



A GREEN APPROACH FOR COATING AND CHARACTERISATION OF PAPER WITH BIODEGRADABLE POLYMER (PVA): A REVIEW

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(Received : 17.11.2012; Revised : 30.11.2012; Accepted : 02.12.2012)

ABSTRACT

Coatings find their application in various fields depending upon the purpose for which they are required. Paper coated with whatsoever type and nature of polymer, finds its extensive applications depending upon the nature of utility. Coated papers, since several years, are used for lining of containers to protect the contents from damage during transportation and handling. Paper bags of coated papers are used to handle and protect the material from humidity. Currency notes are made from coated papers. Coating is of great importance in order to enhance the physical and mechanical properties of paper, to increase the durability of paper and to give extra strength to paper. Coating with conventional polymer like HDPE, LDPE, PVC, PP is quite suitable for the purpose but it is not biodegradable. Hence it is harmful to environment. Search of PVA made it possible to serve as eco-friendly polymer. Earlier, PVA coating by making aq. solution of PVA was done on papers for packaging purposes. Thickness increased to 158 μm , density increased to 0.46 g/cm^3 . Tensile and bursting strength improved remarkably. PVA coating was done for improving fastness properties of ink jet prints. Light fastness of paper improved from 2.32 for unprinted paper to 44.7 for printed paper. PVA coating was done on food granules for their protection from dust formation, moisture gain and breakage. Water content of uncoated paper was 5.17% whereas that of coated paper was 4.58%. PVA coating was done on SPIONs for functioning of medical device systems. MRI was sharp and contrast impression was observed for easy diagnosis of the disease. PVA coating was done on orthopedic implants in bone surgeries. Corrosion inhibition efficiency reached a value of 79.8%.

Key words: PVA, SPIONs, Ink-jet prints, Food granules, Orthopedic implants.

INTRODUCTION

Some mechanical properties of paper were studied with the aim to create biodegradable polymer composites for packaging materials¹. Tensile and tear properties of the tested papers depended not only on paper density (or void content) but also on some other paper structure features. As polymers are applied from solution, the impact of solvent on the mechanical properties of paper was investigated². For primary packaging paper is often treated, coated, laminated, or impregnated with other more resistant and durable material to improve its functional and protective properties³⁻⁶.

Dace Cerpakovska and coworkers studied improvement and enhancement in physical and mechanical properties of paper¹. The result on paper characterization, experimented on seven types of paper is shown in Table 1.

Table 1: Paper characterization

S. No.	Designation of paper	Density, $dpap, g/cm^3$	Grammage, $ms\ pap, g/m^2$	Thickness, $hpap, \mu m$	Voids content, $\phi voids, vol. part$
1	FL 70 (FP)	0.460	73.0	158	0.697
2	ST 70 (KP)	0.566	70.3	124	0.627
3	KP 90 (BP)	0.668	91.4	136	0.560
4	SC 45 (BP)	0.745	45.4	60	0.509
5	SC 115 (BP)	0.786	114.1	145	0.482
6	CY 90 (BP)	0.847	89.4	105	0.442
7	ML 150 (BP)	0.914	151.5	165	0.398

Impact of solvent was studied by testing unsoaked and solvent soaked paper by optical microscope images. The structure of two papers before and after soaking with the solvents is illustrated in Fig. 1. It can be observed that both water and chloroform affect paper structure. Some areas of samples have become more fibrous, while some others look more homogeneous than before treatment. The optical microscopy images as well as results of tests of mechanical properties give evidence that water has a greater impact on structural changes of paper than chloroform.

