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USE OF THE TETRAPAK MATERIAL RESIDUES IN NATURAL FIBRES CONTAINED COMPOSITES

MATERIĀLU ATLIKUMU IZMANTOŠANA DABAS ŠĶIEDRU KOMPOZĪTOS

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Introduction

Natural fiber plastic composites (NFPCs) have gained increasing interest and broad application during the last decades due to desirable properties of natural fibers. Some of the growing applications of biocomposites are in building materials, car industry, housing products, packaging [1-2].

In the last years plastic packaging has becoming the major component of the plastic waste stream because of the short time of use and the long period necessary for degradation. As a result plastic recycling is perceived as an important environmental topic [3-4]. Often multilayered materials are used in the packaging sector, for example Tetra Pak containers, which (depending on packaging content) are composed of two (polyethylene(PE) and carton) or three (PE, Al, carton) layers.

The recycling of the beverage Tetra Pak shows increasing interest for both an environmental point of view and valorization of high value residue The virgin cellulose fibres, used in Tetra Pak products, are specially selected to give maximum strength and stiffness for the lowest possible weight. When recycled, these fibres provide a valuable material for new paper and board products.

According to Tetra Pak Environment and Social Report [5] paper mills recycle Tetra Pak cartons, either separately or together with other paper grades, by separating carton cellulose fibres from PE and Al using a water-based process known as repulping.

Recycled beverage carton fibres are used in products ranging from stationery, kitchen rolls to paper bags and cardboard boxes, however, also other applications can be found.

After the separation of carton cellulose, remaining part is PE (contaminated with cellulose) or mixture of PE and Al foil. Consequently, waste Tetra Pak PE can not be used for producing

of PE film by blown extrusion (most usual product of the reprocessing of secondary PE). Therefore, at present waste Tetra Paks (or separated PE) mainly are incinerated or discarded in landfills, only small part is recycled.
On the other hand, a number of studies on natural fibre (including cellulose fibre) reinforced thermoplastic composites is performed in last decades.
Cellulose fibers (CF) offer several advantages when added to the plastic: low density, high modulus and low price of composite among other features. On the other hand, the incorporation of cellulose fibers in a synthetic polymer is associated with agglomeration of CF what results in insufficient dispersion degree [6], it consequently causes inferior mechanical properties of composites.
Another technical problem is the lack of adhesion between hydrophilic cellulose fiber and the hydrophobic polymeric matrix [7]. There are several possible strategies for improving interaction between cellulose fiber and thermoplastic matrices: fibre surface modification (physical or chemical methods) or addition of coupling agents (CA) in the polymer melt. Last one is among the most extensively used methods in practice (partially maleated CA are widely used to increase the strength of NFPC). Interactions between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fibres can overcome the incompatibility problem and increase tensile and flexural strengh of natural fibre thermoplastic composite [8]. The difference with other chemical treatments is that maleic anhydride is not only used to modify fiber surface, but also the PE matrix to achieve better interfacial bonding and mechanical properties in composites [9].
Different types of commercial maleated polyolefins are widely used, however, not all maleated polyolefins are created equal (they differ by molecular weight and content of maleic groups), consequently, their reactivity also is different.
The purpose of the present work was to study the possibility to use Tetra Pak components (PE film contaminated with CF (TP-PE) and carton cellulose fibre (TC) for preparation of polyolefin-cellulose fiber composites and to determine their mechanical properties, moisture uptake and flowability depending on polymer matrix type, filler type and content.
Taking into account previous research results we use as coupling agent Fusabond E MB100D, which was maleic anhydride grafted high density polyethylene (HDPE) [10], and possesses high MA graft level. Flowability of composites at high level of natural fibre loading is poor [11], therefore we also tested effectiveness of several lubricants (paraffin, PE wax and stearic acid).

