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Selected properties of plasticized PVC modified by recyclate of polylactide film

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ABSTRACT

Purpose: The main aim of this work is to investigate mechanical properties of plasticized PVC modified by recyclate of polylactide film and influence of aging time in humidity chamber on mechanical properties.

Design/methodology/approach: Static test of tensile strength was realized using the testing machine Instron TT-CM 80. Hardness was tested by hardness tester Zwick. Fractures were examined with a scanning electron microscope Zeiss Supra 25. Before the test, the sample was sprayed thin (0.05 mm) silver layer in order to ensure discharge of static electricity from the surface of the sample. PVC granules used is prepared by mixing together at 70°C: PVC 70, plasticizer – dioctyl phthalate FDO Boryszew Erg production and stabilizing lubricant composition. The final materials being studied, obtained by subjecting of the homogenizing extrusion the mixture of granules PVC and recycled PLA.

Findings: The analysis of the results gives a real chance to avoid long-term retention of product made from the plastic in the landfill after the end of his exploitation.

Research limitations/implications: For the blends of plasticized PVC and recycled PLA derived from films, further structural and tribological resistance examinations are planned.

Practical implications: Obtained materials are characterized by satisfactory mechanical properties which make them ideal for use in the packaging industry. The effect of the addition of biodegradable recyclate postconsumer waste in the form of PLA film on plastic susceptibility to degradation under conditions of moisture was confirmed.

Originality/value: The article presents selected properties of blends of plasticized PVC and recycled PLA derived from films. The content of recyclate in tested materials varied from 0% to 50%. Introduction to poly (vinyl chloride) degradable additive made it susceptible to degradation in the presence of water, which initiates the biodegradation of polylactide.

Keywords: Engineering polymers; Biodegradable material; Mechanical properties; Electron microscopy

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PROPERTIES

1. Introduction

In connection with the inevitable prospect of running out of oil and gas resources, which are essential raw materials for the synthesis of macromolecular materials and the associated increase in their prices, alternative to traditional polymers are biopolymers. Their success, they also facilitated compared to traditional plastics capabilities biodegradability. This gives you a real chance to avoid long-term pollution of their environment. It should be noted that with the depositing on the final landfill such a product after the operating period, also forfeited all his energy put into the production. This is particularly important in the case of plastics produced from renewable raw materials, the production of which is much more energy-intensive than synthetic materials.

One solution to this problem would be a waste and recycling post-consumer plastics are degraded allowing partial recovery of energy used to synthesize and production. Remains an open question is the influence of degradable recyclates additives on the properties of mixtures containing them. In particular, it is important to question the impact of recycled plastics degradable additive on the stability properties of the modified material. Necessity undertake research in the field of material recycling of polymer blends traditional and biodegradable polymers also stems from the fact of their simultaneous use, mainly in the packaging industry, and after the use to storage without segregation [1-7].

1.1. Biodegradability

One way to solve the problem of the accumulation of plastic waste is an introduction to general use cost-effective methods for the preparation of macromolecular materials from renewable biological resources. Such materials are generally able to degrade in the environment [8-10].

The mechanism of degradation of polymers may be physical, chemical or biological. Physical degradation occurs for example due to friction, chemical by photolysis, hydrolysis or oxidation, while the process of biodegradation caused the action of enzymes produced by microorganisms. The most important mechanisms of degradation of polymeric materials is shown in Fig. 1 [11-14].

Biodegradation of material occurs gradually, inducing degradation of the polymer, followed by reduction of the chain length and the elimination of its fragments, reducing the degree of polymerization and molecular weight, etc.

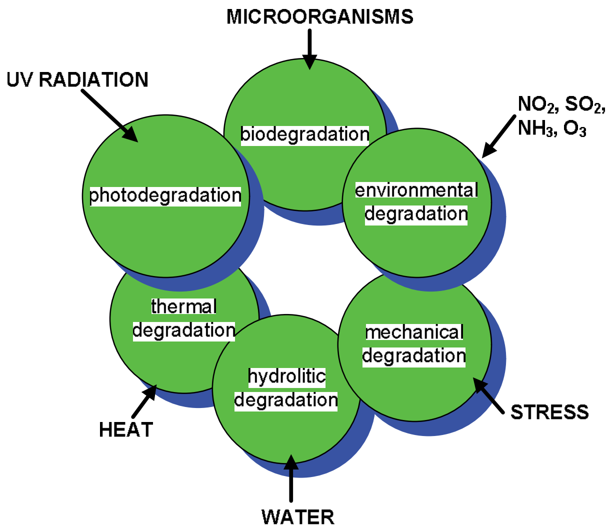

Fig. 1. Mechanisms of degradation of polymeric materials [15]