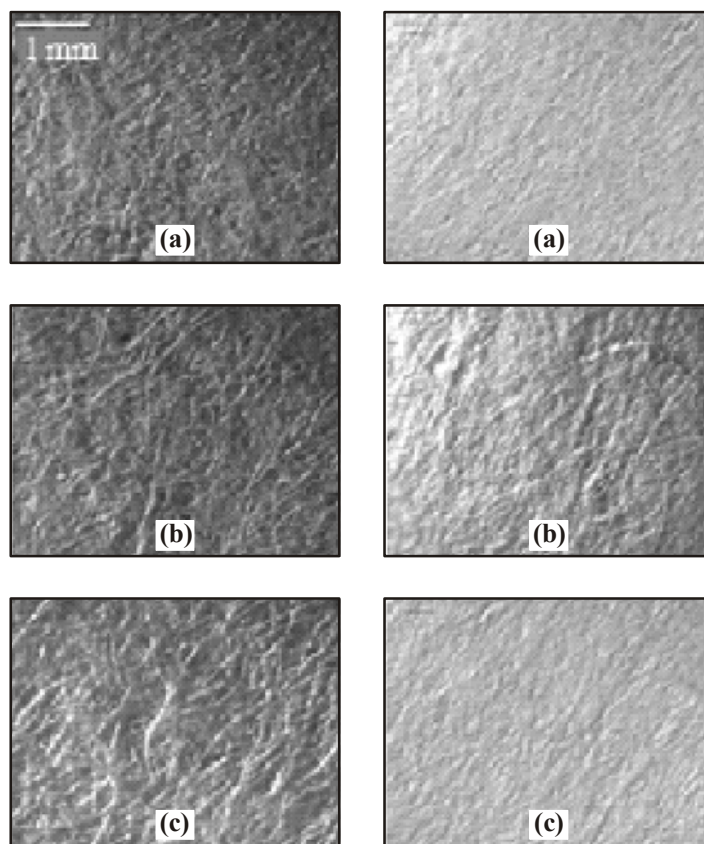


Fig. 1: Optical microscopy images of FL 70 (1) and ML 150 (2). A – Non-soaked paper; B – Water-soaked paper; C – Chloroform-soaked paper

Katri Vikman⁷ studied fastness properties of ink jet prints on coated papers.

EXPERIMENTAL

The focus of the experimental work is on the influences of the coating polymer system of kaolin coated papers on light fastness. Consequently, a pilot paper set was generated, where the absorption properties and thenet-charge of the coatings were altered by means of variations in the polymer system, see Table 2⁸⁻¹⁰.

Table 2: Polymer compositions of the coating colors of the pilot paper set¹¹

Paper	Binder type	Amount [pph]	Dispersant type	Amount [pph]
A1	PVA	5	CMC	1
A2	PVA	10	CMC	1
A3	PVA	15	CMC	1
A4	Anionic SA	5	-	-
A5	Anionic SA	10	-	-
A6	Anionic SA	15	-	-
A7	Anionic SA	20	-	-
A8	Anionic SA	10	Oxidized starch	4
A9	Weakly cationic SA	10	Weakly cationic starch	4
A10	PVA	5	Poly-DADMAC	3
A11	PVA	10	Poly-DADMAC	3

Light fastness was measured with SCAN-P 60:87 standard and results are shown in Table 3.

Table 3: The data on paper properties and on light fastness¹²

Paper	Porosity		Roughness		Unprinted paper	Light fastness ΔE^* (100 h)		
	Av. Pore diameter [μm]	Bendtsen air perm [mL/min]	A [deg.]	Bendtsen roughness [mL/min]		AR 249	DY 86	DV 107
A1	0.099	27	4.80	90	2.32	44.70	23.92	24.98
A2	0.088	15	4.55	100	2.55	45.86	21.39	23.05
A3	0.096	8	5.35	140	3.06	43.45	15.17	21.93
A4	0.089	30	4.12	75	2.61	45.42	32.16	30.46
A5	0.085	24	4.10	60	2.79	45.61	33.42	31.51
A6	0.082	14	3.95	105	3.11	43.37	31.57	26.33
A7	0.076	5	4.18	85	3.30	38.32	26.54	21.71
A8	0.088	11	4.43	110	3.12	44.94	30.11	20.29
A9	0.089	20	4.86	115	2.12	43.03	30.56	22.43
A10	0.096	95	4.78	135	2.34	53.76	30.69	24.51
A11	0.092	75	4.97	150	2.48	49.99	22.82	20.85

Giacomo Perfetti et al.¹³ studied influence of PVA coating on strength and damage of granules. Many of the food granules produced have an outer coating to prevent the deterioration, dust formation and in the end the breakage of the particle. It should be strong enough to survive forces exercised during handling and transportation.

