

PHYSICOMECHANICAL PROPERTIES OF COMPOSITES
FROM RECYCLED POLYETHYLENE AND LINEN YARN
PRODUCTION WASTES

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The possibilities of utilizing wastes of linen thread production (chaffs, spinning and roving losses) in recycled polyolefin composites have been investigated. The wastes were mixed with recycled polyethylenes (produced from domestic and industrial film production wastes). The physico-mechanical properties (tensile strength, bending and tensile moduli, and water resistance) and the fluidity (melt flow-behavior index) for systems with a different filler content are estimated. Almost all the composite materials obtained have satisfactory fluidity (melt flow-behavior index is not lower than 0.07-0.15 dg/min). For all types of the composites, a slight increase in tensile strength and a considerable increase (3-7 times) in bending and tensile moduli were observed. The water resistance of the composites decreased with an increase in the filler content. The modification of filled systems with diisocyanates (diphenylmethane diisocyanate) improved the useful properties and water resistance of all the composites investigated.

In our previous investigations [1, 2], it was shown that linen yarn production wastes could be used for the modification of low-density polyethylene (LDPE). Such composites have good physico-mechanical properties (increased tensile strength, tensile and bending moduli), and they are ecologically promising materials. One of the main deficiencies of composites containing natural fibers is their inhomogeneity and relatively low water resistance [3, 4]. This disadvantage is the feature of systems containing linen yarn production wastes [1]. For reducing the inhomogeneity of the composites and increasing their physico-mechanical properties and water resistance, stearic acid and diphenylmethane diisocyanates (DIC) are used [2]. These coupling agents promote adhesion between the matrix and filler and improve the physico-mechanical properties and water resistance of the investigated composites. The best results are obtained for composites containing the DIC modifier (3% of the polymer weight) [2]. Thus, the tensile strength of the composite containing 40 wt.% linen wastes and 3 wt.% DIC is 1.4 times higher than that for the polymer matrix. Almost all modified systems (10-50 wt.% filler content and 3 wt.% DIC) maintain good fluidity. The melt flow-behavior index is not lower than 0.2-0.3 dg/min, and the absorbed water content (140 days in water at 23°C) of the composites (filler content up to 40 wt.%) is not higher than 4.5 wt.%. Therefore, the same modifier (coupling agent) is used in composites based on recycled LDPE and linen yarn production wastes.

Recycled polyolefins are widely used materials for obtaining different thermoplastic composites, because the main component in domestic polymer wastes are polyolefins. The utilization of recycled polymers provides not only additional material resources, but also solves ecological problems. From this aspect, wood

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TABLE 1. Physicomechanical Properties of Raw Matrix Materials

Materials	T_m , C	H_m , J/g	E_b , MPa		E_t , MPa	
RPE, grade A	122.3	85.1	220	230*	332	423*
RPE, grade B	109.8	89.4	106	110*	139	140*
LDPE, 15813-020	107.3	71.6	103		130	
HDPE, 276	134.1	164.7	-		-	

*Contains 3 wt.% of DIC

T_m and H_m are the melting temperature and the heat of melting, according to DSC data.

E_b and E_t are the elastic moduli in bending and tension.

and other natural vegetable fibers (NVF) are very promising for the production of environmentally friendly composite materials [3-6]. Composites containing NVF have technological advantages in comparison with traditional thermoplastic systems reinforced with high-modulus fibers. The authors of [3, 4], who utilized recycled polyolefins and wood fibers for the production of thermoplastic polymer composites by using different mixing technologies, concluded that the best quality of blends was observed when applying twin-screw extruders. In this case, the maximum filler content reached 60 wt.%. The tensile and flexural moduli of the investigated composites increased, while the tensile strength decreased with increase in the content of wood fibers. The relationship between the bending strength and the filler concentrations had a maximum at 40-50 wt.% filler content. Since especially low tensile strength was exhibited by systems with untreated wood fibers, the authors of [3-7] used interfacial compatibilizers. Low-molecular compounds like stearic acid and different high-molecular modifiers — maleated polypropylene (PP), PP modified with phenolic resins, ethylene vinylacetate copolymers (vinylacetate content 45-55 wt.%), bromobutyl rubber (20 wt.% bromine content), chlorinated polyethylene (40 wt.% chlorine content), etc. — were applied as coupling agents.

