basis weights of 63, 56, or 45.5 g/m² were soaked successively in 5, 11, or 23% BP emulsions, previously determined for the composite sheets (basis weight 70 ± 3 g/m²) to contain 10, 20, and 35% BPs, respectively. To evaluate further strength enhancement, PAE with and without the PVAm was added to the EM901 emulsion at the designated concentrations under vigorous stirring. The previously prepared paper sheets were soaked in the mixtures and treated in a manner similar to that described above.

After being soaked for 1 min, the wet sheets were mounted on a polished flat brass plate. Three pieces of standard blotting paper were laid centrally on the paper attached to the plate and a brass couch roll was placed gently over the edge of the blotting paper. To remove excess emulsion from the surface, the roll was then rotated twice forward and backward, without application of any further pressure, and removed. The blotting papers were consequently removed and the plate with its attached wet sheet was fitted onto metal rings for drying. A heavy weight was attached to the pile of rings, which were immediately placed in a convection oven to be cured. The sheets were cured at 80, 100, or 120°C for 20 min. After curing, the composite sheets were conditioned at 23°C and 55% relative humidity (RH) for more than 24 h. Some wet sheets were air-dried in an air-conditioned chamber at 23°C and 55% RH for more than 48 h. The sheets were then cut into 15-mm-wide strips and cured under a pressure of 1, 2, or 4 kg/cm² at 100°C for 10 s. They were also conditioned at 23°C and 55% RH. BP content was estimated from the difference between the dried weights of the sheets before and after soaking.

All samples were subjected to tensile strength tests under dry and wet conditions according to TAPPI

TABLE II
Characteristic Parameters of the Cationic Polymers

Parameter ^a	PVAm-1	PVAm-2	PVAm-3	PVAm-4	PVAm-L	PEI
DP $\times 10^{-3}$	42.3	42.3	42.3	42.3	0.15	0.24
CD	1.5 (10)	6.7 (40)	11.1 (61)	20.5 (80)	18.5	16.3

^a DP, degree of polymerization; CD, charge density (meq/g). Number in parenthesis: degree of poly(*N*-vinylformamide) hydrolysis.

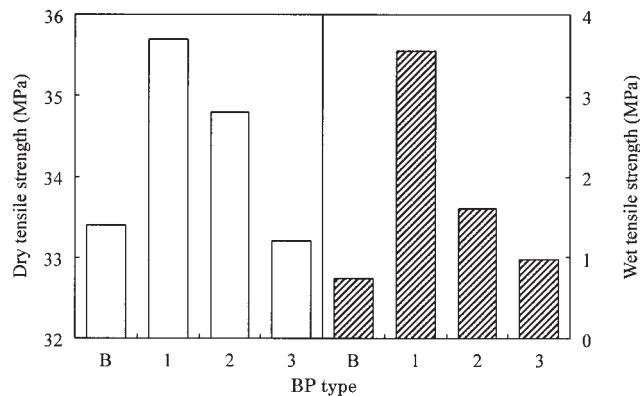


Figure 1 Effect of biodegradable polymer (BP) additions on composite sheet strength. B: Blank paper; 1: EM901; 2: EM301; 3: PL-1000.

T494 om-88 and T456 om-87, respectively. Ten replicates were tested for each sample.

Outdoor biodegradable tests were carried out by burying disrupted sheet samples inserted in plastic nets in soil (pH 7.5) at a depth of 10 cm. Trials were performed in the summer from the beginning of June to the middle of August. Samples were removed, washed very gently with water, dried, and weighed. Weight losses were recorded.

RESULTS AND DISCUSSION

Effect of biodegradable polymers with different minimum film-forming temperatures on composite sheet strength

At first the retention systems,²¹ which used only cationic retention aids or dual polymers consisting of cationic and anionic aids, were examined in connection with the internal addition of BP emulsions to the pulp suspensions. Retention was very poor, probably as a result of the nonionic property or very weak negative charge of the BP particles in the emulsion. The soaking method was then applied to obtain basic data on the strength and biodegradability of the composite sheets consisting of paper and BP, with and without other additives, with the aim of using simple and reproducible experiments, because the retention was almost 100% as a result of the physical entrapment.

