ISSN 1407-7353

MATERIĀLZINĀTNE UN LIETIŠĶĀ ĶĪMIJA
MATERIAL SCIENCE AND APPLIED CHEMISTRY

2008-16

BLENDS OF PVA WITH NATURAL FILLERS

PVS MAISĪJUMI AR DABĪGĀM PILDVIELĀM

Nataļja Jeļinska, *master's programm student*
Institute of Polymer Materials, Riga Technical University
Address: Azenes str. 14/24, LV 1048, Riga, Latvia
Phone: 371 22336226
E-mail: nloginova@inbox.lv

Velta Tupureina, *reseacher, M.sc. ing.*
Institute of Polymer Materials, Riga Technical University
Address: Azenes str. 14/24, LV 1048, Riga, Latvia
Phone: 371 7089219
E-mail: veltupur@ktf.rtu.lv

Anda Dzene, *assistant, Engineer*
Institute of Polymer Materials, Riga Technical University
Address: Azenes str. 14/24, LV 1048, Riga, Latvia
Phone: 371 7089219
E-mail: veltupur@ktf.rtu.lv

Marianna Laka, *leading researcher, Dr. ing.*
Latvian State Institute of Wood Chemistry
Address: Dzerbenes str. 27, LV 1006, Riga, Latvia
E-mail: lamar@edi.lv

Key words: poly (vinyl alcohol); biodegradable polymers; starch; irradiation; thermocell

Introduction

The request for biodegradable disposable packaging or single use items capable of overcoming or at least reducing the issues bound to the management of their post consume status is attracting increasing attention for the utilization of poly (vinyl alcohol) (PVA) in the production of environmentally friendly plastic items. The good processability and the well-known biodegradability of PVA have been the guidelines at the basis of the formulation of PVA-based water-soluble films and composites with natural polymers and fillers that do not affect PVA propensity to biodegradation in aqueous medium.

The main objective of the present study was to investigate filled biocomposites (PVA) and to evaluate mechanical characteristics, thermal properties and biodegradation of PVA based films.

Experimental

Several blends of polyvinyl alcohol, glycerol and natural fillers (starch, thermocell and thermocell gel) have been prepared by solvent casting. The influence of fillers in blend systems on the properties of the prepared films was investigated. After drying PVA composites were irradiated by γ–radiation using ^{60}Co (dose 25 kGy). It is well known that the exposure of polymers to γ-rays induces structural defects. The radiation induces the degradation of the initial structure by scission and emission of atoms. PVA biocomposites have been characterized by IR spectroscopy, DSC method and biodegradation in soil. The elongation at break (ε) and tensile strength (σ) of films were determined.

Partially crystalline water soluble PVA (0.8-2.0 wt% acetate groups) was used for investigations. Constant content of glycerol (30 wt% from PVA) was used as plasticizer. Local origin potato starch (Aloja) and microcrystalline cellulose – thermocell (in forms of powder material and thermocell gel) were chosen as fillers for plasticized PVA biocomposites. Thermocell is commonly obtained from softwood pulp by the hydrolysis method, treating with hydrochloric or other acid solution at elevated temperature and then washing-off from the acid. Thermocell is homogeneous powder with a particle size of 10-30 nm. Powder thermocell differ from thermocell gel with average degree of polymerization, degree of crystallization and with particle sizes [1]. Modified PVA films were prepared by solvent casting technique from aqueous systems of all components. After drying PVA composites were irradiated by γ–radiation using ^{60}Co (dose 25 kGy). The elongation at break (ε) and tensile strength (σ) of films were determined by use of Universal testing machine. Laboratory-accelerated soil degradation tests were carried out gravimetrically at 25±2 ^{o}C in the microbial active garden soil as described at [2], thermal properties of modified PVA films were investigated by DSC method. The structure of PVA films, obtained from solution, was determined by using Infra Red Spectroscopy (IR).

Results and Discussion

The formation process of modified PVA films was performed and developed by casting from 10 wt% PVA water solution plasticized with glycerol and blended with natural fillers (potato starch, thermocell and thermocell gel). PVA water solution was prepared at 95-100^{o}C till complete PVA powder dissolving. Prepared PVA water solution was plasticized with glycerol (30 wt% from PVA). As the next step natural fillers such as potato starch, thermocell and thermocell gel were added to plasticized PVA solution. It was ascertained from experimental results that such film preparation technique – casting of blended suspension – ensures homogenous distribution of used additives and obtaining promising product.

