Proceedings of the Estonian Academy of Sciences,
2009, **58**, 1, 40–44
doi: 10.3176/proc.2009.1.07
Available online at www.eap.ee/proceedings

MATERIALS SCIENCE

Characterization of various kinds of paper as reinforcement for biodegradable polymer composites

Dace Cerpakovska*, Martins Kalnins, Velta Tupureina, and Anda Dzene

Institute of Polymer Materials, Riga Technical University, Azenes 14/24, LV-1048 Riga, Latvia

Received 2 June 2008, accepted 9 October 2008

Abstract. Some structural characteristics and properties of a diverse paper selection were studied with the aim to create biodegradable polymer composites for packaging materials. Paper in such composites would serve as a reinforcement and biodegradable polymer as a matrix. 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 for composite production are applied from solution, the impact of solvent on the mechanical properties of paper was investigated.

Key words: polymers, paper, biodegradable polymer composite, tensile strength, tear resistance.

INTRODUCTION

The principal functions of food packaging are to carry the food product, to protect the product from outside impact and damage, and eventually to provide consumers with ingredient and nutritional information on the product. The key to successful packaging is the selection of proper material and package design that best satisfy competing needs. In particular, interaction between the packaged product and the properties of the packaging material plays an important role in maintaining an acceptable quality of the product for a prolonged time. Materials that provide optimum protection and safety of product are preferred [1].

Paper and paperboard are the oldest and most versatile packaging materials available on market today. Besides their undeniable practical qualities, paper and paperboard are manufactured from natural and renewable raw materials and are both recyclable and biodegradable [2,3]. Environmental concerns, including the growing cost of petrochemical products, have made renewable materials more attractive as an alternative for synthetic packaging materials [4,5]. In addition, the use of long-lasting polymers as packaging materials for short-lived applications is not entirely reasonable [6].

However, because of poor functional barrier properties of paper, particularly its high moisture sensitivity, and because it cannot be heat sealed, paper is not used to protect food products for long periods. When used as primary packaging (direct contact with product), paper is often treated, coated, laminated, or impregnated with other more resistant and durable materials to improve its functional and protective properties [1–3,7,8]. Moisture loss or gain can result in food quality loss and even spoilage [9].

In the current work essential characteristics of paper are studied with the aim to develop thereafter paper-based polymer composites in which paper functions as a reinforcing component but polymer is a matrix. To maintain the biodegradability of the composite material it is planned to combine nature friendly biodegradable polymers – polyhydroxybutyrate (PHB) and polyvinyl-alcohol (PVA) – with paper in the further examinations. Paper is a low-cost material, so it can reduce the cost of free film packaging material, because there is less polymer material needed for such reinforced product. Besides, biopolymers are of interest in the context of environmental protection [5,10,11].

As polymers for composite production will be applied from solution (water solution of PVA and chloroform solution of PHB), the influence of these solvents on paper characteristics and structure was

* Corresponding author, dace.cerpakovska@inbox.lv

examined. In this work properties characterizing the macrostructure of untreated and solvent-treated paper were measured and compared and also the tensile strength and tearing resistance of non-soaked and soaked papers were measured.

MATERIALS AND METHODS

Seven types of paper were chosen for the experiments. Strong wrapping paper, kraft paper (KP) ST 70; bleached papers (BP) SC 45, CY 90, KP 90, SC 115, and ML 150; and filter paper (FP) FL 70 were tested. Designation of paper contains abbreviation of paper name given by the manufacturer and approximate value of grammage (weight of 1 m^2).

As the characterization of the papers specified by the manufacturers was incomplete, essential macrostructure characteristics of paper were determined. Paper samples 100 cm^2 in area were prepared and their thickness was measured with a 'Mitutoyo' flat digital micrometer. Samples were weighed on a 'Precisa XB 220A' balance. From the obtained data density, the exact grammage and voids content were calculated, assuming that the paper constituents were cellulose and voids and ignoring other possible constituents of negligible quantity (Table 1).

The tensile strength and tear resistance of paper were determined with a 'Zwick/Roell' universal testing device. For tensile experiments samples were prepared and tested according to standard LVS EN ISO 1924-2 in machine and cross directions (MD and CD, respectively). For performing paper tear resistance tests, the test standard of trouser tear method LVS EN ISO 6383-1 was adjusted, and samples of 150 mm × 35 mm were examined both in MD and CD. Tear resistance was calculated dividing tearing force by sample thickness.

To evaluate the influence of solvents on paper structure the paper was soaked with solvent. The duration of solvent soaking was chosen taking into consideration the evaporation rate of the solvent in the process of composite production. Samples were soaked with water for 24 h and with chloroform for 1 h. After soaking the samples were dried at room temperature, weighed, and prepared for the determination of tensile and tear properties as described above.