Alke Petri-Fink et al.¹⁴ studied effect of cell media on SPIONs after coating with PVA. The synthesis and characterization of nanoparticles have been a focus of intensive research for more than 10 year since they play an important role in electronics, catalysis, biology and medicine. Nanoparticles that can be biochemically functionalized are potential medical device systems that can be used in many different biological and medical fields of application.

Transmission electron microscopy

Transmission electron microscopy (TEM) was carried out with individual and coated particles (Fig. 2). Primary uncoated SPIONs showed ellipsoidal iron oxide particles with an average size of 9 nm (Fig. 1a). Two perpendicular diameters were measured for 100 particles, and average axle lengths of 10 ± 2 nm and 8 ± 2 nm were determined. An aspect ratio of 1.2 ± 0.2 was determined, corresponding to the results obtained by other groups¹⁵. PVA-coated iron oxide particles (PVA-SPION) were also observed by means of transmission electron microscopy (Fig. 2b). Although the polymer was responsible for image blurring (due to film formation), it seemed that the particle spatial distribution was more homogeneous and that the minimum distance between the particles was larger compared to the uncoated particles for equivalent concentrations. Iron oxide particles embedded in a PEI polymer matrix (Peispion) are shown in Fig. 2c. Each nanoparticle was associated with more than one strand of the PEI and, likewise, each strand of PEI attached to more than one nanoparticle, resulting in a bridging aggregation. An average bead size of 27 ± 12 nm was obtained for sample R = 2 (PEI : Fe mass ratio of 2) using 25 kDa PEI by measuring 360 beads by transmission electron microscopy. Comparable PEI iron oxide nanobeads using higher molecular weight (800 kDa) PEI showed an average size of 200 nm¹⁶.

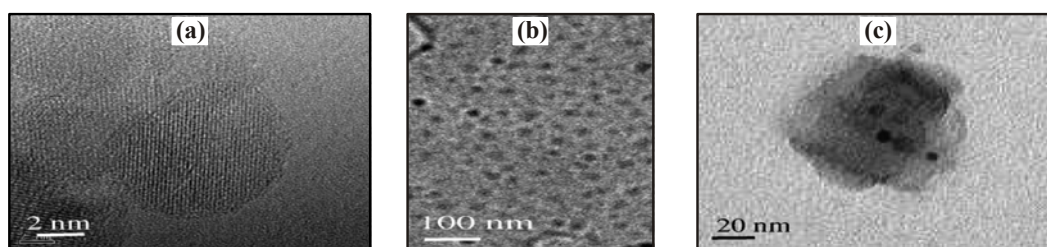


Fig. 2: (a) High resolution transmission electron micrograph showing slightly faceted crystalline particles in the 10 nm range, (b) Bright field TEM picture showing a homogeneous spatial distribution of the PVA coated iron oxide particles, (c) Bright field transmission electron micrograph showing one Peispion bead

A. Samide et al.¹⁷ formed thin film of PVA on stainless steel for orthopedic implant applications. The metal materials used as implants must be biocompatible. Biocompatibility means absence of corrosion or allergic reactions. Corrosion is one of the most important processes that affects the physical properties, functionality and the durability of medical devices made of metals and their alloys used as implants^{5,10,17,18}. The 304L steel with high chromium (18-20% in weight) and nickel (8-15% in weight) contents is usually used for making an implant such as femur prosthesis. This steel is well tolerated by the human body but after a long contact of the metallic prosthesis with the body fluids some leaching of the alloy ions into the human fluids occurs. It has been proved that chromium hexavalent ions are even carcinogenic^{7,19}. PVA and its composites may be applied to tissue engineering as a long-term or permanent scaffold due to their good

biocompatibility, elasticity and hydrophilicity²⁰. Furthermore, it was found that PVA are very stable in the body because no degradation product was detected in the urine and feces²¹. The results of corrosion data of 304L stainless steel showed that the corrosion current density decreased and polarization resistance increased in presence of PVA, which indicates that this compound acts as inhibitor. The value of inhibition efficiency reached an approximate value of 79%¹⁷.