The most effective modifier for the investigated systems is found to be maleated polypropylene [7]. In [6], it is shown that by using coupling agents it is possible to realize chemical interaction between natural fibers (the main component of NVF is cellulose with hydroxyl groups) and different modifiers, for example, polyisocyanates.

Some papers dedicated to investigations of the service characteristics of composites on the basis of polypropylene and natural vegetable fiber wastes show that addition of wheat and flax straw fibers leads to a significant increase in tensile modulus of the composites, in comparison with the unfilled polypropylene [7, 8], despite the lack of strong interfacial bonding. A further increase in the tensile strength is achieved by adding 5 wt.% of maleated polypropylene, which promotes adhesion between the fibers and the polymer matrix. Maleated polypropylene is known as a coupling agent for sisal-polypropylene composites [9]. For the intensification of interfacial interaction, the authors recommend washing the fibers before chemical treatment to eliminate pectin substances. This favors an increase in mechanical properties and a decrease in water sorption of composites.

Two kinds of recycled polyethylene (RPE) from the firm "Polyethylene Industry" (Latvia) were used as a matrix material. Grade A is a recycled polyethylene produced from domestic polyethylene film wastes. It contains 2 wt.% carbon black. Grade B is a recycled polyethylene obtained from industrial film production wastes. The main component of RPE of grade B is LDPE of grade 15813-020; additives are 10 wt.% virgin high-density polyethylene, grade 276, and a 0.7 wt.% high-molecular lubricant (blend of LDPE and ethylene-vinylacetate copolymer). The thermal-physical characteristics of used raw RPE obtained on the basis of differential scanning calorimetry (DSC) measurements are given in Table 1 and the DSC curves are shown in Fig. 1. Linen yarn production wastes (LW) were used as a filler analogously in [1, 2].

Composites with filler content of 10-50 wt.% were prepared by mixing ($T = 160^\circ\text{C}$, $n_{\text{rot}} = 80$ rev/min, $t = 10$ min) in a Banbury mixer (the fillers before mixing were dried at 80°C , 24 h). The mixed compositions were passed through rolls for producing sheets which then were crushed in a rotary knife granulator. Plates for specimens used in physicomechanical tests were pressed at a temperature of 140°C and a pressure of 10

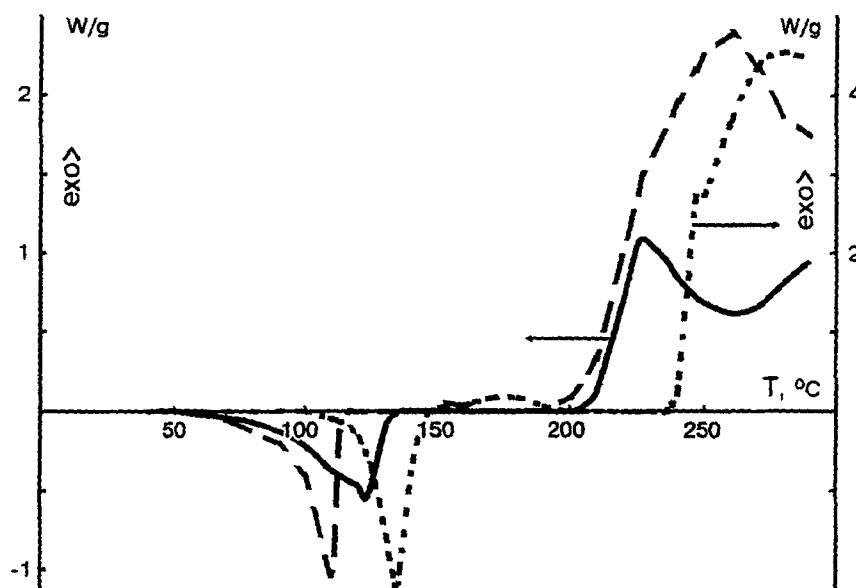


Fig. 1. DSC curves of raw recycled polyethylenes. Wastes of domestic film production, grade A (—), wastes of industrial film production, grade B (---), and HDPE, grade 276 (-·-).