This process in favorable conditions is completed depolymerization and form a simple chemical compounds that may constitute a breeding ground for microorganisms. Biodegradation of polymers are most easily distinguished by the absence of side branches and linearity as possible to increase the susceptibility of macromolecules to the enzymes. In addition, susceptibility is the greater, the more the macromolecule is a chemical group sensitive to their action. In general, biodegradable polymeric materials do not pose a serious threat to the environment, and its effect is to produce biomass and simple chemical compounds that may turn up in the cycle of matter circulation [4,8,16-20].

1.2. Poly(Vinyl Chloride)

Poly(vinyl chloride) is one of the oldest synthetic polymers known to mankind. It was the first time, completely by accident, synthesized in the first half of the eighteenth century. By the French chemist Henri Regnault. However, the widespread use came only about a hundred years later. Since then, he has found numerous applications in almost every industry. Despite the dynamic growth resulting from improvements to other polymers, especially polyolefins, PVC market position seems to be threatened. Since the poly(vinyl chloride) is, in addition to polyethylene and polypropylene, the most commonly used polymer. Contribution of individual species in the polymer depending on the industry, see Fig. 2 [21-26].

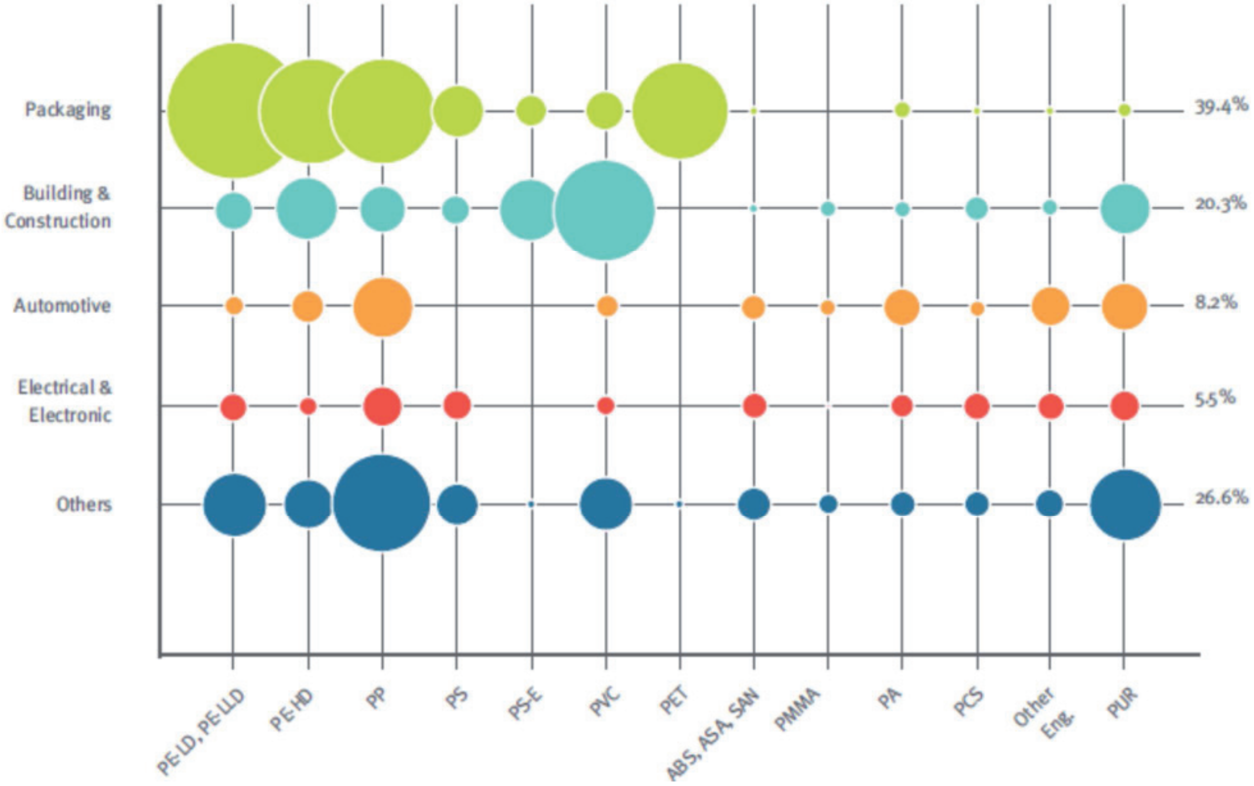

Fig. 2. The share of individual types of polymers, depending on the industrial sector [25]

The great market success of PVC owes its unique properties arising from a wide range of possible modify it and low prices, chemical resistance and non-flammability. As a pure poly(vinyl chloride) is technically meaningless, but its modification allows for optimal material for many applications. The basic modifiers include plasticizers should affect the mechanical properties of the material, stabilizers greatly enhance the heat and UV radiation resistance of the material and processing aids lubricants [26-32].

Numerous opinions about the potential dangers of PVC and mainly stabilizers used for improving the properties of the material, necessitated the development of safer substitutes already used compounds. The first substances removed from the plastic PVC were stabilizers based on cadmium and lead compounds. They have been replaced by a much safer for human health compounds of calcium, zinc and magnesium. Currently, due to concerns about the impact of phthalate compounds (the most commonly used PVC plasticizers) on the human endocrine system, also seeks to replace them with safer substances [33-38].

