

**THE INFLUENCE OF WATER SORPTION-DESORPTION  
CYCLES ON THE MECHANICAL PROPERTIES  
OF COMPOSITES BASED ON RECYCLED POLYOLEFINE  
AND LINEN YARN PRODUCTION WASTE**

**G. Bakradze,<sup>\*,\*\*</sup> J. Kajaks,<sup>\*</sup>  
S. Reihmane,<sup>\*</sup> R. Krutohvastov,<sup>\*\*</sup>  
an V. Bulmanis<sup>\*</sup>**

**Keywords:** recycled low-density polyethylene, linen yarn production waste, eco-composites, cyclic influence of water, mechanical properties, coupling agent

*The effect of water on the mechanical properties (tensile modulus, ultimate tensile strength, tensile strain, and specific work at break) of both chemically treated and untreated composites based on a recycled low-density polyethylene and linen yarn production waste is analyzed. It is found that three water sorption-desorption cycles change the tensile properties of both the materials irreversibly. This effect is considered as the result of partial fracture of the fiber-matrix interface.*

**Introduction**

Some natural vegetable fibers have an outstanding potential as a reinforcement material in many widely-used thermoplastics [1-2]. Lately plant-fiber-reinforced composites have attracted growing attention of materials scientists because of a number of advantages of natural fibers over such traditional reinforcing materials as glass fibers and other inorganic fillers, namely the low cost, the relatively high toughness, the high specific strength and stiffness, the low density, the good acoustic and thermal properties, biodegradability etc., [2-3]. Plant fibers are also easily recyclable and fast renewable raw materials.

Currently there exists a technology for the manufacture of high-performance plant-fiber-based thermoplastic composites mainly from recycled materials [3, 4]. It was shown earlier [5] that polymer composites based on recycled low-density polyethylene (RLDPE) and linen yarn production waste (LW) have good strength and processing properties. This makes them attractive and ecologically prospective materials for various applications. The utilization of secondary polyolefines and linen yarn production waste can also solve some ecological and technological problems, thus providing a solution to environmental pollution by finding new uses for the polymer materials wasted previously.

Together with a number of good exploitation properties, natural-fiber-based composites have also some undesirable ones. The main drawback of the materials is their high hydrophilicity owing to the presence of hydroxyl groups in cellulose fibers. This defect can be overcome by treating the fibers with suitable chemicals to decrease the number of hydroxyl groups in the cellulose present in them [1-4].

The high level of moisture absorption, the poor wettability, and the insufficient interfacial adhesion between untreated fibers and a polymer matrix may lead to their debonding with age or during weathering. Chemical modifications of the fibers

---

\*Institute of Polymer Materials, Riga Technical University. \*\*Institute of Solid State Physics, University of Latvia, Riga, Latvia. Russian translation published in *Mekhanika Kompozitnykh Materialov*, Vol. 43, No. 6, pp. 839-848, November-December, 2007. Original article submitted December 28, 2005; revision submitted January 18, 2007.

TABLE 1. Decrease in Weight (%) after Several Water Sorption-Desorption Cycles

Cycle	Untreated fibers	DIC-treated fibers
I	0.99	0.98
II	0.98	0.92
III	1.68	1.32

make it possible to retard the moisture sorption process and, at the same time, increase the water resistance of such systems [3, 6]. Selected correctly, chemical modifications can also enhance the interfacial adhesion between the polar fibers and the nonpolar polyolefin matrix. This results in a considerably improved mechanical performance of compounds reinforced with chemically treated natural fibers [1-5]. In [5], it was found that, for RLDPE/LW systems, optimal technological and performance properties has a composite with 40 wt.% filler treated with 3 wt.% (of matrix weight) of diphenylmethane diisocyanate (DIC).

A second essential disadvantage of composites based on natural fibers is the significant variation in some of their characteristics caused by heterogeneity of the materials. Therefore, many parallel measurements are needed to obtain extensive and exact experimental information on the mechanical and other characteristics of the systems [5-7].