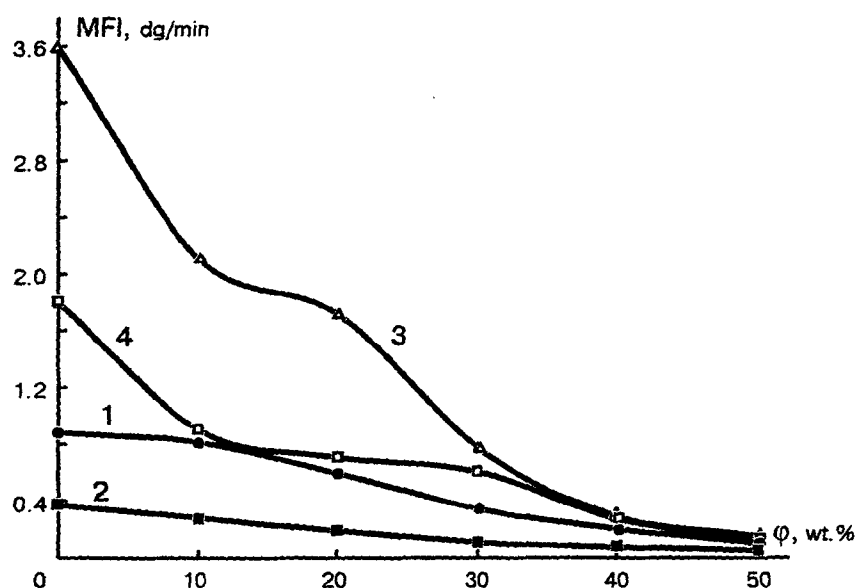


Fig. 2. Melt flow-behavior index as a function of LW content in RPE/LW composites. (●) — grade A, (■) — grade A with 3% DIC, (△) — grade B, and (□) — grade B with 3% DIC.

MPa for 3 min. Samples for tensile and bending investigations were prepared as in [2]. Diphenylmethane diisocyanate (DIC) with 3 wt.% of the polymer matrix was used as a modifier. The technological properties of the prepared composites were evaluated by measurements of the melt flow-behavior index ($T = 190^{\circ}\text{C}$, load = 31 N). The water sorption testing was performed as in [1, 2].

An increase in the filler content (Fig. 2) diminished the fluidity of all the composites (curves 1, 3 — without the coupling agent, curves 2, 4 — with addition of DIC). The coupling agent DIC in composites with a filler content of 0–40 wt.% caused an additional decrease in the melt flow-behavior index. This may be due to enhanced adhesion between the fibers and the polymer since DIC forms strong covalent bonds with the flax