The structural features of non-soaked and soaked paper were evaluated with an optical microscope 'Leica MZ16 A' with magnification ×30. For this examination the papers were previously glued on glass to achieve an even surface of the sample.

Table 1. Paper characterization

No.	Designation of paper	Density, d_{pap}, g/cm^3	Grammage, $m_{s\,pap}$, g/m^2	Thick-ness, h_{pap}, µm	Voids content, φ_{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

RESULTS AND DISCUSSION

No strict correlation between density and strength (σ_B) or elongation at break (ε_B) was observed in tensile experiments (Figs 1 and 2). Although there was a tendency for tensile strength and elongation at break to grow with increasing density, strength deformation characteristics of paper strongly depended on its category and structure, which are determined by the cellulose fibre length, aspect ratio, and the distribution of these characteristics.

The obtained results demonstrated that density alone did not determine the tensile properties of paper. The smallest elongation at break in MD was observed for FL 70 and SC 45, whereas the elongation of the other

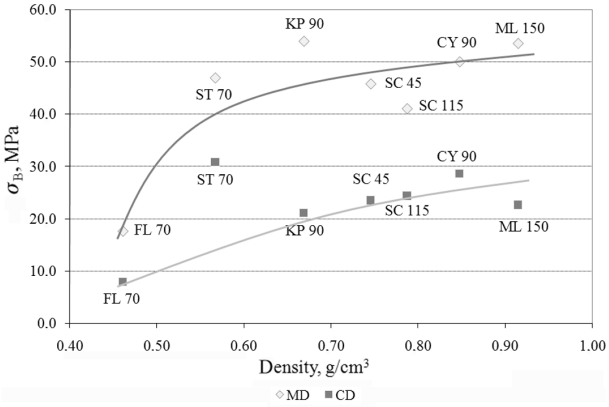

Fig. 1. Tensile strength of untreated papers.

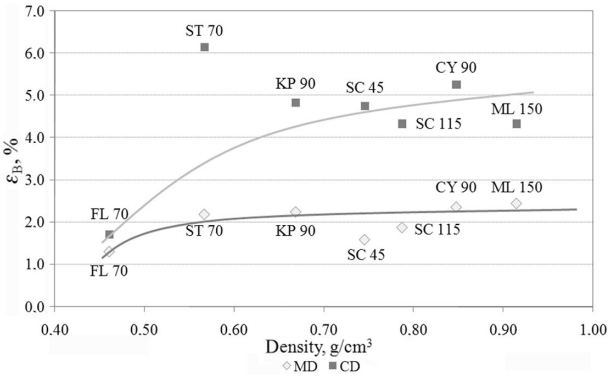

Fig. 2. Tensile elongation at break of untreated papers.

five papers was similar to one another – between 2% and 2.5%. The elongation of FL 70, the paper with the smallest density, had risen from 1.3% in MD to 1.7% in CD, but the elongation of other papers had increased twice and more. Remarkably diverse tensile strength and elongation data were shown by kraft paper ST 70 tested in CD. It had both the highest tensile strength and the largest elongation at break.

Tear test results are given in Fig. 3. The significant role of paper category and structure is the reason for lack of interconnection between tear resistance and paper density. Besides, there is no great difference between tear resistance (R) in MD and CD for papers ST 70 and SC 45, but for KP 90, CY 90, and ML 150 the difference between the two test directions is considerable.

Comparison of tensile strength data with tear resistance results did not disclose any direct relationship between these characteristics. Tensile properties of paper (Figs 1 and 2) are more dependent on density, whereas the results of tear experiments obtained indicate a considerable influence of paper structure parameters, e.g. fibre length and location, on tear characteristics. Both good tensile strength and tear resistance were demonstrated by ST 70. The poorest tensile strength was shown by the most porous paper FL 70; however, its tear resistance was the average of all paper test results. The thinnest paper, SC 45, had the weakest resistance to tear.

Mechanical properties of untreated paper and paper soaked with solvent were compared. Relative values of tensile strength in MD are demonstrated in Fig. 4. Here the tensile strength of solvent-soaked paper $(\sigma_{\mathrm{B\,MD1}})$ is related to the initial strength, which is the strength of non-soaked paper $(\sigma_{\mathrm{B\,MD0}})$ in this experiment, and also the non-soaked paper strength was related to itself $(\sigma_{\mathrm{B\,MD1}}/\sigma_{\mathrm{B\,MD0}} = 1)$ for more obvious depiction of changes in strength after soaking.