Development of technologies for synthesis of poly (vinyl chloride) has been a sharp reduction in the proportion of unreacted monomer. Vinyl chloride, which could be released from PVC during its operation, is absorbed into the human body through the skin, mucous membranes, and above all by the aspiration of air. In high concentrations quickly shows irritant effect on skin and eyes, but much more serious threat is the continuous exposure to even low levels of vinyl chloride. Medical studies have unequivocally confirmed the carcinogenic effect of vinyl chloride in the body man- especially the liver, lungs and brain. After getting into the body of vinyl chloride is metabolized in the liver by specific enzymes chloroethylene oxide. This compound, in turn, have a strong tendency to combine with cell DNA chains, resulting in mutations and leads to the development of tumors. Now, thanks to the development of techniques for synthesizing polymers unreacted monomer – vinyl chloride, is much lower than found in products from years ago, and its maximum permissible content should not cause adverse effects on human health (less than 1ppm free vinyl chloride). As can be concluded that the admission of the products of poly (vinyl chloride) into contact with body fluids in medical equipment. After the fulfillment of additional requirements related to the content of auxiliary substances such as plasticizers, dyes and stabilizers, PVC is used in the manufacture of containers for blood, dialysis equipment or operational tubing [39-44].

Although poly (vinyl chloride) is a material known for over a century and widely used for seventy years, it still shows great potential application. Introduction of new synthesis techniques made of PVC material has become safer for the health of its users. Also, the use of innovative modifying substances, specifically expanded range of applicability of this material. Currently, poly (vinyl chloride) is widely used in almost all branches of industry, and its susceptibility to modification by the use of suitable auxiliaries or filling, opens before him the prospect of being one of the most important polymers XXI century. One of the dominant areas of development PCV-based materials are modification techniques of their structure by pore-forming additives. Modern techniques of pore formation used in the plastics macromolecular materials processing injection and extrusion methods allow you to get the product characterized by a smooth surface, low weight and very good functional properties [45-51].

The most commonly used PVC fillers are currently still mineral particles (chalk and talc) as well as glass fibers. However, intensive research conducted on the use of naturally occurring mineral particles or organic in order to improve the properties of plastics based on poly (vinyl chloride). Due to the relatively low temperature processing of PVC, it is possible to fill it with organic particles, such as sawdust, coconut fibers and flax or sisal and nutshell meal. After an appropriate dissected of surface organic fillers in order to improve their adhesion to the polymer matrix component is prepared significantly affects on the characteristics of the material. The WPC Composites (Wood Plastic Composites) based on PVC filled with sawdust are now used mainly for the production of building profiles. Thanks to its specific properties and appearance are successfully compete with wood and wood-based products such as paneling, siding (facing) and furniture boards [47,52,53].