Materials

Tetra Pak polyethylene (TP-PE) – MFI =1.79g/10min (T=190°C P=2,16kg), virgin low density polyethylene (LDPE -640 M) – MFI =2,0 g/10min (T=190°C P=2,16kg), and mixture of both were used as composite matrix.
Maleated PE (Fusabond E MB100D, acid number - high) was used as coupling agent.
Three type fillers were used: talc, hard wood flour (HW) and Tetra Pak carton cellulose fiber (TC)
Paraffin(Tm=34.8 and 53.9°C), PE wax (Tm=77.2 and 100°C, stearic acid (Tm=70 and 110°C) were used as lubricants

Compounding

Tetra Pak carton was shredded at RECH mill and obtained cellulose fibres (length ≤ 1 mm) were dried at 105° C during 24 hours.Tetra Pak PE film contaminated with cellulose fiber was dried at 80° C during 24 hours. The blending of materials was done at 160-180° C on two-roll mill during 20 min.

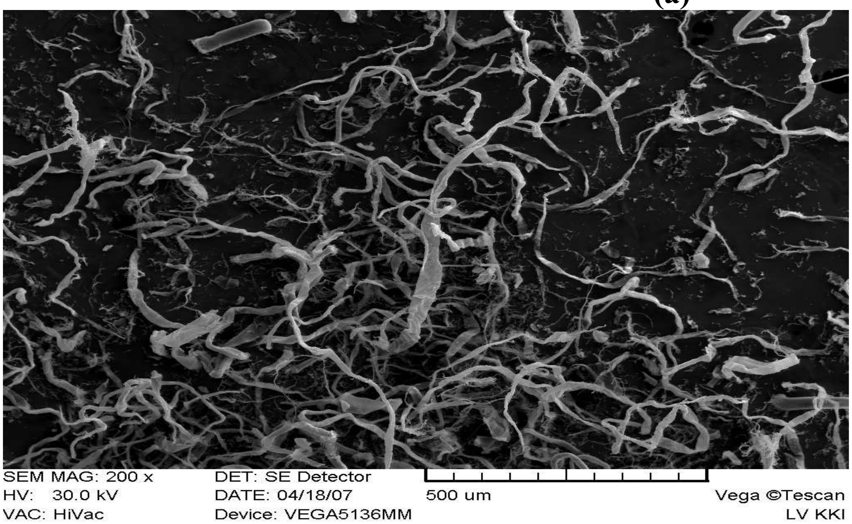
Testing

Tensile properties (tensile strength, elongation) and flexural strength and modulus were determined on an universal testing machine UTS 100. Determination of tensile strength and elongation was done according to standard ISO 527-1:1993. Specimens were prepared by compression moulding at 180° C 3 min.
Determination of flexural strength was in accordance with ISO -178:1993.Specimens were prepared by injection moulding at 200° C
Determination of Charpy Impact strength was done on Zwick 5102 according to standard ISO 179:1993. Specimens were prepared by injection moulding at 200° C
Moisture absorption (RH=97%, T =20°C) was determined by measuring weight gain of samples in the form of plate (length = 4 cm, width = 4 cm, thickness = 0.1cm).
DSC thermogramms were perfomed by differential scanning calorimeter "Mettler 300".

Results and discussion

Two natural fibres (TC and HW) were used as reinforcing fillers in PE composites. They differ between themselves by length and aspect ratio, as it is seen from Fig.1

(a)



(b)

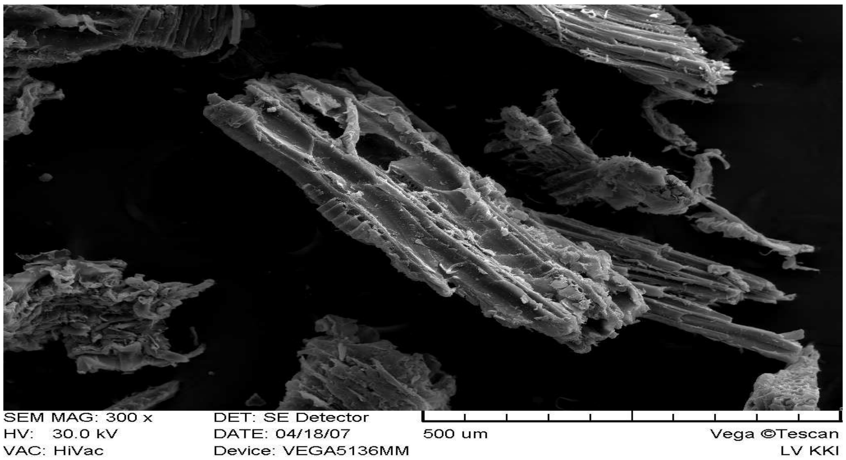


Fig.1 *SEM micrographs of (a) tetrapak carton cellulose fiber and (b) hard wood flour*