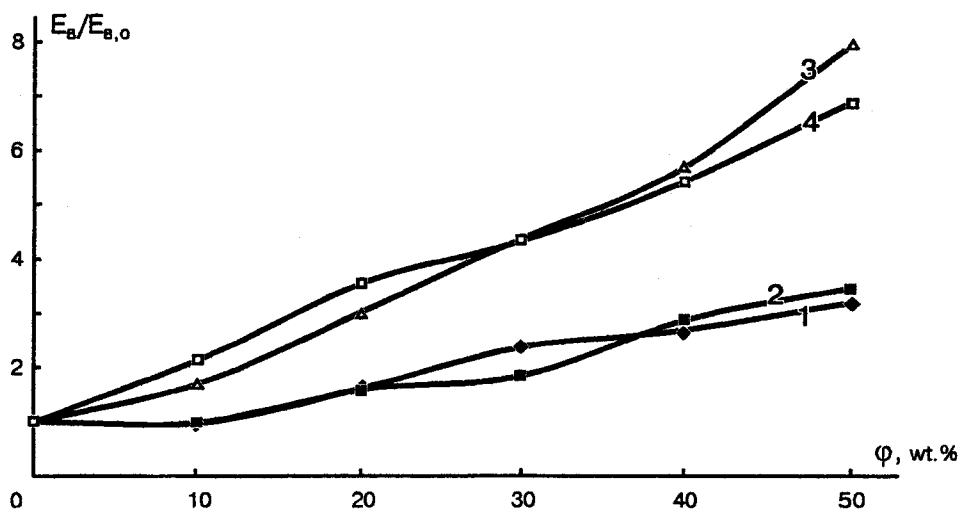


Fig. 3. Relative elastic modulus in bending as a function of LW content in RPE/LW composites. Notations as in Fig. 2.

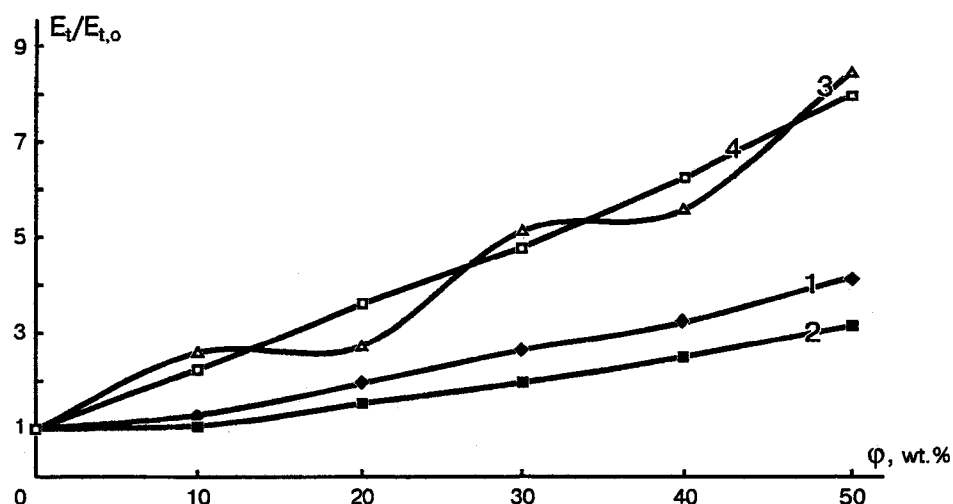


Fig. 4. Relative tensile modulus as a function of LW content in RPE/LW composites. Notations as in Fig. 2.

fibers. Intensification of interfacial interaction in NVF/thermoplastic composites in the presence of DIC was also observed in [6, 10-12]. Still the fluidity of the highly filled systems (40-50 wt.%) based on the secondary polyethylene and the wastes of linen yarn production was satisfactory: the melt flow-behavior index depending on the composition was not lower than 0.07-0.15 dg/min. Therefore, the traditional methods (extrusion, compression molding, etc.) of processing the composites can be used.

Investigations of the physicochemical properties show that a significant improvement of bending (3-8 times) and tensile (2-7 times) moduli (Figs. 3, 4) was achieved in composites with LW content more than 20 wt.% for both kinds of RPE matrices (curves 1, 2 — domestic film wastes, curves 3, 4 — industrial film production wastes). Greater reinforcing efficiency of LW was observed in the case of the polymer matrix of industrial film production wastes. The results obtained are in good agreement with the results presented in [1].