The influence of water on paper strength was higher than that of chloroform. Because water evaporates more

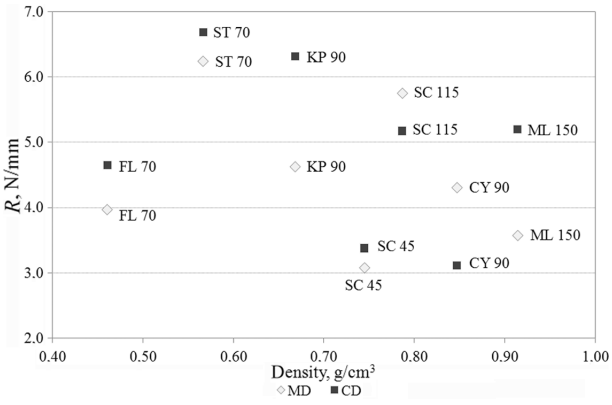

Fig. 3. Tear resistance of untreated papers.

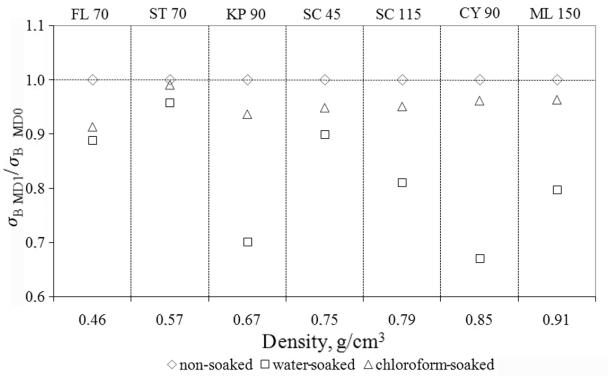

Fig. 4. Relative tensile strength in MD of non-soaked and soaked papers.

slowly than chloroform, it takes more time to dissolve paper constituents and somewhat destroy the structure of paper. On the other hand, the tensile strength of FL 70 obtained in CD after soaking had increased. Tear resistance decrease after soaking is not unambiguous. There were samples where the tear resistance had increased as a result of soaking (Fig. 5). It is clear that water absorption causes certain transformations in paper structure, most probably some changes in the distribution and loss of water-soluble paper adhesives.

Figure 6 demonstrates changes in paper weight after 5 and 60 min in water as compared to the initial weight of non-soaked paper dried at 105 °C. Paper soaks up its maximum water very rapidly. After 5 min its weight had grown to 100% of the weight of absolutely dry paper for ML 150, the paper with the highest density (smallest void content), and to 245% of the initial weight of FL 70, the most porous paper. However, afterwards a gradual increase in the amount of soaked water was observed until 60 min from the beginning of the experiment when equilibrium was reached. For ML 150 it was 126% while FL 70 soaked up 275% water of dry paper

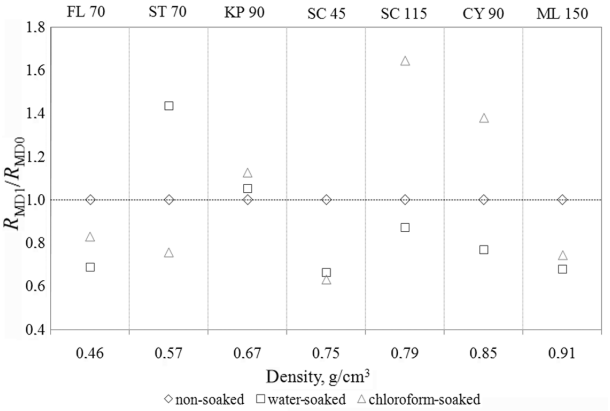

Fig. 5. Relative tear resistance in MD of non-soaked and soaked papers.

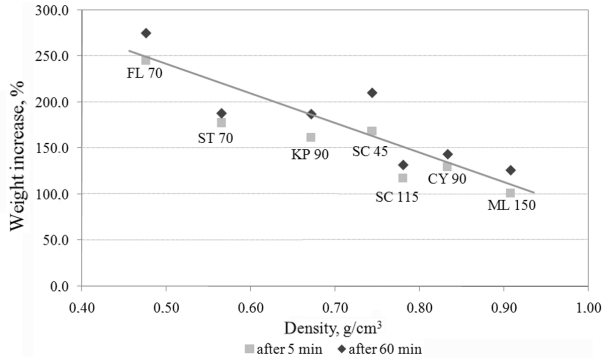

Fig. 6. Equilibrium water content as a function of paper density.

weight. Experimental data reveal that the amount of soaked water was directly related to paper density. The higher the density, the less water the paper could take up. On the other hand, there was no obvious influence of the water quantity that could be soaked up by paper on its mechanical properties. Tensile strength and tear resistance decreased for both FL 70 and ML 150 by a similar percentage.