Figure 1 illustrates the dry and wet tensile strengths of the composite sheets prepared with paper and 20% additions of EM901, EM301, or PL-1000. The samples were cured at 100°C for 20 min. EM901 and EM301 improved both the dry and wet strengths of the composite sheets, although EM901 was much more effective than EM301, probably because of its lower minimum film-forming temperature (MFT) (Table I). In contrast, PL-1000 did not improve either dry or wet sheet strengths. These results are probably attributable

to its very high MFT (Table I) and suggest that no PL-1000 film was formed on the composite sheets. However, if the curing temperature was increased above the MFT, it is believed that PL-1000 and EM301 would have a greater effect on tensile strength; from an energy-saving perspective, however, it is preferable for papermaking to be carried out under low temperatures. Therefore, the feasibility of EM901 as a component for composite sheets consisting of wood pulp paper and BPs was investigated.

Figure 2 demonstrates the effect of curing temperature on the strength of composite sheets prepared with 20% EM901. There was an obvious increase in both dry and wet tensile strengths, up to a curing temperature of 100°C, after which it leveled off. These results indicate that as a result of its MFT (60°C), EM901 melted and formed a thin continuous film tightly incorporated into the integrated structure of the composite sheet during 20 min of curing at 100°C. Thus, hereafter, the curing temperature was fixed at 100°C.

Figure 3 shows the effect of curing pressure at 100°C on the dry and wet strengths of the composite sheets. Both strengths increased only slightly with increasing pressure. For example, dry and wet strengths were enhanced by only 5–6% with a pressure of 4 kg/cm² compared with those without pressure. This might be the result of the very low compatibility between hydrophobic EM901 and hydrophilic cellulose, and the good film-forming nature of EM901, even at low pressures because of its very low MFT (60°C). This is supported in part by the densities of the sheets, which were identical regardless of pressure. Consequently, curing was undertaken in a convection oven without pressure for convenience and simplicity.

Effect of EM901 on wet and dry composite sheet strengths

Figure 4 shows sheet strength as a function of EM901 content; the basis weights of the sheets were identical

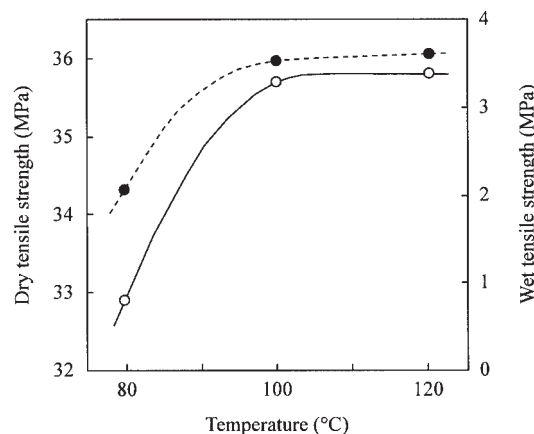


Figure 2 Effect of curing temperature on the strength of composite sheets composed of EM901 and paper (20 : 80). ○: Dry; ●: wet.