2. Material and methods

PVC granules used is prepared by mixing together at 70°C: PVC 70, plasticizer – dioctyl phthalate FDO Boryszew Erg production and stabilizing lubricant composition. The above components were mixed together in a weight ratio of 100 parts PVC to 55 parts plasticizer to 3 parts stabilizing lubricant composition. After cooling obtained PVC blend to ambient temperature, it was subjected to an extrusion process using a twin screw extruder, a counter-manual Gőetffert of L/D 25, to give granules. PLA films recycled materials in the form of granules obtained by the rib post-use films made from the PLA on a twin screw extruder. Upon delivery film was free of impurities, due to omission typical for recycling process the washing step and the associated waste drying the film.

The final materials being studied, obtained by subjecting of the homogenizing extrusion the mixture of granules PVC and recycled PLA. Because of the large water absorption exhibited by the polylactide, before the processing of recyclate dried in a laboratory oven at 100°C for 6 hours. Mixtures contained 15%, 25%, 35% and 50% recycled PLA. As a reference sample of PVC treated with granules which contained no polylactide. To eliminate the effect of variations in the processing properties of the resulting polymer blend, all blends, including a reference sample, were subjected to repeated homogenizing extrusion to give granules. Individual granules obtained were characterized by a uniform color, glossy surface and no discontinuities in the form of gas bubbles visible to the naked eye in cross-section of individual granules.

Materials for the study were a mixture of granulated plasticized PVC and recyclate film made of polylactide (PLA). Test samples were cut from the tape having a thickness of approx. 1 mm extruded pellets previously obtained. These tapes were extruded using a single screw extruder PLASTI-CORDER PLV 151 BRABENDER with an L/D ratio equal to 25, equipped with a slot die.

The thickness of the strips equal to 1 mm was chosen because of projected possible use of test materials in the packaging industry. In addition, the relatively small thickness of the sample allows faster penetration of the material by such external factors – water or micro-organisms. It is very important from the point of view of biodegradability, as polylactide acting as prodegradant before it becomes available to the microorganisms that cause its degradation, must be hydrolyzed.

In order to evaluate the properties of the materials were subjected to the following tests:

1. Tensile strength and elongation at break according to the methodology of the [54], using a tensile speed of 200 mm/min. The study was conducted using the testing machine Instron TT-CM 80.
2. Density, according to the methodology of the [55], using as auxiliary liquid distilled water. The study was conducted using an analytical balance Mettler Toledo equipped with an adapter for immersion density test.

3. Hardness, according to the methodology of the [56], using the hardness tester Zwick.
4. Research fracture samples using a scanning electron microscope SEM. Fracture photos taken with a scanning electron microscope using a Zeiss Supra 25. Before the test, the sample was sprayed thin (0.05 mm) silver layer in order to ensure discharge of static electricity from the surface of the sample.

To check the susceptibility to degradation, especially hydrolytic degradation, which should be sensitized poly (vinyl chloride) by mixing it with the polylactide, the sample was subjected to artificial aging. All the strips were placed in a humidity chamber at 45°Cand a relative humidity causes condensation steam on their surface for a period of 500 hours and 1000 hours [57-60].

3. Results and discussion

The results of strength tests mixtures of PVC and recyclate PLA, shows in Table 1 and Figs. 3-8, demonstrated the influence of recyclate PLA film on the value of defined parameters. The addition of recyclate causes a marked reduction in tensile strength, while greatly increasing the value of the elongation at break.

Table 1.
The results of mechanical properties

Content of recyclate PLA	Tensile strength			Elongation at break		
	Aging time					
	0 h	500 h	1000 h	0 h	500 h	1000 h
%	MPa			%		
0	18.4	18.6	18.0	236	232	220
15	18.1	18.0	17.6	295	291	277
25	17.8	17.2	16.5	318	312	312
35	17.3	16.3	16.0	366	357	347
50	16.2	15.7	15.4	453	445	440

Pure PLA is a brittle material, which is characterized by high Young modulus and low elongation at break. However, polylactide used recycled materials in the initial state was already modified with plenty of plasticizer, which showed the FTIR study done for the postconsumer waste film. For this reason, the elongation at break, increase with increasing content of biodegradable recycled in the material.