TC fiber exhibited greater length and aspect ratio compare to HW flour.We also determined Tetra Pak PE characteristics by DSC method (Fig.2). As it is seen from figure, thermogram of Tetra Pak PE exhibited two endothermic peaks at 109°C and 181°C, what means that PE is contaminated with some unknown matter (possibly it can be residue of adhesive which is used to glue carton and PE layers.). TP-PE is comparable with virgin LDPE by tensile strength (13.2 MPa and 16.5 MPa) but is significantly more brittle (elongation, consequently 51% and 1040%). Flowability of both polyethylenes is similar: 1.79 (TP-PE) and 2.0 g/10min (LDPE).

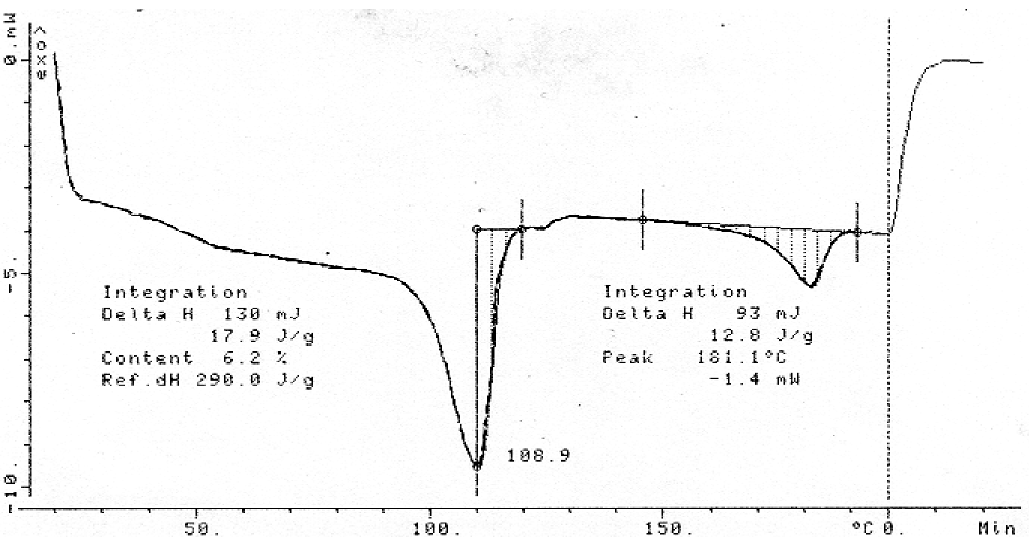


Fig. 2. *DSC thermogram of TP-PE*

Therefore, it was expected that composites on the base of TP-PE could be comparable by strength properties with composites on the base of virgin low density polyethylene. Influence of polymer matrix on the several strength parameters (tensile, flexural, impact strength and flexural modulus) of composites with Tetra Pak carton cellulose fiber was determined and results are compiled in Table1. Composition of tested composites was similar : 40%TC and 5% coupling agent.