It was not possible to estimate chloroform uptake of paper because of the fast evaporation rate of this solvent.

Weight of soaked and afterwards dried paper related to initial non-soaked paper weight (m_1/m_0) is shown in Fig. 7. There was a certain weight loss during solvent absorption, which explains changes in mechanical properties of the soaked paper. The greatest weight decrease and consequently the greatest tensile strength decrease was observed for water-soaked papers (Fig. 8). Data points of chloroform-soaked samples regarding weight changes look as dispersed as those of water-soaked samples in this figure, but the values of tensile strength of chloroform-soaked samples are located much closer to the initial position $(\sigma_{\mathrm{B\,MD1}}/\sigma_{\mathrm{B\,MD0}} = 1)$ than those of the water-soaked samples.

It could be predicted that the decrease of paper weight in the process of composite manufacturing will be negligible. Composite preparation technology

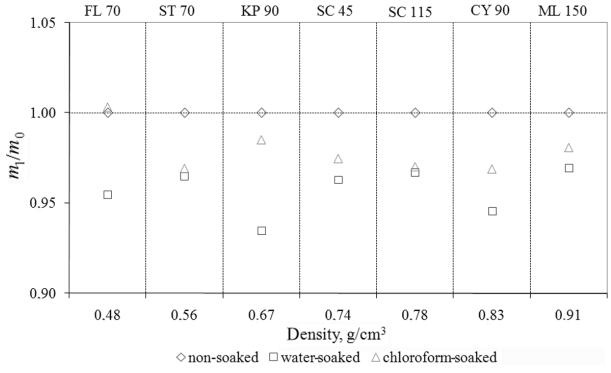

Fig. 7. Influence of solvent on paper weight.

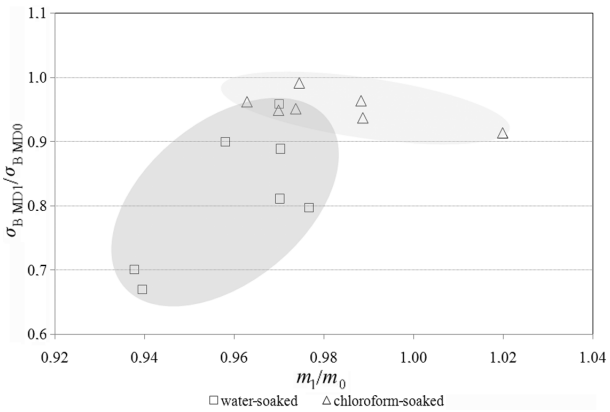

Fig. 8. Influence of changes in paper weight on tensile strength after soaking.

envisages quick soaking of paper with the polymer solution followed by drying. Hence extracting constituents will mostly remain in the composite. However, paper in the composite cannot lose its weight, and it is not excluded that some structural changes of paper will occur.

The structure of two papers before and after soaking with the solvents is illustrated in Fig. 9. It can be

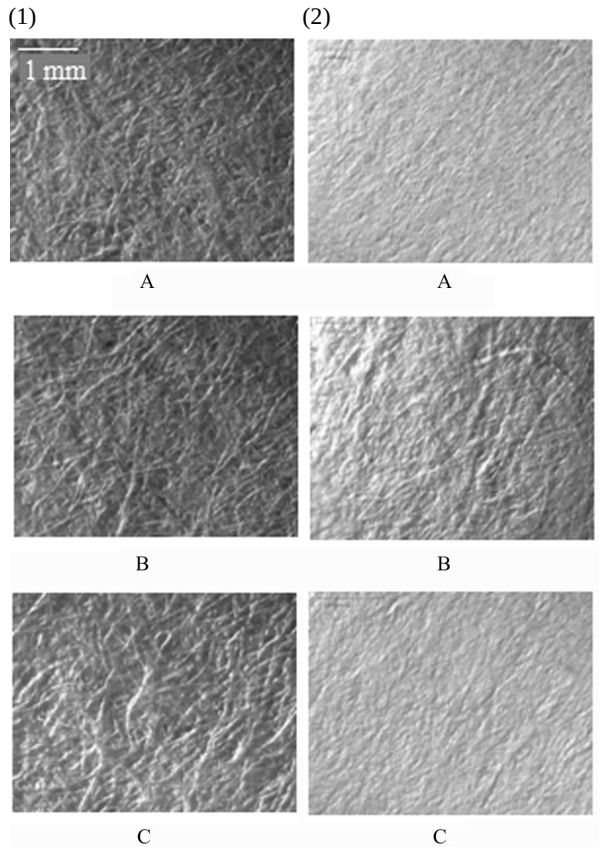

Fig. 9. Optical microscopy images of FL 70 (1) and ML 150 (2). A – non-soaked paper; B – water-soaked paper; C – chloroform-soaked paper.