After irradiation the colour of the films changed to yellowish-brown. Additional changes observed in IR absorption bands revealed the possibility of liberation of –H and –OH groups as well as scission of the main chain.

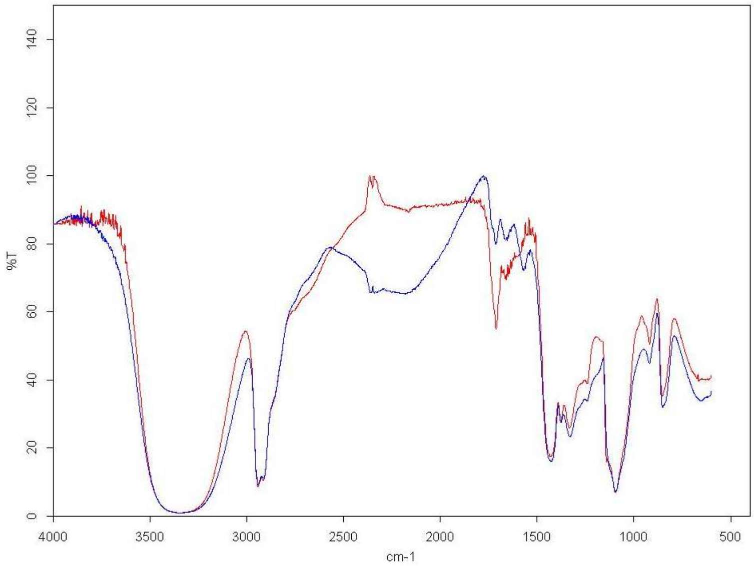

Fig. 1. *Pure PVA films IR spectrum. Irradiated pure PVA film – underneath line; non-irradiated pure PVA film – upper line.*

Careful consideration of the IR spectrum of PVA films shows that intensity of the absorption band at 1736 cm^{-1} increases rapidly after the γ-radiation (Fig.1). The absorption band at 1736 cm^{-1} arises due to the carbonyl bond (C=O) of aldehyde. Thus it is evident that when PVA is irradiated by γ-radiation (in presence of air) scission of the main chain occurs making 'C' available for the bonding with the oxygen.

Results of γ–radiation used show different influence of irradiation on the changes of mechanical properties of modified and pure PVA films. Tensile strength and elongation at break of irradiated modified PVA films decreased but tensile strength of pure PVA films increased ~2.5 times (Fig. 2). Content of all PVA compositions is shown in Table 1.

The high energy of radiation causes the –H and –OH groups of the PVA molecule to get affected and breaks the bonds. This leads to transformations in the bonding mode and formation of aldehyde group as well as scission of the main chain [3].

a) b)

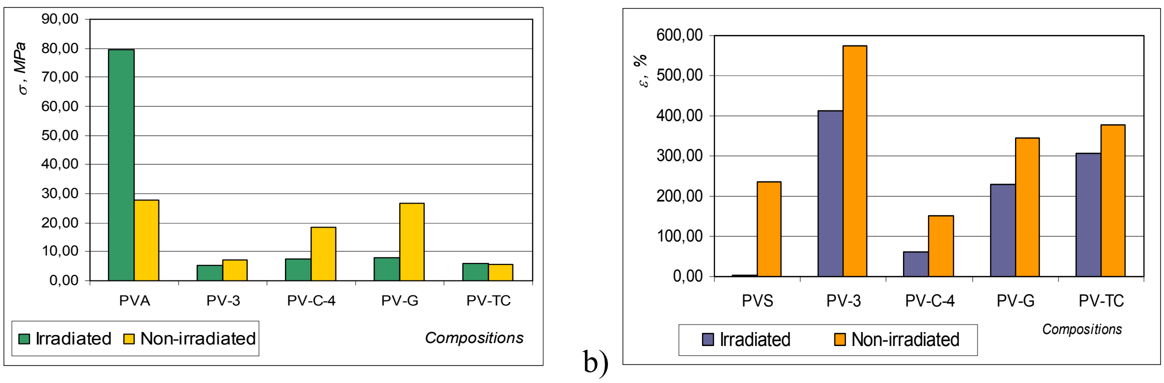

Fig. 2. *Tensile strength (a) and elongation at break (b) of modified PVA films.*

Table 1

Compositions of PVA based films

Composition	Content
PVA	10%-tage PVA water solution
PV-3	PVA+30% glycerol from PVA
PV-C-4	PVA+30% glycerol from PVA +30% starch from PVA
PV-G	PVA+30% glycerol from PVA +10% thermocell gel from PVA
PV-TC	PVA+30% glycerol from PVA +10% thermocell from PVA

The possible interaction of γ-radiation at the molecular level of PVA is depicted in the scheme below (Fig. 3).