Surface characterization

The electrochemically corroded stainless steel samples by Tafel polarization in both a PS solution without PVA and PS with 0.6 mM PVA were tested by SEM/EDS and XPS surface analysis; these indicate formation of superficial layer providing a very good protection on the corroded electrode, in the presence of PVA.

SEM observation

The SEM images of 304L stainless steel surface before corrosion (Fig. 3a) and after occurrence of the corrosive processes in PS (Fig. 3b) and in PS containing 0.6 mM PVA (Fig. 3c) are presented. In case of corroded 304L stainless steel in PS without PVA a non-uniform layer can be observed (Fig. 3b). When PVA was used the texture is modified and the layer which was formed on the surface is more uniform. It can be seen that the surface morphology shown in the case of PS containing 0.6 mM PVA (Fig. 3c) is significantly different and more regular than that obtained in PS without PVA (Fig. 3b).

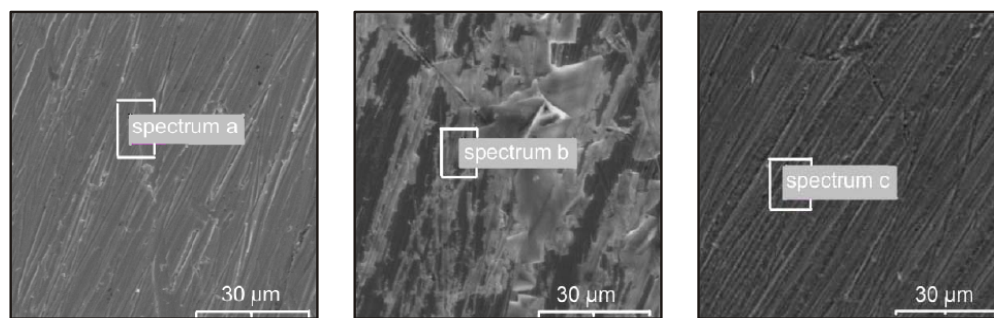


Fig. 3: SEM images of 304 L Stainless steel semi column a-before corrosion, after corrosion, b-in PS without PVA, c-in PS containing 0.6 mM PVA

EDS surface composition

The 304L stainless steel spectrum before corrosion process (uncorroded sample) is presented in Figure 4 (spectrum a). The main difference between of the corroded sample in PS without PVA (spectrum b) and the uncorroded sample (spectrum a) consists in a considerable decrease of Fe, Cr and Ni peak heights. Moreover, after corrosion in PS blank (spectrum b) the presence of a considerable amount of Cl and Na elements on the surfaces of stainless steel can be noticed. This demonstrates the formation of a thick, non-uniform and porous layer on the corroded sample surface, consisting of NaCl; the surface layer on stainless steel is not stable and the composition changes by incorporation of ions and molecules. For the sample corroded in PS containing 0.6 mM PVA (spectrum c) a superficial layer on stainless steel was formed. From estimation of the EDS peaks of Fe, Cr, Ni and Mn (spectrum c), this layer has a smaller thickness than the one formed in the corrosion process without PVA, indicating that a thin film on the stainless steel surface was formed.

The EDS peaks of oxygen and carbon (elements which are found in the chemical structure of PVA macromolecule) are also observed in the “spectrum c”. This indicates that the substrate is covered with an organic thin film which containing small amount of Na and Cl, in good agreement with previous

considerations. The ratio between carbon atoms and oxygen atoms is 2/1 (see spectrum c), indicating that this film consists in PVA; then, it can be considered that the composition of layer measured by EDS consists in PVA thin film containing of small amount of other elements, such as: Na, Cl.