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.

CONCLUSIONS

The tensile properties and tear resistance of paper depend on its structure. There is a tendency for tensile properties to increase with increasing paper density, whereas tear resistance is not directly connected to this structural characteristic of paper.

Paper soaks up its maximum amount of water very rapidly. Although paper takes up almost the whole amount of water in the first 5 min after immersion, equilibrium is achieved in an hour. The amount of soaked water is directly related to paper density. The higher the density, the less water the paper can take up.

The tensile strength of paper decreases after soaking with a solvent (water or chloroform) and subsequent drying. The decrease of tear resistance after soaking is not unambiguous. There were paper samples which showed an increase of tear resistance after soaking. This suggests that during solvent sorption some transformation in paper structure occurs that is more unfavourable to tensile properties than to tear resistance.

No obvious influence of the amount of water absorbed by paper on changes in its mechanical properties was observed. All mechanical test results revealed that the influence of water on decreasing paper strength was greater than that of chloroform. Optical microscopy images confirm this.

REFERENCES

1. Marsh, K. and Bugusu, B. Food packaging – roles, materials and environmental issues. *J. Food Sci.*, 2007, **72**, 39–55.
2. Gastaldi, E., Chalier, P., Guillemin, A., and Gontard, N. Microstructure of protein-coated paper as affected by physico-chemical properties of coating solutions. *Colloid. Surface. A*, 2007, **301**, 301–310.
3. Rhim, J.-W., Lee, J.-H., and Hong, S.-I. Increase in water of paperboard by coating with poly(lactide). *Packag. Technol. Sci.*, 2007, **20**, 393–402.
4. Gallstedt, M., Brottman, A., and Hedenqvist, S. M. Packaging-related properties of protein- and chitosan-coated paper. *Packag. Technol. Sci.*, 2005, **18**, 161–170.
5. Krook, M., Hedenqvist, M. S., Albertsson, A.-C., Hellman, A., Iversen, T., and Gedde, U. W. Barrier and mechanical properties of pulp fiber/polymer laminates and blends. *Polym. Eng. Sci.*, 2000, **40**, 143–156.
6. Kale, G., Auras, R., and Singh, S. P. Degradation of commercial biodegradable packages under real composting and ambient exposure conditions. *J. Polym. Environ.*, 2006, **14**, 317–334.
7. Pawde, S. M. and Deshmukh Kalim, A. R. Studies on surface properties of polymeric coated paper material. *J. Appl. Polym. Sci.*, 2006, **101**, 4167–4171.
8. Lauzier, C. A., Monasterious, C. J., Saracovan, I., Marchessault, R. H., and Ramsay, B. A. Film formation and paper coating with poly (β-hydroxyalkanoate), a biodegradable latex. *Tappi J.*, 1993, **76**(5), 71–77.
9. Steven, M. D. and Hotchkiss, J. H. Comparison of flat film to total package water vapour transmission rates for several commercial food wraps. *Packag. Technol. Sci.*, 2002, **15**, 17–27.
10. Lim, H.-A., Raku, T., and Tokiwa, Y. A new method for the evaluation of biodegradable plastic using coated cellulose paper. *Macromol. Biosci.*, 2004, **4**, 875–881.
11. Sanchez-Garcia, M. D., Gimenez, E., and Lagaron, J. M. Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohyd. Polym.*, 2008, **71**, 235–244.

Eri paberiliikide iseloomustus biolagunevate polümeerkomposiitide armeerimiseks

Dace Cerpakovska, Martins Kalnins, Velta Tupureina ja Anda Dzene

On uuritud eri paberiliikide mõningaid struktuuri iseärasusi ja omadusi eesmärgiga moodustada biolagunevaid polümeerkomposiite pakkematerjalide tootmiseks. Sellistes komposiitides on biolagunev polümeer maatriksiks ja paber tugevdavaks komponendiks. Testitud paberite tõmbe- ja rebimisomadused ei sõltu ainult paberi tihedusest (või vabast mahust), vaid samuti mõnest teisest paberi struktuuri iseärasusest. Kuna kasutatava polümeeri tootmine toimub lahuses, on uuritud ka lahusti mõju paberi mehaanilistele omadustele.