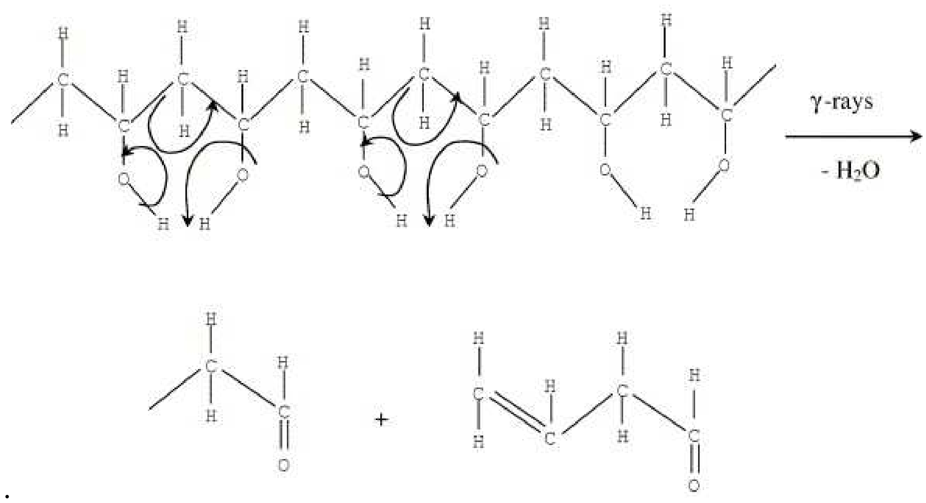

Fig. 3. *The possible interaction of γ-radiation at the molecular level of PVA* [3].

The influence of different kind of modifiers on the thermal properties of PVA films was tested. In Table 2 it was demonstrated that melting temperature (T_m) of all modified PVA films decreased after irradiation but glass transition temperature (T_g) decreased only in case of pure or plasticized PVA films.

Tendency of changes in the crystallinity percentage of PVA films after irradiation with γ-rays calculated from DSC data are in accordance with data received by x-ray diffraction analysis [3].

Presence of plasticizer and diminishing the length of main chain makes segmental motion easier and promotes decrease of T_m and T_g.

Table 2

Properties of modified PVA biocomposite films

Composition	Non irradiated films			Irradiated films		
	T_m, °C	Crystallinity of PVA, % 2nd heating	T_g, °C	T_m, °C	Crystallinity of PVA, % 2nd heating	T_g, °C
PVA	224,0	43.88	76,6	221.1	30.00	45.6
PVA+30% glycerol	208,1	43.60	28.7	186.0	21.22	19.7
PVA+30% glycerol +30% starch	208.3	39.66	53.7	184.4	17.16	69.0
PVA+30% glycerol +10% thermocell	193.3	21.61	17.6	186.9	18.60	43.8
PVA + 30% glycerol +10% thermocell gel	189.0	18.87	36,6	180.3	17.17	55.3

T_m – melting temperature
T_g – glass transition temperature

The biodegradation process of modified PVA biocomposite films with natural fillers (powder thermocell and thermocell gel) and of pure PVA in soil is shown in Fig. 4 and Fig. 5.

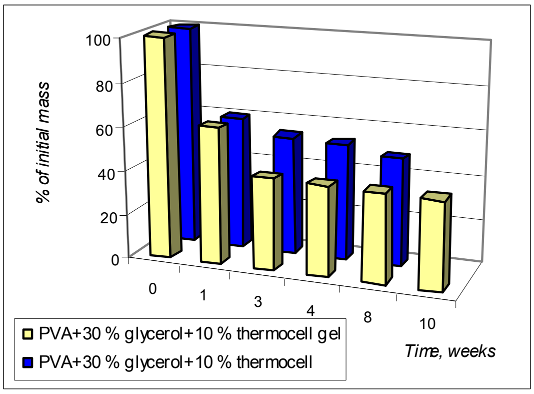

***Fig. 4.** Biodegradation in soil of modified PVA films.*

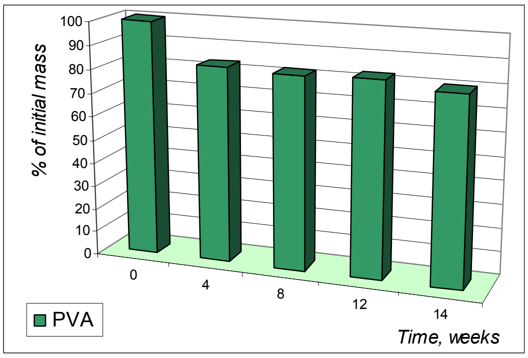

***Fig. 5.** Biodegradation in soil of pure PVA film.*

The incorporation of thermocell or thermocell gel facilitates PVA biodegradation. The results become clearly evident comparing data of eight week on both diagrams.