The increase in the tensile strength σ_r of the investigated composites (Fig. 5) was insignificant. At the same time, there was observed a rapid decrease in the relative elongation ϵ_r at rupture for composites with a low (10-20%) LW content. The relative deviation of average values of ϵ_r and σ_r increased from 6-8 and 8-14%,

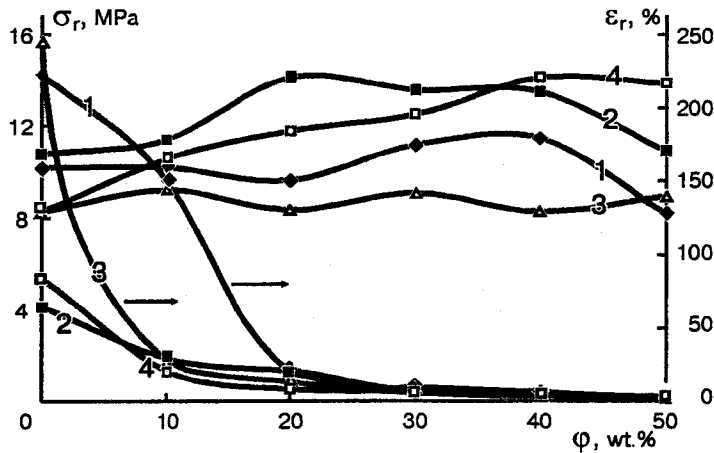


Fig. 5. Tensile strength σ_r and deformation at rupture ϵ_r , as a function of LW content in RPE/LW composites. Notations as in Fig. 2.

respectively, to 16–22 and 25–34% with increase in the filler content from 10 to 50 wt.%. These results are in good agreement with the previous investigations of similar systems on the basis of virgin LDPE [1, 2].

In [2], it was found that the coupling agent DIC promoted an increase in the physicomechanical properties of virgin LDPE of grade 15813-020/LW systems. The maximum bending modulus was exhibited by systems with 40–50 wt.% linen wastes. For composites based on recycled polyethylenes and LW, modifications with DIC did not give the expected enhancement of bending (Fig. 3) and tensile (Fig. 4) moduli. The bending and tensile moduli as a function of the filler content practically coincided for both systems containing the coupling agent (curves 2, 4) and without the modifier (curves 1, 3). The results obtained contrasted with those in similar systems with a virgin polyethylene [2, 4, 6]. Probably, the presence of carbon black and other admixtures in recycled polyethylenes inhibited diisocyanates from intensifying the intermolecular interaction between the natural fibers and polyolefins. The experimental results for the RPE of grade B/LW systems without and with a modifier showed a small increase in the flexural modulus in the presence of DIC at a low filler content (10–20%). For higher filler concentrations (>30 wt.%), no increase in the bending modulus was observed. Obviously, highly filled systems become more inhomogeneous because the real content of DIC, which promotes interfacial interaction in the NVF-polyolefin systems [2, 6], diminishes with a decrease in the matrix content in composites.

The positive influence of DIC as a coupling agent and the negative role of carbon black are better revealed in tensile strength tests (Fig. 5). For filled systems based on RPE of grade B, the addition of a modifier enhanced the tensile strength more significantly (curves 3, 4) than in composites with RPE of grade A containing carbon black (curves 1, 2). The relative rupture strength increased 1.7–1.8 times after the filler treatment with DIC, in comparison with unmodified systems. For analogous RPE composites with a carbon black addition, the tensile strength increased only 1.3–1.4 times. This partially testifies to the negative influence of carbon black on the interfacial interaction between flax fibers and the polyolefin matrix.

The efficiency of the reinforcement action in composites containing natural fibers can be explained in different ways [12, 14]. The improvement of the mechanical properties is due to an increase in the shear stresses at the interface of components and entanglements between the chains of the polymer matrix and of the modifier at the surface of fibers [12]. The authors of [15] have observed that the enhancement of physicomechanical properties is provided by the transcrystalline morphology in the layers at the fiber-matrix (PP-cellulose) interface. The interfacial absorption yields an ordered transcrystalline PP interphase having a high density of intermolecular secondary bonds with the cellulose interface. An increasing efficiency of shear transfer with an increase in the thickness of the transcrystalline layer was also observed.