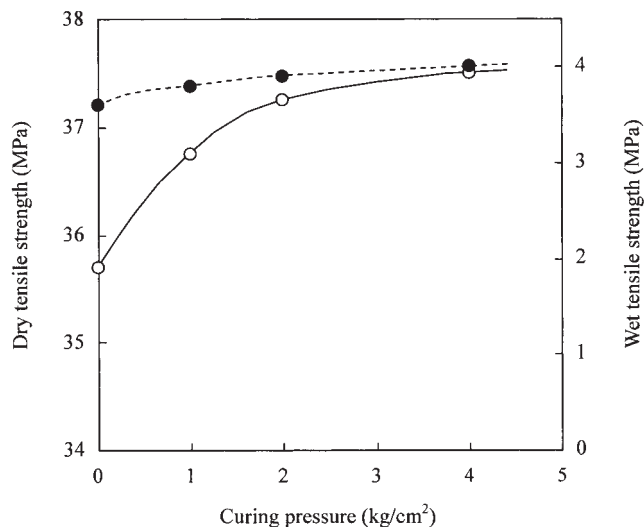


Figure 3 Effect of curing pressure on the strength of composite sheets composed of EM901 and paper (20 : 80). Curing temperature: 100°C; duration: 10 s. ○: Dry; ●: wet.

(70 g/m²). Dry strength increased only slightly with increasing EM901 content; for example, the strengths of composite sheets with 20 and 35% EM901 increased by only 7 and 10%, respectively, compared to paper sheets without EM901. This slight enhancement of strength might be the result of the somewhat higher strength of BP sheets (~ 55 MPa) compared to that of paper-only sheets. Both materials might behave independently in the composite sheets because there is little compatibility between pulps and poly(alkylene succinate) as a result of the hydrophilicity of the former because of its abundance of hydroxyl groups and the hydrophobicity of the latter because of its ester-only groups. In the future, it will be necessary to find a compatibilizer between the two to further improve the physical properties of the sheets. Wang et

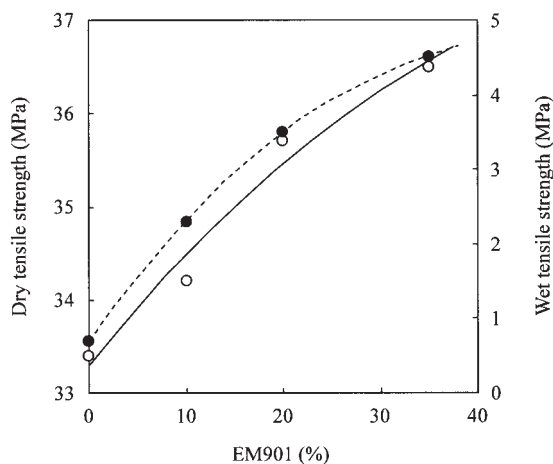


Figure 4 Effect of EM901 content on the strength of composite sheets composed of EM901 and paper. ○: Dry; ●: wet.

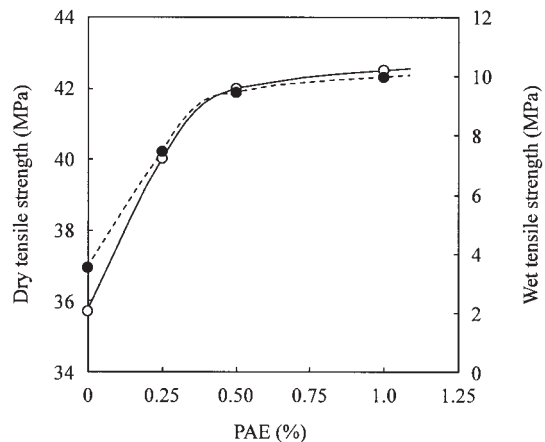


Figure 5 Effect of PAE on the strength of composite sheets composed of EM901 and paper (20 : 80). ○: Dry; ●: wet.

al.²² investigated the use of methylenediphenyl diisocyanate as a compatibilizer in starch/poly(L-lactide) blends.

On the other hand, wet strength increased significantly with increasing EM901 content, and sheets with 20 and 35% BP were approximately five and six times stronger, respectively, than paper-only sheets. This is the result of the high waterproof nature of poly(alkylene succinate) films.