Our previous studies [5-8] have shown that chemically untreated compounds based on recycled low-density polyolefines and linen yarn production waste have a high water sorption ability and that the main mechanical properties of these composite materials strongly depend upon the amount of absorbed water. Modification of these systems with the coupling agent DIC allows one to considerably improve some their mechanical properties and diminish the negative influence of water on their tensile properties [7].

Investigations of the influence of absorbed water on the main tensile strength and deformation characteristics of the composites (with DIC-treated and untreated fibers) have shown [6, 9] that the negative effect of water is almost fully reversible after one water sorption-desorption cycle. However, in reality, materials are often subjected to the influence of a medium with a varying humidity (water sorption-desorption cycles). Therefore, it is important to clarify whether a decreased number of water sorption-desorption cycles will leave an effect on the mechanical properties of the composites or not.

In the present work, results on the effect of up to three water sorption-desorption cycles on the tensile properties (tensile modulus, ultimate strength, ultimate strain, specific work at break) of RLDPE/LW composites with DIC-modified and unmodified fibers are reported.

## Materials and Investigation Methods

In a series of experiments, a recycled polyethylene obtained from domestic films waste (Polyethylene industry, Adazi, Latvia) was used as the matrix material. The main components of the RLDPE were low-density polyethylenes with different melting temperatures; as an additive, 2 wt.% carbon black was used. The linen waste (Larelini, Latvia), used as a reinforcement, was a mixture of linen skin, pulp, and fibers. The content of LW in the composites was 40 wt.%. Fibers both chemically untreated and treated with 3 wt.% DIC were used.

Before compounding, the fibers were dried in an air oven at 75 °C for 24 h. The dried fibers were considered untreated. The fibers and the modifier were melt-mixed with RLDPE at 160 °C during 10 min in a laboratory Banbury mixer at 80 rpm. To rise the degree of dispersion, the batches were melt-blended in a two-roll mill. The resulting composition was removed from the roll mill, cooled, and ground in a knife grinder to obtain 3-mm chips. The chips were compression-molded in a frame-plate molder at 140 °C. The molding cycle consisted of 1-min preheating, 1-min molding under a 10-MPa pressure, and 1-min cooling under the pressure.

Before the first water sorption experiment, the specimen were dried at 25 °C for 24 h. Three water sorption-desorption cycles (30-day water sorption in distilled water up to a constant weight and 30-day water desorption in air up to a constant weight) at 25 °C in a thermostat were carried out to study the effect of water on the composites. The 30-day time was chosen according to the results of our previous investigations [8, 9], where the specimens got fully saturated with water in that time. After 30 days of drying, the weight of the specimens did not change under stationary conditions. After one and three water sorp-

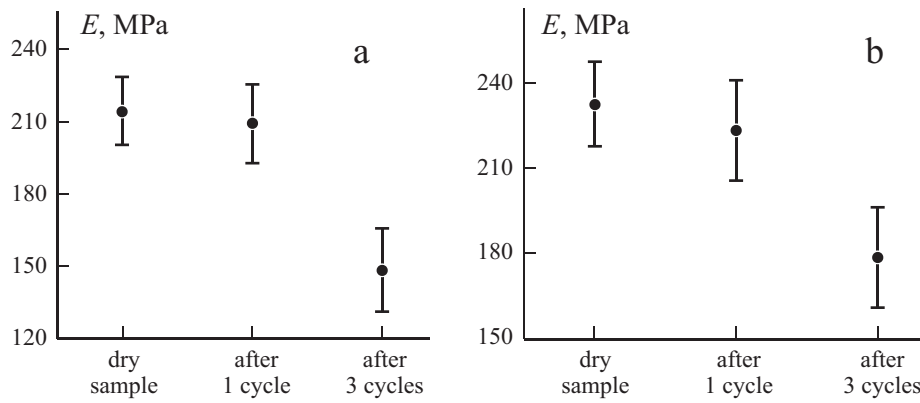


Fig. 1. Elastic modulus  $E$  of the untreated (a) and DIC-treated (b) systems in the initial dry state and after one and three water sorption-desorption cycles