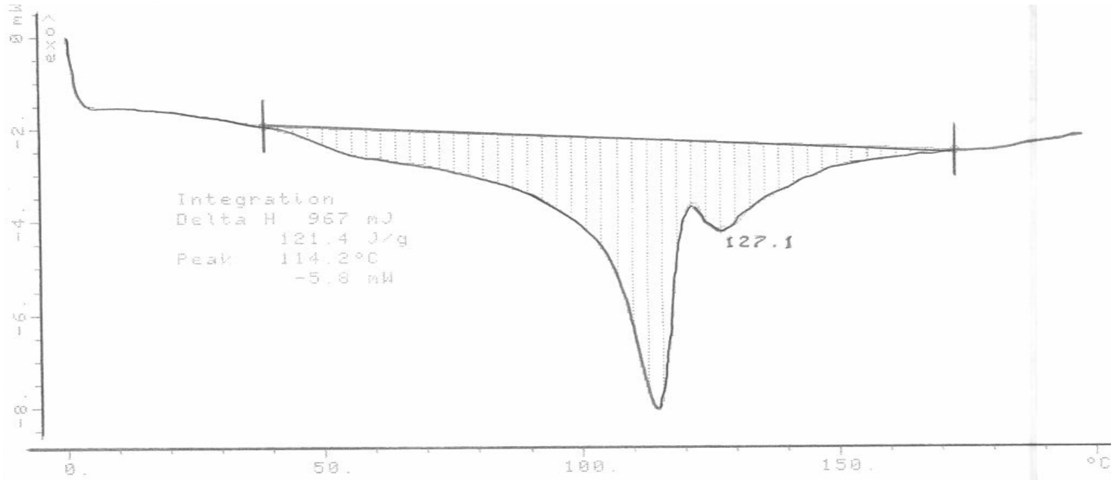


Fig.3 *DSC thermogram of the composite (LDPE+30%TP-PE) + 5% Fusabond +40% TC)*

It can be observed from the table 1, that TP-PE composites had greater tensile and flexural strength and modulus, but lower impact strength compare to LDPE composites. Melt flow index of TP-PE composites also is lower. If blend of both polyethylenes was used as composite matrix, decrease of all strength parameters (except impact strength) was observed with increase of the TP-PE content in the blend. To understand the reason of such behavior, we analysed the thermogram of the composite, where LDPE/TP-PE (70:30) was used as matrix (Fig.3)

Two endothermic melting peaks at 114°C and 127°C present at the thermogram what is evidence of incompatible blend. It is well known that incompatibility of two polymers causes loss of the mechanical properties of the blend.

Table 1

Influence of the matrix type on the mechanical strength parameters of composites

Composite	**Impact strength kJ/m²**	**Tensile strength, MPa**	**Elongation, %**	**Flexural strength, MPa**	**Flexural modulus, MPa**	**Melt flow index, g/10 min, 190°C, P=2,16 kg**
TP-PE + 5% Fusabond+ 40% TC	16,3	26,4	12,5	32,7	1081	0,16
LDPE + 5 % Fusabond + 40% TC	19,18	23,5	19,96	27,2	836,64	0,32
(90 % LDPE + 10 % TP-PE) + 5 % Fusabond + 40 % TC	22,75	21,51	17,63	22,5	812	0,34

(70 % LDPE + 30 % TP-PE) + 5 % Fusabond + 40 % TC	21,17	20,9	14,39	20,9	754	0,21

It is seen that introducing of filler leads to significant decrease of MFI of composites compare to unfilled polyethylenes: the values are about double for virgin LDPE and TP-PE.
Further we have analysed influence of different fillers (talc, hard wood, cellulose fiber) on the TP-PE composites.The results are compiled in the Table 2.
As it was expected, type and content of filler have strong effect on the mechanical strength properties of composites. Increase of filler loading from 10% till 40 % in all cases causes improvement of composite flexural and tensile strength and modulus, opposite to the impact strength which consequently decrease. Flowability of composites (measured by their melt flow index values) also decrease with increase of filler content.
Composites on the base of natural fibres were compared with traditional inorganic filler – talc. At the filler content of 40%, composites with natural fibres had greater values of flexural modulus, however, impact strength is greater in the case of talc filled polymer. Regarding strength parameters, composites which contain TC had greater, but composites with HW had lower tensile and flexural strength compare to talc filled TP-PE. It can be explained by different geometry of TC and HW particles: TC had greater aspect ratio and acts more as reinforcing fiber opposite to HW flour which acts more as particles, therefore had smaller reinforcing effect (see Fig.1). Also flowability of talc filled TP-PE is better compare to natural fiber containing composites.