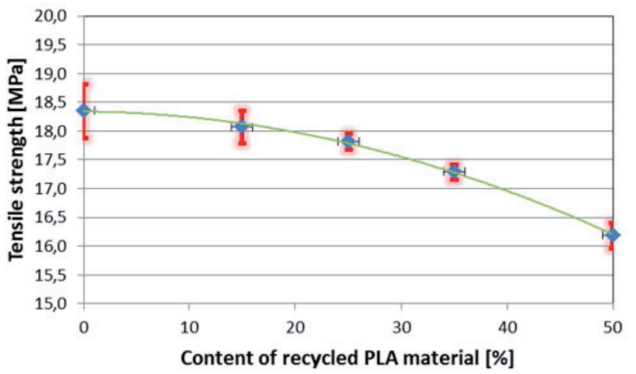

Fig. 3. Tensile strength of non-aged samples

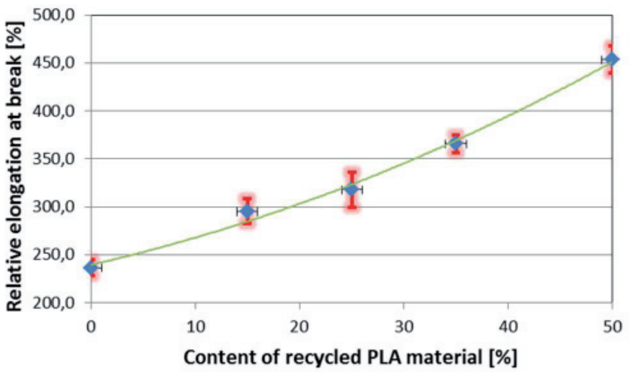

Fig. 4. Elongation at break of non-aged samples

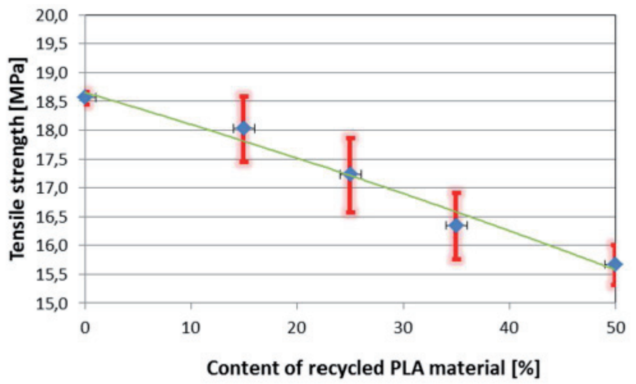

Fig. 5. Tensile strength after 500 h of aging the samples in the humidity chamber

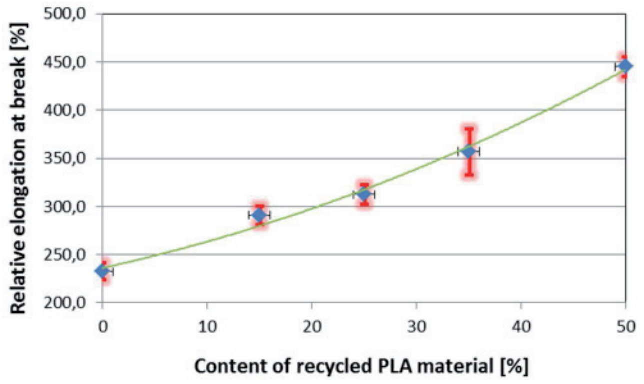

Fig. 6. Elongation at break of the samples after 500 h of aging in a humidity chamber

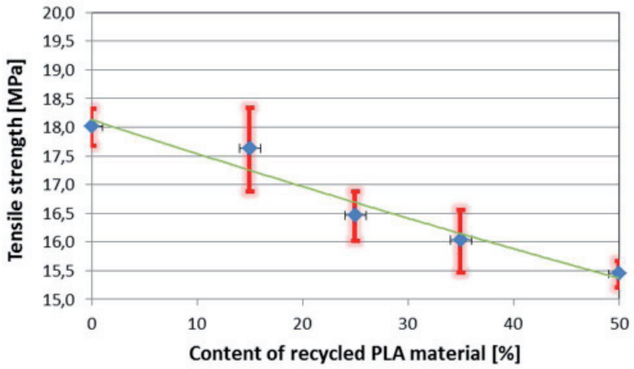

Fig. 7. Tensile strength after 1000 h of aging the samples in the humidity chamber