An interesting interpretation for the enhancement of the strengthening effect of NVF on the mechanical properties is given in [6]. Cellulose fibers are highly polar due to the hydroxyl groups and C-O-C

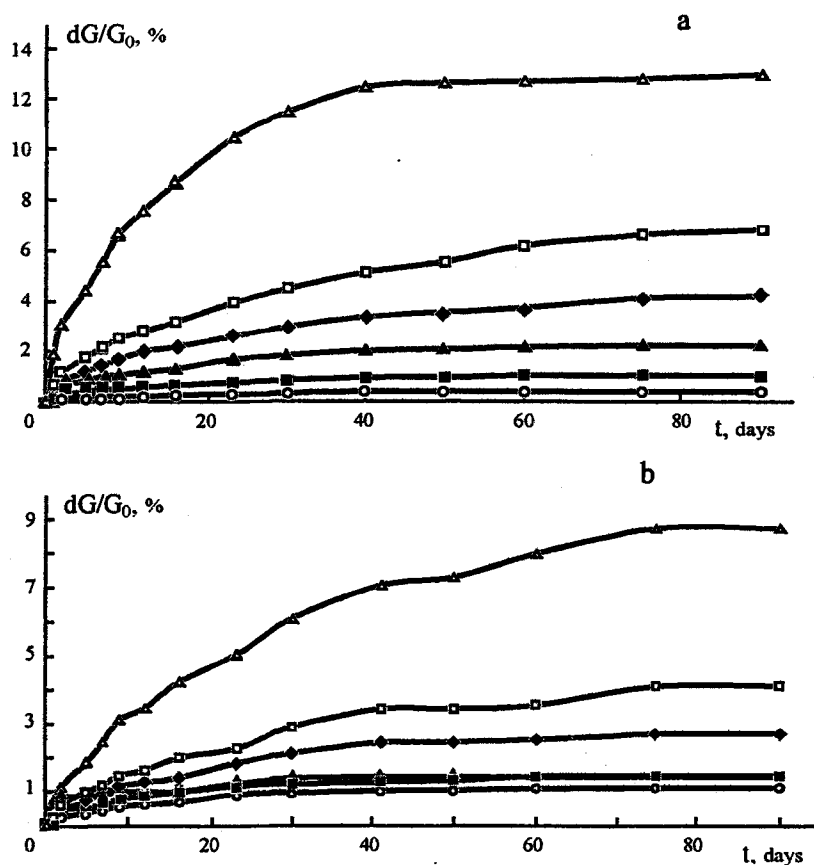


Fig. 6a, b. Water sorption kinetics for composites RPE/LW as a function of LW content: (○) — 0, (■) — 10, (▲) — 20, (◆) — 30, (□) — 40, (△) — 50 wt%. (a) — grade A and (b) — grade A with 3% DIC.

links in their structure. This polarity makes the cellulose-containing fibers more compatible with polar acidic or basic polymers. Virgin polyolefins PE and PP are neutral [15, 16]. There are no data about the acidic/basic character of RPE.

One of the most important service characteristics of NVF-modified composites is their water resistance. The results of water absorption kinetics for the investigated systems are presented in Fig. 6. The scatter of experimental measurements was not more than 2% (of the given average values). The water sorption of NVF/thermoplastic composites increases with an increase in the filler content, and, for highly filled polyolefins (40–50 wt.% filler content), the equilibrium values of absorbed water reaches 10–12 wt.% [1, 2, 11]. Similar results were obtained for RPE/LW composites without a modifier. The water sorption of composites with a high filler content (50 wt.%) reaches 12%. At the same time, all composites produced from recycled polyethylene based on domestic film wastes have lower water sorption than materials based on the industrial waste polymer (Figs. 6a, 7a). The DIC modifier enhances the water resistance of virgin PE/LW composites [2]. The same influence of DIC was observed for RPE/LW composites. The equilibrium water content was not higher than 4 and 3.8% (Figs. 6b, 7b) for the composites with a 40 wt.% filler content. These results correspond to the results presented in [13] and are satisfactory for similar materials [9]. The higher rate of sorption at the beginning of the experiment is due to the emergence of fibers at the surface. This effect in particular is observed for composites with a high filler content (50 wt.%) (Figs. 6b, 7b), which corresponds to a low water resistance (for RPE of grade A/50% LW, the absorbed water content was 8.5%, for RPE of grade B/50% LW, it was 6.6%). It should be noted that all the modified systems containing wastes of industrial film production have better water resistance than the domestic film wastes (Figs. 6b, 7b),