Table 2

Influence of filler type on the mechanical strength parameters of TP-PE composites

Composite	**Impact strenght, kJ/m²**	**Flexural strength, MPa**	**Flexural modulus, MPa**	**Tensile strength, MPa**	**Elongation, %**	**Melt flow index, g/10min, 190 °C, P= 2.16 kg**
TP-PE + 5% Fusabond + 10% talc	39,92	21,5	624	18,1	20,7	0,68
TP-PE + 5% Fusabond + 30% talc	27,74	22.72	74,92	19,3	18,1	0,48
TP-PE + 5% Fusabond + 40% talc	22,48	24,53	905,9	21,6	15,2	0,29
TP-PE + 5% Fusabond + 10% HW	25,26	17,46	529	12,8	22,02	0,51
TP-PE + 5% Fusabond + 30% HW	14,9	19,28	689	14,5	13,27	0,11

TP-PE + 5% Fusabond + 40% HW	10,8	24,66	1179	16,6	11,56	0,09
TP-PE + 5% Fusabond + 10% CF	19,5	28,3	9514	14,9	16,8	0,67
TP-PE + 5% Fusabond + 30% CF	17,7	26,6	8329	22,5	11,12	0,55
TP-PE + 5% Fusabond + 40% CF	14,7	24,1	7638	26,4	7,45	0,16

Processing of natural fibre composites have to be done by the traditional methods –injection moulding and extrusion. Choice of the method depends on the material melt flow index. It was shown previously that flowability of composites decrease with increase of filler content and in the case of composite which contains 40% TC, MFI is only 0,16 g/10min. Therefore effectiveness of three lubricants (paraffin, PE wax and stearic acid) was tested. As it was expected, in the presence of lubricants values of composite MFI increase significantly, the best results was obtained if stearic acid was used (Table 4). However, addition of low molecular, highly crystalline lubricants can affect also strength parameters of composites. Therefore, their influence on composite mechanical properties was tested. As it is seen from Table 3, addition of lubricants mainly affects impact strength of the composite, the lowest decrease was observed if paraffin was used and the greatest decrease – if stearic acid was used as lubricant. Tensile strength, flexural strength and modulus are greater or comparable with values obtained for composite without lubricant. On the base of obtained results, we conclude that the optimal lubricant was paraffin – it significantly improve flowability of composite without negative effect on strength parameters

Table 3

Influence of lubricants type on the mechanical strength parameters of TP-PE composites

Composite	**Impact strenght, kJ/m²**	**Flexural strength, MPa**	**Flexural modulus, MPa**	**Tensile strength, MPa**	**Elongation, %**	**Melt flow index, g/10min 190° C, P=5kg**
TP-PE +5% Fusabond+40% TC	21,8	32,7	1081,7	21,35	12,5	0,16
TP-PE +5% Fusabond+40% TC+10% paraffin	10,8	31,14	944,66	21,49	8,28	0,88
TP-PE +5% Fusabond+40% TC +12% paraffin	19,5	-	-	26,1	13,0	0,94
TP-PE +5% Fusabond+40%	15,3	-	-	23,3	13,5	0,90

TC +1% PE wax						
TP-PE +5% Fusabond+40%TC + 2% PE wax	11,03	32,02	1308,22	19,28	8,31	0,86
TP-PE +5% Fusabond+40%TC + 5% stearic acid	10,04	29,42	1206,53	25,27	9,46	1,16

Disadvantage of all natural fibre composites is their great moisture (water) uptake. Therefore, we also determined moisture absorption of tested composites depending on polymer matrix and type of lubricant (Fig.5). Increase of TP-PE content in the LDPE/TP-PE blend leads to slight increase of the content of absorbed water by the composites. (8,08% and 8,14% for 10% TP-PE and 30% TP-PE accordingly) compare with LDPE based composite.It was expected as far as TP-PE based composites exhibited greater values of moisture uptake.

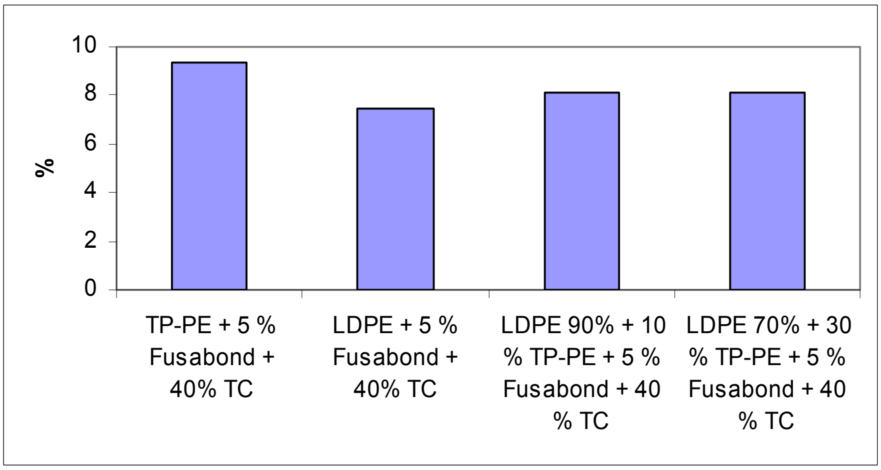


Fig.4 *Moisture uptake of composites depending on the polymer and TP-PE content after 1060 hours.*

