Ageing effect on morphology, thermal and mechanical properties of impact modified LDPE/PP blends from virgin and recycled materials

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Abstract
An experimental study was conducted to investigate the influence of ageing on the morphological, thermal and mechanical properties of virgin and two types of recycled (from technological and postconsumer wastes) modified polyolefin blends. Immiscible blends of virgin low-density polyethylene (LDPE) and polypropylene (PP) in weight ratio 1:1 were modified with the ethylene–propylene diene monomer (EPDM) rubber impact modifier. The efficiency of modification was investigated as a function of modifier content in the range from 7 to 15 wt%. The blends were prepared by extrusion using a corotating twin screw extruder Brabender DSE35/17D at melt temperature in the range from 150 to 200°C and a screw speed of 20 rpm. Compression-molded samples were subjected to natural and accelerated ageing and characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and mechanical testing.

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The experiments show that the ageing process deteriorates the mechanical properties of the PP/LDPE blends, and this is more clearly expressed in the blends of virgin material. The results show that the presence of the EPDM modifier delays the process of ageing in PP/LDPE blends. The DSC and SEM investigations confirm the structural changes in the examined compositions.

Keywords
Polyolefin blends, ageing, modification, thermal properties, mechanics.

Introduction

Blending of different plastic resins has long been practiced in the manufacturing industry for various reasons including (1) tailor-made blends to meet specific processing and performance requirements that cannot be satisfied by a single component; (2) blending of polymers can be used in the field of recycling postconsumer wastes to upgrade their properties; (3) scientific interest and (4) financial incentives.¹

Statistic data show that the most essential part of polymer waste is the volume of polyethylene (PE) and polypropylene (PP).²,³ Usually, the plastics are mixed within the polymer waste and their utilization together as blends is a good solution. Both above mentioned polymers are immiscible, therefore, blending leads to heterogeneous morphology and phase separation.⁴ Strategies for proving the compatibility of the blends include addition of low-molecular weight substances,⁵ inclusion of reactive polymers capable of interchange reactions⁶ or addition of modifying copolymers.⁷ From technological point of view, the modification with a third polymer elastomer is a preferable way for increasing the mutual affinity of the two polymers.⁸–¹¹ The copolymer has affinity to each of the polymers in the blend and is localized at the interphase boundaries,⁹,¹²,¹³ enhancing the stress transfer and contributing to particle size reduction.¹⁴ The resulting blends have fine morphology¹⁵–¹⁷ and improved stress-crack resistance.¹⁸

The changes in the polymer properties under the different environmental and processing conditions are termed ageing. Polymers have been known to demonstrate two kinds of ageing: chemical and physical. Chemical ageing is thermal degradation, photooxidation, and so on and the changes are connected with degradation and lead to molecular chain scission and/or cross-linking. The result is cracking and chemical disintegration of polymers.¹⁹ Physical ageing, also known as structural relaxation is due to the fact that in the moment of producing polymer material is in nonequilibrium state and it is unstable. Physical ageing is the isothermal change in different properties of the amorphous phase of a polymer because the preparation history of the polymer did not leave it in a state of thermodynamical equilibrium, and thus isothermally the polymer steadily evolves toward an equilibrium state. The molecules slowly become more closely packed in the amorphous regions with time, and this reconfiguration decreases both the average energy and the free volume of the system.²⁰
Investigation of natural or accelerated chemical ageing henceforth for convenience referred to as ‘ageing’, is very important because this helps for better understanding and prediction of long-term behavior of polymers in practical applications.\(^\text{21}\) Frequently the degradation products can often act as a compatibilizer for the newly blended system, and this process is more complicated for recycled polymers. For example, carbonyl groups can act as a compatibilizer.\(^\text{22}\)

Although PE and PP oxidize via similar propagation reactions, there are some marked differences in their oxidative degradation processes. In the case of PP, the tertiary radicals are formed predominantly due to the lower dissociation energy of a tertiary C–H bond (ca. 373 kJ.mol\(^{-1}\) at 25°C), compared to that of a secondary C–H bond (ca. 394 kJ.mol\(^{-1}\) at 25°C).\(^\text{23,24}\)