Conclusions

1. It was found that mechanical characteristics, thermal properties and biodegradation of modified PVA films were significantly affected by content and correlation of fillers. Tensile strength and elongation at break of irradiated modified PVA films decreased but tensile strength of clean PVA films mentioned increased ~2.5 times.
2. It was demonstrated that melting temperature (T_m) of all modified PVA films decreased after irradiation but glass transition temperature (T_g) decreased only in case of pure or plasticized PVA films.
3. Addition of biodegradable natural filler thermocell gel facilitates the biodegradation of PVA films in soil to a greater extent than incorporation of powder thermocell in plasticized PVA compositions.
4. Analysis of present results testify that such way of PVA modification with natural fillers could be promising for development of selective kind of ecologically-sound biocomposites providing decrease of environmental pollution.

References

1. M.Laka, S.Chernyavskaya. Obtaining and properties of microcrystalline cellulose from hardwood pulp. Scientific Papers of RTU, *Material science and applied chemistry*, **2007**, Ser. 1, *14***,** 7-14.
2. D.Erkske, I.Viskere, A.Dzene, V.Tupureina, L.Savenkova. Biobased Polymer Composites for Films and Coatings. *Proc. Estonian Acad. Sci. Chem*., *55,* **2006,** *2*, 70-77.
3. N.V. Bhat, M.M. Nate, M.B. Kurup, V.A. Bambole and S. Sabharwa. Effect of γ-radiation on the structure and morphology of polyvinyl alcohol films. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms., Vol. 237,Issues 3-4* , **2005**, 585-592.

N.Jeļinska, V.Tupureina, A.Dzene, M.Laka. PVS maisījumi ar dabīgām pildvielām.
Pētīti polivinilspirta maisījumi ar dabīgām pildvielām. Kartupeļu cieti un mikrokristalisko celulozi (termocelu un termocela gelu) izmanto ar glicerīnu plastificēta polivinilspirta pildīšanai. Novērtētas pildītu, neapstarotu un ar gamma starojumu apstarotu PVS biokompozīciju deformatīvās un termiskās īpašības, kā arī spēja sadalīties augsnē. Konstatēts, ka pēc apstarošanas modificētām PVS plēvēm stiepes robežstiprība un elastība samazinās, taču tīram PVS stiepes robežstiprība pieaug ~2.5 reizes. Ievadītās pildvielas paātrina PVS kompozītmateriālu sadalīšanos augsnē.

N.Jelinska, V.Tupureina, A.Dzene, M. Laka. Blends of PVA with natural fillers.
Several blends of polyvinyl alcohol, glycerol and natural fillers (starch, thermocell and thermocell gel) have been prepared. The influence of fillers in blend systems on the mechanical and thermal properties and biodegradation in soil of the prepared films was investigated. It was found that mechanical characteristics, thermal properties and biodegradation of modified PVA films were significantly affected by content and correlation of fillers. Tensile strength and elongation at break of irradiated modified PVA films decreased but for clean PVA films mentioned tensile strength increased ~2.5 times. Addition of biodegradable natural filler thermocell gel facilitates the biodegradation of PVA films in soil.

Елинска Н., Тупурейна В., Дзене А., Лака М. Смеси на основе ПВС с натуральными наполнителями.

Приготовлены смеси на основе полимера поливинилового спирта (ПВС) с натуральными наполнителями. В качестве наполнителей для пластифицированного ПВС использовались: крахмал, термоцелл и гель термоцелла. Оценено влияние введённых наполнителей на изменение физико-механических и термических свойств, а также на способность композиций к биоразложению в почве. Установлено, что механическая прочность и эластичность модифицированных ПВС плёнок снижается после облучения гамма-излучением, но в случае плёнок из чистого ПВС, механическая прочность возврастает в 2,5 раза. Добавление наполнителей к пластифицированному ПВС значительно ускоряет биоразложение в почве.