Multiplicative effect of PAE/PVAm on the wet tensile strength and biodegradability of composite sheets

It is anticipated that the dry strength of the composite sheets developed here meets the requirements of practical disposable goods such as packaging, mulching, and seeding pots. On the other hand, the wet strengths obtained so far are thought to be insufficient at withstanding many of these applications. Therefore, paper strengthening was carried out using a typical wet-strength additive for papers.

Figure 5 illustrates the dry and wet tensile strengths of composite sheets containing EM901 and paper (20 : 80) prepared with the further addition of PAE. Increasing PAE levels moderately enhanced dry tensile strengths and significantly enhanced wet tensile strengths. When 0.5% PAE was added to the dry base, the wet strength (9.4 MPa) of the composite sheets with a 20 : 80 ratio of EM901 : paper was 2.7 times higher than that of composite sheets without additives (3.5 MPa) and 13 times higher than that of the base paper sheets (0.73 MPa). The dry strengths of the same sheets were 1.17 and 1.25 times higher, respectively. The significant difference between wet and dry strengths might be the result of the enhancement mechanisms.

Dry paper strength is mainly the result of fiber bonds, which are thought to be caused by multiple

hydrogen bonds within the area between the contacting fibers. It is thus preferable for the dry strength additives to be distributed only on the outer surfaces of the fibers. Theoretically, the higher the molecular weight, the higher its effectiveness, although the molecular weights of commercial dry-strengthening additives are usually a couple of hundred thousand because those with an even higher molecular weight have a tendency to disrupt paper formation. On the other hand, wet strength is achieved by restricting fiber swelling and by making interfiber bonds more permanent in the presence of water. With respect to the mechanisms of paper strength improvement with the addition of PAE resin, Espy et al.²³ described that the azetidinium group formed through the intramolecular rearrangement of epoxidized amide groups can theoretically crosslink to other amino groups by homo-cross-linking and to cellulose carboxyl groups by hetero-cross-linking, the former of which is more probable. Furthermore, the molecular weight of wet-strengthening additives is usually lower than 10,000 and therefore they can penetrate into the pores of the fibers.

It was previously indicated that wet tensile strength often approaches a plateau when plotted as a function of resin content. As shown in Figure 5, our results also followed this trend; however, further enhancement of wet as well as dry strength is preferable in expanding the possibility for practical applications.

It is well known that polyethyleneimine (PEI) shows a degree of wet strengthening, although the mechanism by which it works is somewhat different from the resins discussed above, that is, from chemically reactive polymers such as PAE resin. It has been proposed that PEI functions by creating stronger intratomic bonding rather than homo- or cocrosslinked networks.^{23,24}

We tried to use PEI and PVAm-L with low molecular weight (Table II), but they had little effect on strength enhancement when applied with PAE. PAE, PEI, and PVAm-L can penetrate easily into the micropores of cellulose pulps because of their relatively low molecular weights. It is thus considered that these chemicals occupy reaction sites and compete with each other. PVAm with both amine and *N*-formamide groups and a high MW has an effect on paper sizing,¹⁷ suggesting the formation of stable PVAm complexes with resin-sized particles through hydrogen bonds and coordination bonds with aluminum cations. Consequently, a PVAm along with the PAE resin was applied to the composite sheets, resulting in a very high strength.

Figure 6 indicates the effect of PVAm hydrolyzation (amine group contents, Table II) on the dry and wet strengths of composite sheets consisting of EM901 and paper (20 : 80) when 0.5 and 0.2% of PAE and PVAm were added, respectively. Both the dry and wet