Competing reactions of chain scission (molecular weight loss) and cross-linking (molecular weight gain) are expected to occur in PE samples during ageing. The chain scission is less favorable in PE and only becomes important at higher temperatures due to the faster movement of the polymer chains. Chain scission of PP samples is the predominant degradation mechanism owing to the higher reactivity of the tertiary carbon-based radical. Chain scission in PP and cross-linking in PE in mixed blends could have a compensating effect (could be balanced out) on each other and lead to nondegradative effects; although the evidence for this was inconclusive the synergistic or antagonistic effects of each much be considered. It has been shown\(^\text{22}\) that low-density polyethylene (LDPE) acts as a stabilizer for isotactic polypropylene (iPP) by retarding the autocatalytic propagation of tertiary carbon radicals, probably by cross-linking. As would also be expected the temperature at which the photooxidation occurs is also important; it is often cited that a 10°C rise in temperature doubles the rate of decomposition. However, there are many other external factors associated with outdoor polymer degradation – humidity, temperature as well as the polymer sample: sample thickness, degree of branching, melt flow index, tacticity (of PP) and catalyst type.\(^\text{22}\)

Degradation studies of blended plastics are not as well covered as those of their homopolymers. Commercial polymer blends only really became available in the early 1980s, but research into the degradation properties of these materials only really have begun in the late 1990s; much of this is due to the interest in polymer recycling of virgin and recycled resins. The addition of elastomer can influence to a great extent the properties of polymer blends after ageing. The literature does not contain so much data about ageing of similar modified blends and in particular of recycled modified polymer blends. Most investigations have only studied molecular weight distributions or viscosity measurements.\(^\text{22}\)

The main goal of this experimental study was to investigate the influence of ageing on the mechanical properties depending on the changes in morphology and thermal properties. The samples were subjected to natural and accelerated ageing and characterized by wide-angle x-ray diffraction (WAXD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and mechanical testing. Virgin and recycled polyolefin blends from LDPE and PP modified with ethylene–propylene diene monomer (EPDM) rubber from virgin blends ageing were used for optimizations of ageing conditions of recycled blends.
Materials and methods

Materials

The materials used in this study were commercial virgin homopolymers a LDPE ROPOTEN OB-2-102 (labeled as LDPE_{VR}) with melt flow index of 0.8 g/10 min and density of 918 kg/m^3 and an iPP BUPLEN 6631 (labeled as PP_{VR}) with melt flow index of MFI = 2g/10 min and density of ρ = 898 kg/m^3, products of Lukoil Neftochim Co (Burgas, Bulgaria). The recycled polymers used were industrial scrap (labeled as LDPE_{TW} and PP_{TW}) in the form of granulate supplied by Asenova Krepost Ltd (Asenova Krepost, Bulgaria) and postconsumer scrap (labeled as LDPE_{PW} and PP_{PW}) in the form of granulate supplied by Unitrade 2002 Ltd (Sofia, Bulgaria). The used impact modifier was the nonpolar terpolymer EPDM ‘Keltan 512’ (DSM Elastomers, the Netherlands) with content of ethylnorbornene and ethylene 4.3 and 55%, respectively, and Mooney viscosity ML (1 + 4)125°C = 46UM. The blends from recyclates were mixed with 0.5 wt% Irganox 1010.

Blending and samples preparation

The binary LDPE/PP and ternary LDPE/PP/EPDM blends from virgin polymers (labeled as VR) and from recycled polymers from technological and postconsumer wastes (labeled as TW and PW, respectively) were prepared by extrusion using a corotating twin screw extruder DSE35/17D (Brabender Co., Germany) at melt temperature 200°C and screw speed of 20 rpm. The ratio between different LDPE and PP was kept constant at 1:1, because the statistic data show that in plastic wastes both polymers were of approximately equal quantity. The concentration of rubber in the ternary blends was varied in the range from 0 to 15 wt%. The modified polymer blends from virgin materials were labeled as VR, 7.5VR, 10VR, 12.5VR, 15VR and from recycled materials—as TW, 7TW, 10TW, 15TW, PW and 15PW, respectively. The extrudates were cooled between tempered rollers and pelletized by a cutting machine (Vespa 16/22, Bulgaria). Plates with dimensions 160 × 220 × 2 mm were compression molded from VR blends by means of Shpindel press for 10 min at 180°C with average cooling speed of 11°C/min to 70°C. Plates with dimensions 80/100/4 mm were prepared from recycled polymer blends by means of injection molding machine KuASY 25/35L at the following processing conditions: temperature of the cylinder 170–240°C, injection pressure of 15 MPa, packing time—1s and cooling time—90s. Specimens for mechanical tests were punched out from these plates.