Table 4

Diffusion coefficient of LDPE/TP-PE based composites depending on TP-PE content

TP-PE loading %	**Diffusion coefficient (cm²/sek)*10^{-9}**
0	0,61
10	0,63
30	0,73

Further influence of different lubricants (paraffin, PE wax, stearic acid) on the moisture uptake of TP-PE composites was tested (Fig.5)

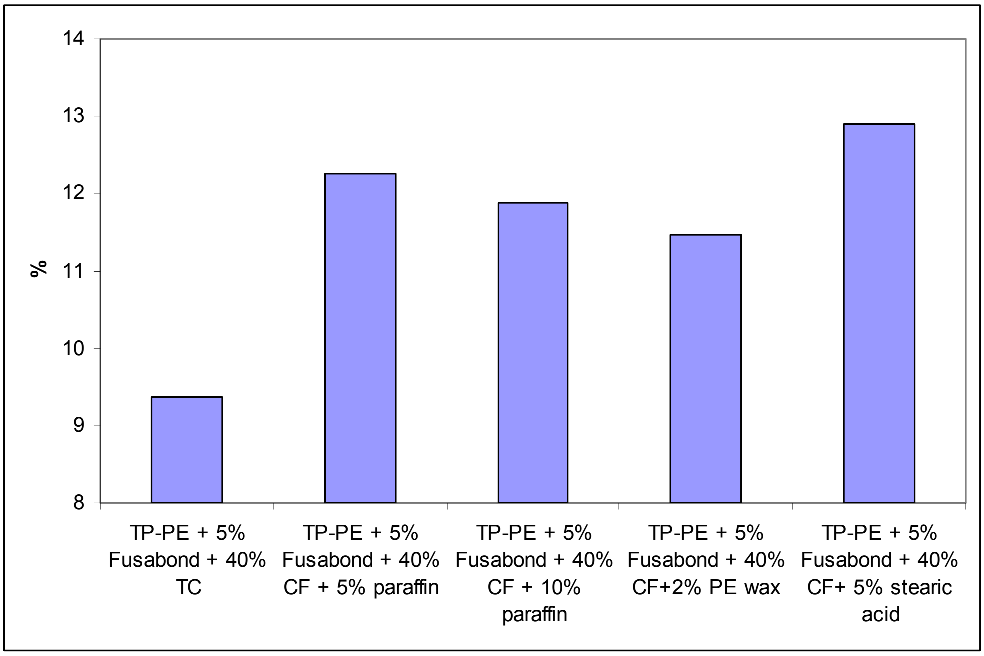


Fig. 5. *Moisture uptake of TP-PE composites depending on the type of lubricant after 1060 hours.*

Table 5

Diffusion coefficient of TP-PE based composites depending on the type and content of lubricant

Composite	**Diffusion coefficient (cm2/sek)*10^{-9}**
TP-PE + 5% Fusabond + 40% CF	0,97
TP-PE + 5% Fusabond + 40% CF + 5% paraffin	1,31
TP-PE + 5% Fusabond + 40% CF + 10% paraffin	2,61
TP-PE + 5% Fusabond + 40% CF+2% PE wax	1,35
TP-PE + 5% Fusabond + 40% CF+ 5% stearic acid	1,57

Conclusions

1. It was shown that Tetra Pak waste materials (separated PE film and carton cellulose fiber) can be successfully used for preparation of PE/cellulose fiber composites, which are comparable with similar virgin LDPE composites by mechanical strength.
2. Addition of TP-PE to virgin LDPE leads to decrease of composite strength parameters with increase of waste PE content in the blend.
3. Addition of lubricants mainly affects impact strength of the composite, the lowest decrease was observed if paraffin was used and the greatest decrease – if stearic acid was

used as lubricant. Tensile strength, flexural strength and modulus are greater or comparable with values obtained for composite without lubricant.