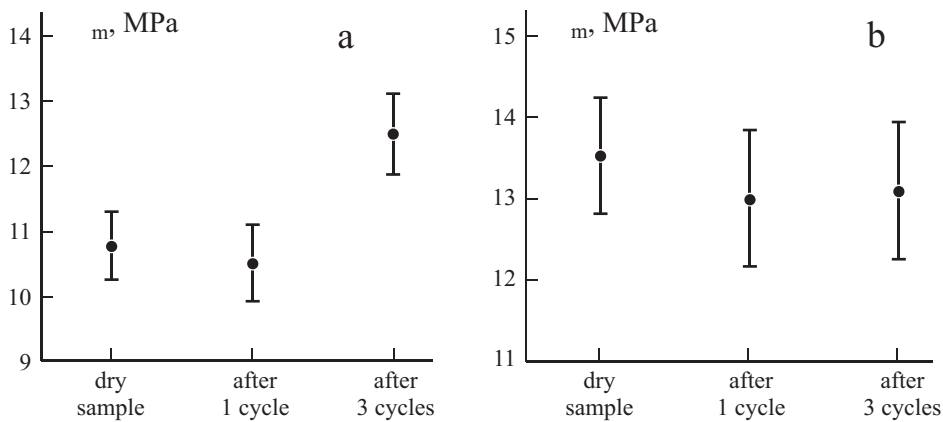


Fig. 2. The same for the ultimate tensile strength  $m$ .

tion-desorption cycles, the specimens were weighted to the nearest 0.001g and tested in tension. The properties of the dry specimens served as reference data.

The mechanical properties of the specimens were determined on an UTS-100 universal testing equipment at a deformation rate of 20 mm/min. The tensile modulus was determined within a deformation interval of 0.1-0.2 mm on a gage length of 10 mm. At least 20 specimens were tested in each experiment to get reliable results in view of the scatter of experimental data, and the results obtained were average. The computations were performed by using the software Statistica 6.0. In all the plots presented, the average values are shown together with their 95% confidence intervals.

The images of fracture surfaces of the test specimens were obtained on a Zeiss EVO 50 Scanning Electron Microscope (SEM) at an accelerating voltage of 6.49 kV. The specimens were previously coated with a 5-nm-thick layer of AuPd by using an SC7620 Sputter Coater.

## Results and Discussion

For both the composites, after the water sorption-desorption cycles, a considerable decrease in weight was observed, as seen in Table 1.

The nearly 1% drop in weight, in comparison with initial values for both the modified and unmodified specimens after the first water sorption-desorption cycle, is essential, taking into consideration that the amount of water absorbed by the modified and unmodified composites was about 5 and 11 wt.%, respectively. Obviously, this result demonstrates that, during exposure to water, not only does the water sorption occur, but also the leaching of low-molecular products from composite materials

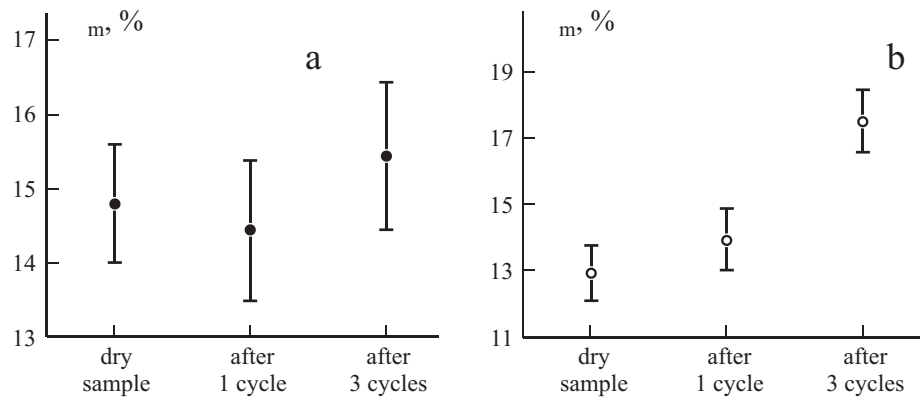


Fig. 3. Tensile strain at break  $m$  of unmodified (a) and DIC-modified (b) systems.