Ageing

The samples from virgin material underwent natural weathering placed on inclined racks for 2 years at a temperate continental climate in Sofia, Bulgaria. These racks were oriented at the sun at an angle of 45°, because this angle ensures exposure to the full spectrum of solar radiation, from infrared to ultraviolet.

Accelerated weathering testing is a laboratory simulation of the damaging forces of weather for the purposes of predicting the relative durability of materials exposed to outdoor environments. The samples from recyclates were exposed to accelerated ageing in Q-sun Xenon Test Chamber (Q-panel Lab Products, Bolton, UK). The tested samples
were exposed to xenon light in accordance with EN ISO 2440 under the following conditions: irradiance $0.51 \text{ W/m}^2$, $\lambda = 340 \text{ nm}$ and $T = 65 \pm 3^\circ \text{C}$. The exposure period was 500 h, and each cycle consisted of 102 min of irradiation and 18 min of distilled water injection. The samples were annealed for 16 h at 23°C after accelerated ageing.

**Thermal behavior**

Differential Scanning Calorimetry (DSC) of VR blends was carried out in a temperature range from $-50$ to $200^\circ \text{C}$ with a ‘TA Q100’ (TA Instruments, New Castle, DE, USA). DSC of recycled polymer blends was carried out with a DSC823e (Mettler Toledo Inc, Columbus, OH, USA). Both the equipments are calibrated with indium and zinc and are connected to a liquid nitrogen cooling system and the testing conditions are as follows: a scanning rate of $10^\circ \text{C/min}$ for first and second runs and a cooling rate of $30^\circ \text{C/min}$.

**Wide-Angle X-Ray Diffraction (WAXD) measurements**

WAXD patterns were recorded in the reflection mode by means of ‘D8 Advance diffractometer’ (Bruker, Germany) containing a PSD Vantec detector. The experiments were carried out using Cu K$\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) operating at 40 kV and 40 mA. The relative portion of $\beta$ form $K_\beta$ in the PP specimen was determined by x-ray diffraction and calculated according to the equation of Turner-Jones et al.:

$$K_\beta = \frac{I_{\beta(300)}}{I_{\beta(300)} + I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)}}$$

where $I_{\alpha(110)}$, $I_{\alpha(040)}$ and $I_{\alpha(130)}$ are the intensities of the peaks for (110), (040) and (130) diffracting planes of monoclinic $\alpha$ form, and $I_{\beta(300)}$ is the intensity of the peak for (300) diffraction plane of the hexagonal $\beta$ form.

**Mechanical characterization**

Tensile tests of VR blends (tensile strength and strain at maximum stress) were carried out in accordance with EN ISO 527 using a Shopper Instron testing machine and for recycled polymer blends before and after ageing was used TIRAtest 2300 machine (TIRA GmbH, Germany). At least five dumbbell-shaped specimens with gauge dimensions of 30 mm in length and 6 mm in width for each composition were tested.

The impact strength was determined according to the EN ISO 179 standard by means of Charpy impact tester M 1488-4 (CEAST, Italy). Six notched test specimens with dimensions of 80 mm in length and 10 mm in width for each sample were tested. The U-shaped notch was cut at the center of each specimen with a depth of 2 mm.

**Morphology observation**

The phase morphologies of the blends were characterized from cryogenically fractured samples using a JSM 5510 (JEOL Ltd, Japan) SEM in a regime of secondary electrons and 10 kV accelerating voltage. The examined fracture surfaces were coated with a thin layer of gold (2 nm) in argon atmosphere.
Results and discussion

A preliminary study to understand the behavior of materials and especially their thermal behaviorstudy is necessary in the case of the recycled materials (T and W) for proper selection of processing conditions. Recycled polymers possess their own ‘prehistory’ which defines the possibility for reusing them for different applications. The industrial scrap has the so-called thermomechanical prehistory due to the big shear forces and the high temperatures in the processing machines. Postconsumer polymer wastes have also, apart from it, the so-called thermooxidative prehistory as a result of their exploitation conditions.

A polymer may be degraded by chemical changes due to reaction with the components in the environment, for example with the oxygen, with impurities or structural defects responsible for the photodegradation. This degradation may be less pronounced when an ultraviolet absorber (antioxidant) is incorporated into the polymer. Therefore, the problem with the ageing process can be due to the synergistic action of factors like electromagnetic radiation, thermal energy on the oxidation, favoring the initiation of degradation by excision of chain and radicals.