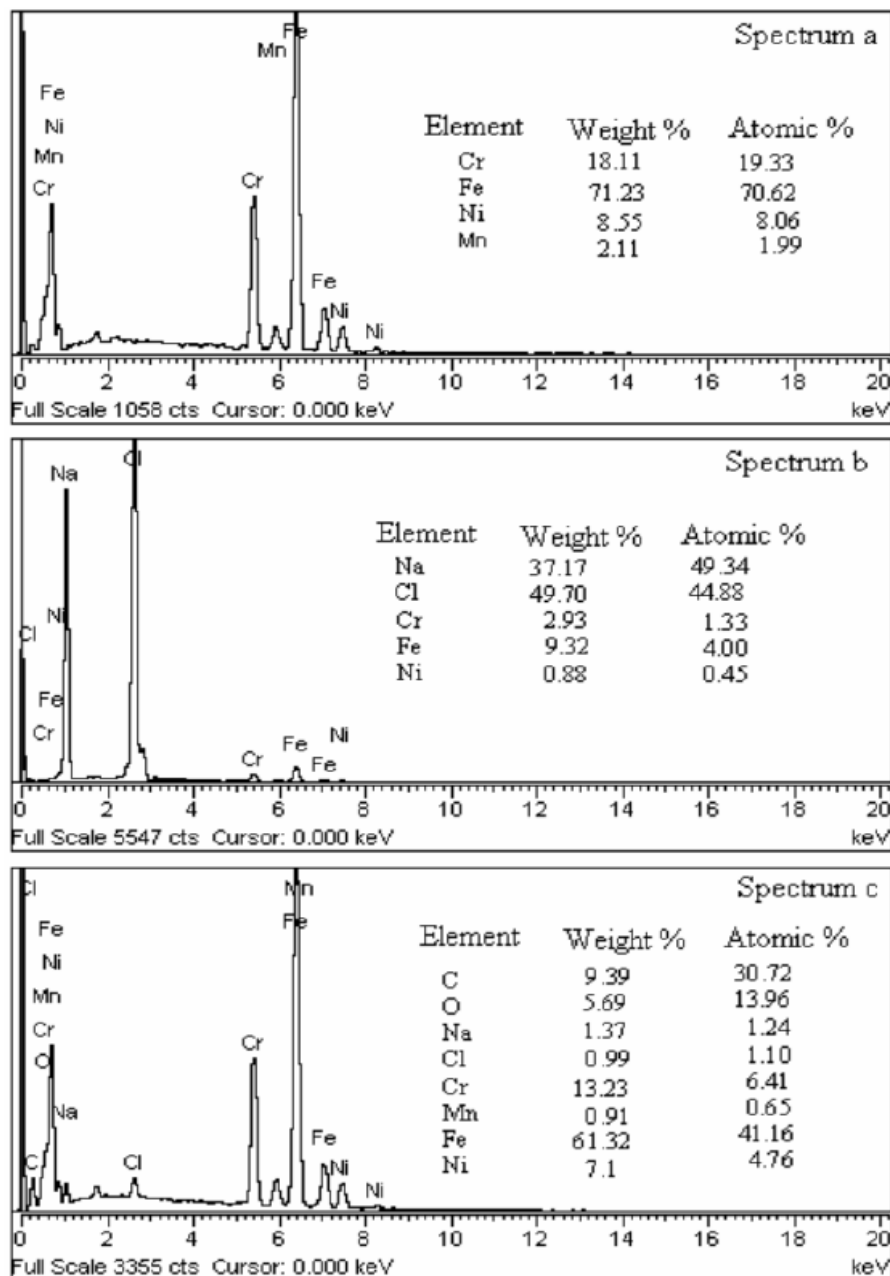


Fig. 4: EDS spectra of 304 L stainless steel semi column, a-Before corrosion, After corrosion, b-in PS without PVA, c-in PS containing 0.6 mM PVA

RESULTS AND DISCUSSION

Performance tests

As prescribed & specified by TAPPI (Technical Association of Pulp & paper Industries) taken from “Testing of paper”.

Test result of uncoated paper and PVC coated paper

Test	Values for uncoated paper	PVC coated paper
GSM (10 × 10) cm	45	55
Thickness (µm)	5.0	5.4
Bursting strength (Kg/cm ²)	1.00	1.25
Tearing strength (mN)	-	-
Average tearing force (gm- force)	36.65	44.85
Tear factor	52.3	81.549
Cobb value	22	0

CONCLUSION

PVA coating on paper showed remarkable improvement in bursting strength, tensile strength, tearing strength and cobb value. Formulation of aq. PVA solution with ingredients' like starch solution and Japanese clay could make development in further research with an intention to –

- (i) Maintain the various physical and mechanical properties.
- (ii) Bring out glaze look to paper.
- (iii) Curtail PVA consumption to minimum possible extent.

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