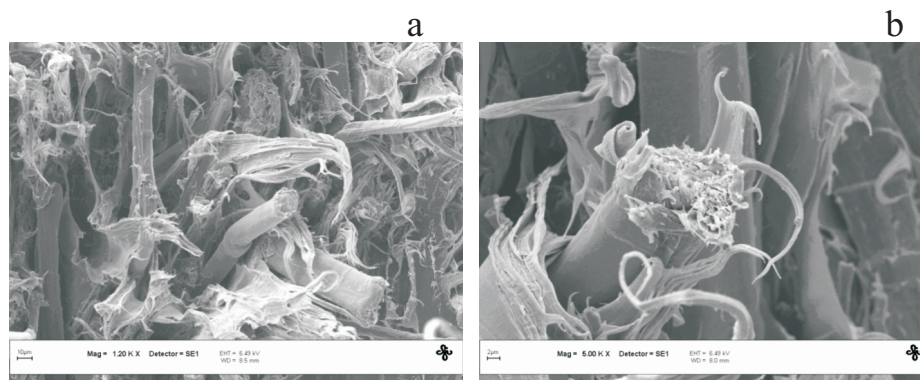


Fig. 4. SEM images of untreated (a) and DIC-treated (b) specimens in the initial dry state.

takes place. A similar phenomenon was also observed in [6, 10]. The source of the low-molecular products can be LW. Investigations [10] have shown that some species of LW can contain up to 3-4wt.% different low-molecular leaching products (e.g., pectines, inorganic salts, and terpenes), which, during water sorption, can migrate on the polymer/fiber interface and significantly weaken the interfacial interaction between the filler and the polymer matrix.

Figures 1-3 depict changes in the tensile properties of the composites studied after one and three water sorption-desorption cycles in comparison with their initial values.

The change in Young's modulus after the action of water, for both the untreated and DIC-treated systems, is presented in Fig. 1. As can be seen, after three water sorption-desorption cycles, the decrease in the modulus reaches 30% for the untreated system and 21% for the DIC-treated one.

The final values of the ultimate tensile strength  $m$  for the unmodified system, after one water sorption-desorption cycle, practically did not differ from its initial values (Fig. 2a), but  $m$  of the DIC-treated composites practically did not change even after the third cycle (Fig. 2b).

Figure 3 shows the influence of the number of water sorption-desorption cycles on the tensile strain at break  $m$  during the process. As in the case of elastic modulus  $E$ , after one water sorption-desorption cycle, the value of  $m$  almost did not differ from that of the specimens not subjected to the action of water. A slight increase in  $m$  for the untreated system (Fig. 3a) and a pronounced growth in  $m$  for the DIC-treated system (Fig. 3b) was observed after three water sorption-desorption cycles.

A similar dependence was also revealed for the specific work at break  $A_b$ . After one water sorption-desorption cycle, for both the treated and untreated systems,  $A_b$  reached its initial values in the dry state. After the third water sorption-desorption cycle, a significant increase in  $A_b$  for the treated system was observed.