Preliminary DSC and WAXS measurements of the single recycled materials

The changes in the shape of the DSC first melting endotherms provide some qualitative information about the content of other different phases, as well as about the perfection of the crystal structure, depending on the prehistory of the material. Figure 1 shows the first melting thermograms of the recycled polymers used—industrial scrap (labeled as LDPE_T and PP_T) and postconsumer scrap (labeled as LDPE_PW and PP_PW).

Recycled polymers may be more or less pure according to their origin. As indicated in Figure 1, the melting temperature of LDPE_T of about 109°C corresponds to that of a LDPE. A small broad peak at around 60°C is observed, which is due to the physical ageing effect or annealing. This annealing process happens when polymer with lower molecular weight or branching polymer does not have enough time for full crystallization during the cooling process. This peak is achieved when the polymer stays at room temperature for at least 24 h. In the second melting, this peak disappears. LDPE_PW shows more complicated behavior and multiple peaks appear at 105°C, 114°C and 121°C obtained at melting of LDPE_PW. Multiple peaks can appear in (i) a sample that consists of more than one plastic; (ii) a sample that consists of only one plastic but with different molecular weight; (iii) a sample that consists of different size and/or type of crystals and (iv) a degraded sample. Chemical ageing take place essentially in the amorphous phase. Smaller chain fragments resulting from the scissions taking place in the amorphous region are then able to crystallize. This means that after prolonged chemical ageing, increments of total crystallinity are to be expected as well as new peaks corresponding to the smaller crystallites formed. Also this material should consist only of LDPE, but depending on how successful the sorting process has been made, the material may consist of other plastics or mechanical contaminants. Perhaps the triple peak of initial single polymer LDPE_PW is due to the melting and recrystallization processes as well as to the possibility for simultaneous sample degradation and formation of imperfect
crystals.\textsuperscript{26} The second melting curve of LDPE\textsubscript{PW} proves that it may be a binary blend of LDPE or a linear LDPE (LLDPE) and high-density polyethylene (HDPE).\textsuperscript{27,28}

The PP\textsubscript{TW} shows a melting peak at about 163°C and a small peak at 109°C, which indicates the presence of certain amount of PE or existence of PE/PP block copolymer or ethylene–propylene copolymer.\textsuperscript{29}

The first melting curve of PP\textsubscript{PW} also shows three peaks. The main characteristic peak at about 162°C is in the region of the melt temperature of homopolymer iPP. The peak at 123.5°C may be due to the existence of small quantity of PE or PE/PP block copolymer. The quantitative assessment of melting enthalpies shows that its content is about 6%.\textsuperscript{27} The peak at 144°C and the shoulders at about 151°C and 158°C of PP\textsubscript{PW} could be explained with the specificity of the PP crystal melting process, namely melting recrystallization of the forming crystals, or the presence of β phase. Generally, iPP under usual industrial thermal conditions crystallizes into the monoclinic α form. The processing conditions that assist the formation of imperfect β crystals of iPP are (i) presence of additives resulting in chain mobility retardation; (ii) presence of shear stress changing the chain structures\textsuperscript{30} and (iii) fast cooling conditions at foil production when the β phase has not enough time to be transformed into the more stable α form.\textsuperscript{31} Also semicrystalline polymers obtained under rapid crystallization conditions are in a nonequilibrium state, the physical and mechanical properties of the quenched PP exhibit slow changes during subsequent

\textbf{Figure 1.} DSC first melting thermograms of technological and postconsumer polymers.
ageing at room temperature to establish equilibrium conditions, and this phenomenon is called physical ageing. We suppose that the presence of the β phase results mainly from the blend processing conditions.

In order to obtain additional information about the structural characterization of these blends, different x-ray diffraction experiments were performed. The x-ray diffractograms of the technological and postconsumer wastes (LDPE\textsubscript{TW/PW} and PP\textsubscript{TW/PW}) are shown in Figure 2.

The PP\textsubscript{TW} and PP\textsubscript{PW} exhibit the characteristic diffraction peaks of the monoclinic α phase at scattering angles 2θ of 14.2(110), 17.1(040), 18.6(130) and a complex peak 21.9 (111 + 131 + 041),\textsuperscript{32} as well as characteristic peaks for LDPE—(110) (200),\textsuperscript{33} located in the figure from left to right, respectively. Besides the characteristic peaks of the α phase in the PP\textsubscript{PW}, the β phase is also clearly observed. The relative portion of β form (\(K_β = 0.45\)) in PP\textsubscript{PW} calculated by equation (1) confirms our assumption that as a result of the exploitation period, the presented α polymorph transforms into β form, while PP\textsubscript{TW} indicates only α phase.