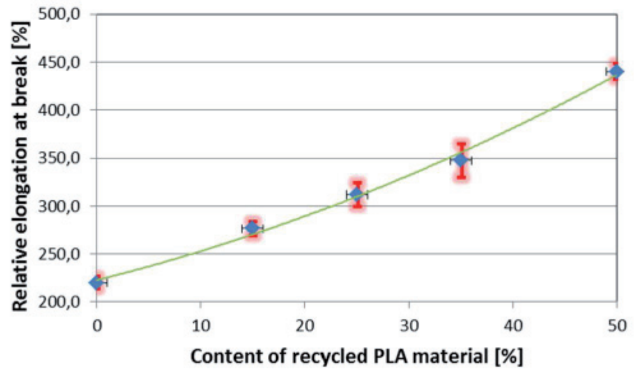

Fig. 8. Elongation at break of the samples after 1000 h of aging in a humidity chamber

Aging in laboratory made in a humidity chamber showed the effect of external conditions on the properties of a material. 500 hours of aging in a humidity chamber has slightly reduced tensile strength of samples containing recyclate polylactide. A clear decrease in tensile strength values can be observed only after 1000 hours of aging in a humidity chamber. It is correlated with the content of biodegradable material. The test samples indicates that the dominant factor in the change of strength of the material is the amount of polylactide, which is hydrolysed in the presence of water. In addition, elevated temperature aging carried out will also adversely affected the mechanical characteristics of the material speeding up the chemical reactions of its decomposition.

For samples subjected to aging in a humidity chamber was decreased elongation at break. For all samples, either after 500 hours and after 1000 hours of aging, the changes of elongation observed are similar the value of 2% and 5% respectively.

The hardness of the tested materials tested by the Shore durometer is another parameter is affected by the content of recyclate PLA. With the increase in the biodegradable additive content increases the hardness of the sample strongly as shown in Fig. 9. This change is approximately linear. The resulting standard deviation is another parameter statistical demonstrating the homogeneity of the samples tested.

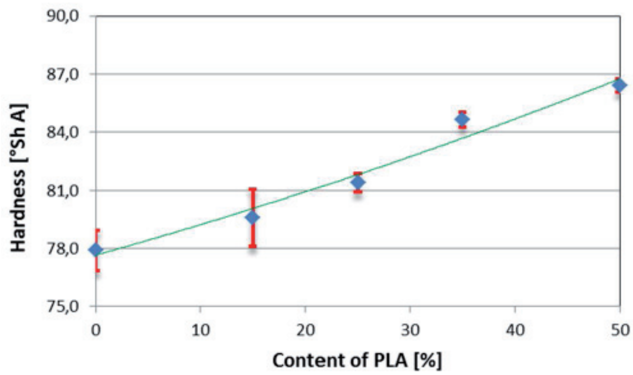

Fig. 9. Influence of recycled PLA on hardness

By analyzing microscopic pictures fractures samples obtained using a scanning electron microscope, it can be seen that the structure is homogeneous. In the Figs. 10 and 11, there are no inclusions, which could use some evidence of limited miscibility of applied materials. In addition, there was no evidence in the structure of the material trapped in the bubbles of gas, which confirms that the drying of recyclate PLA has been carried out successfully and possible moisture granules that may occur due to the high hygroscopicity of PLA, had no effect on the reduction of mechanical properties of the tested materials.