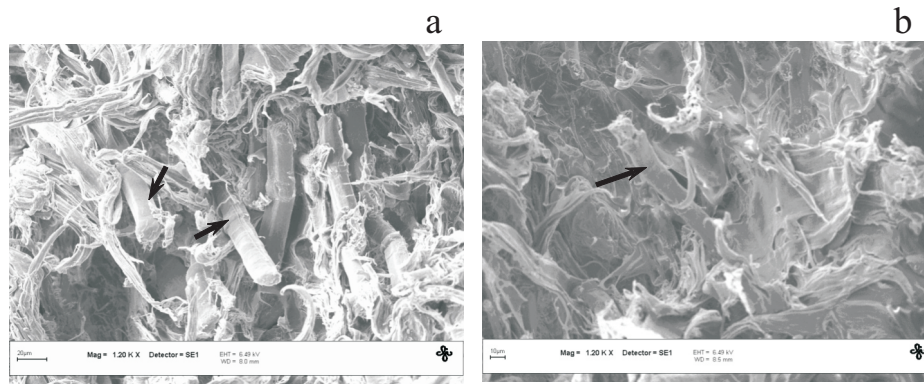


Fig. 5. The same after one water sorption-desorption cycle.

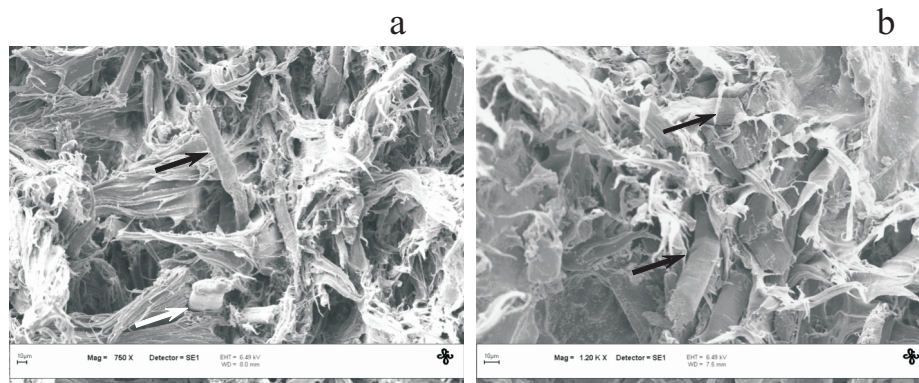


Fig. 6. The same three water sorption-desorption cycles.

The increase in  $\epsilon_m$  and  $A_b$  (as well as the decrease in the elastic modulus) for the modified system can be explained by the residual plasticizing effect of water molecules. It has been found earlier [6, 9] that DIC not only retards water penetration into the composite, but can also lower the water desorption rate. Therefore, it can be assumed that, even after 30 days of desorption, the modified specimens contained some residual amount of water, which had a plasticizing effect on the mechanical properties of the materials.

In order to correlate the data of the mechanical tests with microstructure of the composites, the SEM technique was used. Figures 4-6 show the fracture surfaces of the initial and water-affected specimens.

Figure 4a displays the fracture zone of an untreated specimen before its exposure to water. The clean fiber surface results from the poor bonding of the polar fibers to the nonpolar polyolefin matrix and from the failure at the fiber-matrix interface. When DIC is added (Fig. 4b), the linen fibers have the polymer on their surfaces, and the failure appears to have taken place in the matrix rather than at the fiber-polymer interface.

Figure 5 shows the failure zones of both treated and untreated specimens after one water sorption-desorption cycle. The fracture modes shown in Fig. 5 practically do not differ from those shown in Fig. 4, i.e., the clean fiber surface in the chemically untreated system (Fig. 5a) results from a poor bonding between the linen fibers and the RLDPE matrix, and therefore composite seems to have fractured along the fiber-matrix interface. If DIC is added (Fig. 5b), the linen fibers are still covered with the polymer, and the failure appears to have taken place in the matrix. This fact is in a good agreement with the tensile test data, which showed almost unchanged tensile properties of the materials after one sorption-desorption cycle.

However, after the third water sorption-desorption cycle, both the systems fractured along the fiber/polymer interface (Fig. 6). On the images of the systems with and without DIC, clean linen fibers without any trace of polymer are seen.