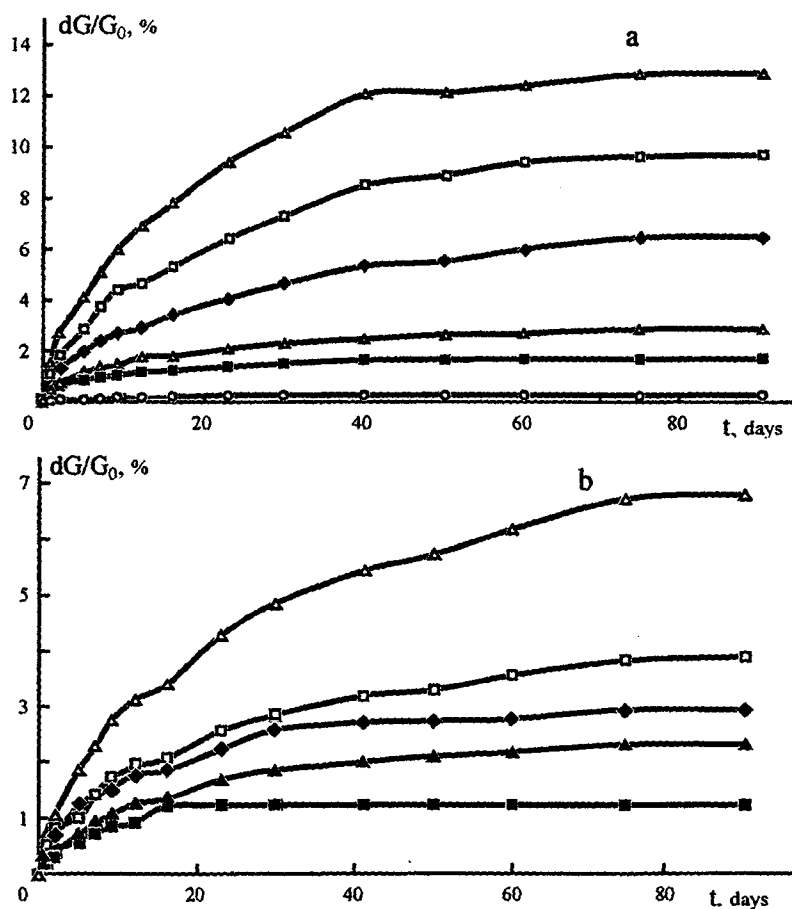


Fig. 7a, b. Water sorption kinetics for composites RPE/LW as a function of LW content: (○) — 0, (■) — 10, (▲) — 20, (◆) — 30, (□) — 40, (△) — 50 wt.%. (c) — grade B and (d) — grade B with 3% DIC.

especially for the composites with a 50 wt.% LW content. This once more confirms the negative influence of carbon black on the interfacial interaction between the polyolefin matrix and linen wastes in the presence of DIC.

The investigations of technological and service characteristics confirm promising perspectives for the production and utilization of composites based on recycled polyolefins and the wastes of linen yarn production. RPE/LW composites have satisfactory physico-mechanical properties and fluidity. The modification with DIC increases the water resistance of these materials. RPE/40% LW modified with 3% DIC is the optimum composition of the investigated systems.

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