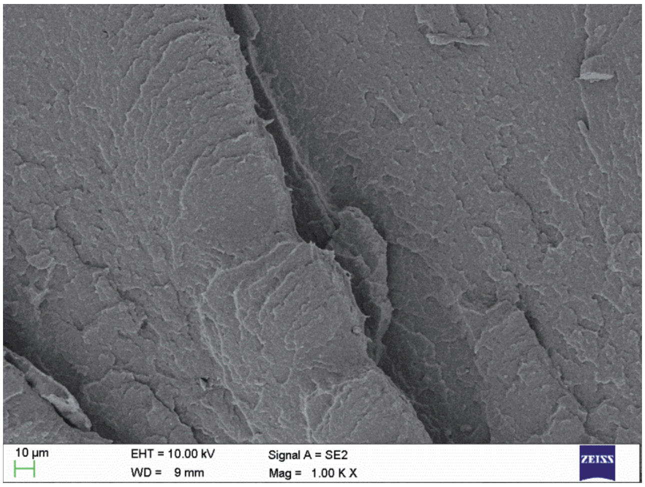

Fig. 10. Fracture of the sample containing 25% of recyclate PLA

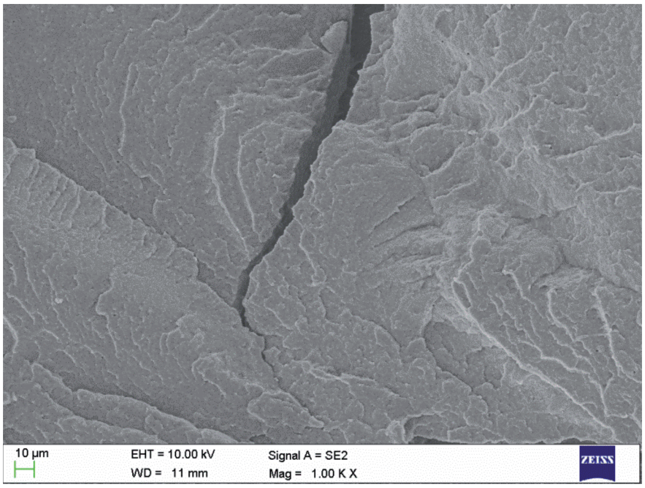

Fig. 11. Fracture of the sample containing 50% of recyclate PLA

The density of test materials is an important parameter characterizing the material during aging. As shown in Figure 12, after aging in a humidity chamber, the biggest change of a density is characterized by the reference sample. With the increase polylactide density change of was lower. This probably indicates migration of PVC plasticizer into the environment in which the samples were conditioned. Stable two-component sample density value tends to adopt the belief that hydrolytic degradation, manifested by a change in the strength and elongation at break, caused the degradation of polymer chains, however, has not led to the removal of polylactide blends. It is not excluded that after the long term degradation of the biodegradable PLA would be falling to such an extent that it would be possible to remove from the mixture. However, aging conducted for 1000 h was definitely too short for removing PLA.

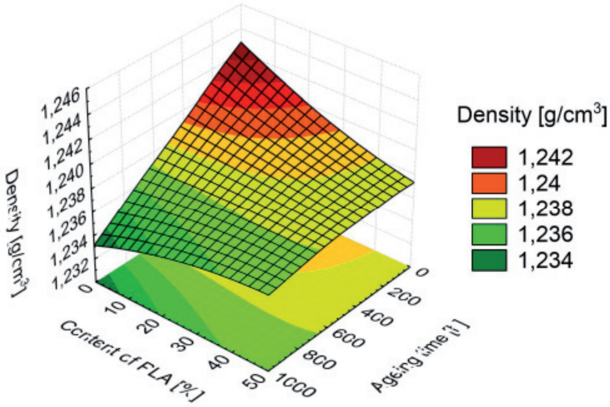

Fig. 12. The density of the test material, depending on the aging time in a humidity chamber and content of PLA recyclate

4. Conclusions

Obtained materials are characterized by satisfactory mechanical properties which make them ideal for use in the packaging industry. It was thus shown that it is possible preparation of the plasticized blend of PVC and PLA having satisfactory performance and processing properties. The effect of the addition of biodegradable recyclate postconsumer waste in the form of PLA film on plastic susceptibility to degradation under conditions of moisture was confirmed. This is an extremely desirable feature for the packaging material, which is usually used only for a short period of time, and it goes to the landfill. With a tendency to degrade when exposed to water after getting the material to the landfill, will undergo gradual disintegration and dispersion. This disintegration is initiated by the hydrolysis of PLA chains will then be intensified by microorganisms.

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