The debonding at the fiber/matrix interface in the DIC-treated composites can be explained by several factors. First, as an aggressive polar medium, water can migrate through fiber lumens on the fiber/polymer interface and damage the bonds ex-



isting between the two materials. This will result in a poor bonding on the interface. Second, as noted above, different leaching products from fibers can migrate in the wet environment on the interface and can weaken the interfacial interaction between the fibers and polymer. Finally, during water sorption, the linen fibers swell (the relative increase in their diameter can amount up to 40%) [4], as a result of which local concentrations of internal stresses arise at the fiber/matrix interface, and the fracture along the interface will require minimum energy.

## Conclusions

Thus, the results of the present research have shown that three water sorption-desorption cycles considerably deteriorate the tensile properties of the chemically treated and untreated composites considered, but the treated ones are affected less. The irreversible changes in their characteristics can be explained by partial debonding of the polymer matrix from the fiber surface during the water sorption-desorption process and by failure of the plant fiber/polymer matrix interface.

*Acknowledgements.* Georgii Bakradze would like to express deep thanks to the Latvian Education Foundation and the Riga Warnishes and Paints Factory for the financial support in this research.

## REFERENCES

1. R. M. Rowell, "A new generation of composite materials from agro-based fiber," in: P. N. Prasad, J. E. Mark, and T. J. Fai eds. *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities*, Plenum Press (1995), pp. 659-665.
2. A. R. Sanadi, D. F. Caulfield, and R. E. Jacobson, "Agro-fiber thermoplastic composites," in: *Paper and Composites from Agro-Based Resources*, Lewis publishers (1997), pp. 377-401.
3. Y. Li, Y.-W. Mai, and L. Ye, "Sisal fiber and its composites: a review of recent developments," *Compos. Sci. Technol.*, **60**, 2037-2055 (2000).
4. A. Bismarck, I. Aranberri-Askargota, J. Springer, T. Lampke, B. Wielage, A. Stamboulis, I. Shenderovich, and H.-H. Limbach, "Surface characterization of flax, hemp and cellulose fibers: surface properties and the water uptake behavior," *Polym. Compos.*, **23**, No. 5, 872-894 (2002).
5. J. A. Kajaks, S. A. Reihmane, and M. G. Tsiprin, "Physicomechanical properties of composites from recycled polyethylene and linen yarn production waste," *Mech. Compos. Mater.* **35**, No. 2, 139-146 (1999).
6. G. Bakradze, J. Kajaks, S. Reihmane, and V. Bulmanis, "Weathering effect on mechanical properties of natural fibers based recycled polyolefines composites," *Sci. Proc. Riga Tech. Univ. Ser.: Mater. Sci. Appl. Chem.*, **11**, 23-29 (2005).
7. J. E. Lejnieks, J. A. Kajaks, and S. A. Reihmane, "Evaluation of deformation and strength characteristics of composites based on low-density polyethylene and linen yarn production waste by the methods of mathematical statistics," *Mech. Compos. Mater.*, **40**, No. 1, 67-74 (2004).
8. J. A. Kajaks, S. A. Reihmane, and J. E. Lejnieks, "Effect of water on the physicomechanical properties of composites containing secondary polyethylene and linen yarn production waste," *Mech. Compos. Mater.*, **38**, No. 4, 351-356 (2002).
9. G. G. Barkadze, J. A. Kajaks, S. A. Reihmane, and J. E. Lejnieks "Correlation between the mechanical properties and the amount of desorbed water for composites based on a recycled low-density polyethylene and linen yarn production waste," *Mech. Compos. Mater.*, **43**, No. 5 (2007).
10. J. E. Lejnieks, J. A. Kajaks, and S. A. Reihmane, "Correlation between the mechanical properties and the amount of desorbed water for composites based on low-density polyethylene and linen yarn production waste," *Mech. Compos. Mater.*, **41**, No. 4, 351-356 (2005).
11. J. Biagotti, S. Fiori, L. Torre, M. A. Lopez-Machando, and J. M. Kenny, "Mechanical properties of polypropylene matrix composites reinforced with natural fibers: a statistical approach," *Polym. Compos.*, **25**, No. 1, 26-36 (2003).