4. Comparing influence of paraffin, PE wax and stearic acid on melt flow index of composites it can be concluded that the optimal lubricant was paraffin – it significantly improve flowability of composite without negative effect on its strength parameters.
5. Increase of TP-PE content in the LDPE/TP-PE blend leads to slight increase of the content of absorbed water by the composites.

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M.Coņeva, A.Vīksne. Materiālu atlikumu izmantošana dabas šķiedru kompozītos.
Pasaules dabīgo resursu krājumi pakāpeniski izsīkst, tajā paša laikā pieaug apkārtējās vides piesārņojums ar sintētiskiem materiāliem. Lielā mērā to rada iepakojuma materiāli, tai skaitā Tetra Pakas, kuras ir divslāņu vai trīsslāņu (kartons-PE-AL) materiāli. To reciklēšanas procesā tiek iegūts kartons un ar kartona celulozes šķiedru piesārņots PE. Mūsu darba mērķis bija izpētīt vai ir iespējama Tetra Pak iepakojumu atlikumu izmantošana dabas šķiedru kompozītos. Tika konstatēts ka mehāniskās stiprības parametri (triecienizturība, lieces un stiepes stiprība, lieces modulis) kompozītiem, kuros kā matrica tika izmantots Tetra Paku PE, kā armējošā pildviela – kartona celulozes šķiedra, ir salīdzināmi ar analoga, uz pirmējā PE bāzes iegūta kompozīta īpašībām. Pamatojoties uz saņemtiem eksperimentālajiem datiem, var secināt ka Tetra Pak iepakojumu atlikumi ir piemēroti izmantošanai kompozītos uz PE/lignocellulozes šķiedras bāzes, kuru mehāniskas īpašības ir salīdzināmas ar tradicionālajiem kompozītiem uz LDPE bāzes.

Coneva M., Viksne A. Material Residues Using in Natural Fibres Contained Composites.
The world's supply of natural resources is decreasing and the environment pollution with synthetic materials continues to rise mainly due to packaging materials, among which there are also Tetra Paks based on 2-layer

and 3-layer (carton-PE-AL) materials. As a result of Tetra Pak recycling process, carton and PE film contaminated with CF (TP-PE) are acquired. The purpose of the present work was to study the possibility to use Tetra Pak components for preparation of polyolefin-cellulose fiber composite. Study results established that mechanical strength parameters (impact strength, tensile strength, flexural strength and flexural modulus) demonstrated by composites with Tetra Pak PE as a matrix and carton cellulose fibre as a reinforced filler are comparable with virgin LDPE composites. It was shown that Tetra Pak waste materials (separated PE film and carton cellulose fiber) can be successfully used for preparation of PE/cellulose fiber composites, which are comparable with similar virgin LDPE composites by mechanical strength.

***Цонева М., Викснe A. Использование материальных отходов в композитах содержащих натуральные волокна*.**

Мировые природные ресурсы с каждым годом сокращаются и в тоже самое время увеличивается загрязнение окружающей среды синтетическими материалами. Львиную долю составляют упаковочные материалы, в том числе Тетра Пак упаковки, содержащие двух- и трехслойные (картон-ПЭ-Ал) материалы. Целью этой работы являлось исследование возможности использования отходов Тетра Пак упаковок в композитах содержащих натуральные волокна, в нашем случае целлюлозные волокна полученные в результате переработки макулатуры. Установпено, что механические свойства композитов (прочность на растяжение, на изгиб, модуль упругости, сопротивление удару) где в качестве матрицы был использован ПЭ из Тетра Пак, в качестве армирующего наполнителя целлюлозное волокно из картона сравнимы со свойствами композитов на базе первичного ПЭ. На основе полученных экспериментальных данных сделан вывод, что отходы Тетра Пак упаковок могут быть успешно использованы в производстве композитов на основе полиэтилена и переработанного целлюлозного волокна, механические свойства этих композитов сравнимы с традиционными композитами на основе полиэтилена низкого давления.