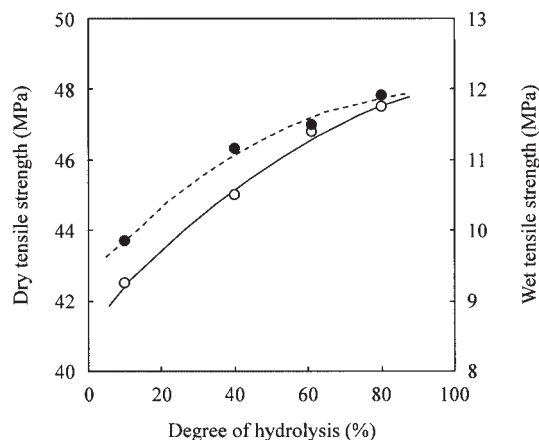


Figure 6 Effect of poly(*N*-vinylformamide) hydrolyzation on the strength of composite sheets composed of EM901 and paper (20 : 80). PAE: 0.5%; PVAm: 0.2%; ○: Dry; ●: wet.

strengths increased with increasing amine content. A 0.2% addition of PVAm-4, which was hydrolyzed by 80%, intensified the dry and wet tensile strengths by 14 and 27%, respectively, when added with 0.5% PAE, whereas only PAE slightly enhanced (1–3%) the strengths upon further addition of 0.2 to 0.5% PAE (total 0.7%). A very high wet strength can thus be achieved by a combination of PAE and high MW PVAm. It has been suggested that such a high molecular weight polymer cannot move into the micropores and remain on the outermost surfaces of the pulp²⁵; however, PAE can penetrate into the pores of fibers as described earlier. These observations thus suggest that the wet-strengthening mechanisms of these two polymers are independent, whereas their wet-strengthening effects are additive or possibly multiplicative.

Under usual papermaking conditions approximately half of the amine groups on PVAm are dissociated, allowing electrostatic interactions with the fibers, whereas the unprotonated amines are available for hydrogen bond formation. It is supposed that charged amines interact electrostatically with the paper fibers, whereas the free amines combine with the fiber surfaces, particularly in the presence of water. However, this observation remains unexplained and further investigation is required. This finding suggests, however, the possibility of a new class of cooperative polymer combinations.

Figure 7 shows weight loss in soil versus degradation time for genuine papers, composite sheets, and composite sheets with PAE/PVAm. Composite sheets with PAE/PVAm degraded with a lag time, however, showed little degradation. This suggests that a higher wet strength reduces biodegradability to some extent because hydrolytic attack by enzymes is restricted. The weight loss of composite sheets with PAE/PVAm reached 65% after 30 days, whereas the weight losses of composite sheets and genuine paper were 82 and

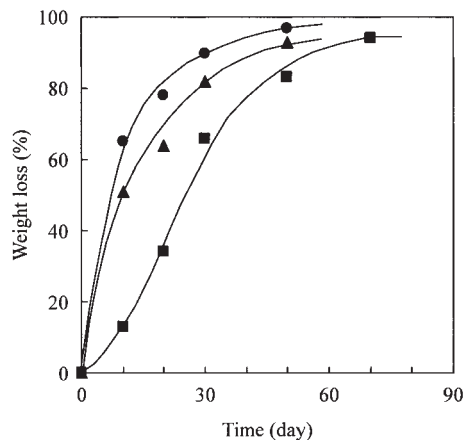


Figure 7 Weight loss in soil (pH 7.5) of genuine paper (●), and composite sheets composed of EM901 and paper (20 : 80) with (■) and without PAE-PVAm (▲).

90%, respectively, over the same period. Although the biodegradability of composite sheets was impeded by the addition of wet-strengthening additives, a 90% weight loss was realized after 60 days. Therefore, it is anticipated that the biodegradability of such composite sheets is within a permissible range.

CONCLUSIONS

Composite sheets with biodegradable polymers and paper had an increasing tendency to be stiff with increasing biodegradable polymer content, and the polymer films were formed on the surface of these sheets when the biodegradable polymer content exceeded 20%. It was qualitatively revealed that these films showed water repellency and heat sealability. It is suggested therefore that the physical properties and biodegradability of composite sheets or molds are easily controlled by varying, for example, the kinds and contents of biodegradable polymer and/or strength-

ening additives used, and by altering the curing conditions.

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