**DSC measurements of ageing blends**

Most of the ageing effects occurring in intercrystalline domains in the thermoplastics are related to a reduction in mobility of the amorphous fraction, lamellar thickening and lowering of free volume of amorphous fraction. Recrystallization behavior of semicrystalline polymers was considered as the consequence of the concentration and strain of
taut-tie molecules. Among ageing effects, oxidative chain scissions and possible sliding of non-scission tie molecules can cause change in crystalline domains. Effects of taut-tie chain scission led to reorganization of the crystalline phase with consequent decrease in its perfection to relief of strained regions of the crystal.\textsuperscript{21} Here we studied the ageing effects on the three kinds of modified polymer blends—virgin, technological and post-consumer blends on two types of ageing—natural and accelerating as a result of the chemical and physical processes that took place.

The DSC second melting curves of virgin blends LDPE/PP 1:1 in Figure 3 show the different thermal behavior of both polymers before and after ageing with and without compatibilizer. All curves have two peaks of melting due to the incompatible blend with the compatibilizer. In the blend LDPE\textsubscript{VR} and PP\textsubscript{VR}, the peaks of both thermoplastic move to lower temperatures especially the melting thermograms of iPP with the addition of compatibilizer.

After natural ageing in both cases, significant changes are observed, decreases in temperature and broadness of the peak size have places due to structural changes as a consequence of chemical aging as we see in previous work.\textsuperscript{27} In the blend with 15\% of EPDM, which have undergone natural ageing, the iPP melting curve at lower temperature appears at the shoulder. It may be due to the recrystallization of the $\alpha$ phase to $\beta$ and $\gamma$ modification as was discussed earlier in the postconsumer blends.

Figure 3. DSC second melting thermograms of virgin LDPE/PP blends modified with 15 wt\% EPDM before and after natural ageing.
The curves of crystallization process are shown in Figure 4. The blends VR and 15VR present separated process of crystallization, it is normal in uncompatibilized samples.\(^{34}\)

In both blends after natural ageing process important changes are observed. In VRag only one peak appears (Tc-108°C) and its position is between both the components (LDPE and iPP), but 15VRag presents only one double peak (Tc-110°C). The next second melting process presents the two melting corresponding of the LDPE and iPP (Figure 3). It means existence of separated phases that cocrystallized together in VRag and in minor quantities in the 15VTag. In other words, the iPP is considerably inhibited, since it melts at a much lower temperature and crystallizes simultaneously with the LDPE component. This effect is dependent on the molecular weight of the polymer.

A polymer ageing under natural weathering may be degraded under the influence of the light due to the electromagnetic energy emitted by the sun, although the total intensity is subject to wide variations according to geographical and atmospheric conditions. The energy necessary for the photochemical degradation are supplied by sunlight. Most ordinary chemical reaction on polyolefins involves energies of activation between 165 and 420 kJ.mol\(^{-1}\) which correspond to the radiation of wavelengths from 710 to 290 nm. This mean that the energy near the ultraviolet region (300–400 nm) is sufficient to break most single covalent bond, but it reported the PE and PP are not absorbed at wavelength longer than 300 nm owing to their ideal
structure and are not be affected by sunlight. However, it is known that these polymers often do degrade when subjected to sunlight and has been attributed to the presence of small impurities or structural defects that absorb the light and initiate the degradation.\textsuperscript{24} Observing crystallization behavior (Figure 4) could be concluded as due to the availability of smaller molecules because of degradation process that generally crystallizes faster than long ones. The reason is that they are less inhibited by entanglements, but the defects on the molecules in the heavily degraded recycled component can discourage crystallization process because they will not fit into the crystal lattice. Therefore, there are two major characteristics (molecule size reduction and the introduction of molecular defects) that affect the crystallinity in opposite senses in aged and degraded polymer.\textsuperscript{19}

As can be seen in Figure 4, cooling peaks of PP\textsubscript{VR} and LDPE\textsubscript{VR} in the blend without modifier, which has undergone 2 years’ ageing, are overlapping each other, whereas in the blend with EPDM (15VR) two distinct melting peaks are observed. Therefore, it can be concluded that the impact modifier improves the stability of LDPE/PP blends against natural ageing.

The melting curves of technological and postconsumer waste blends are shown in Figures 5 to 8. The melting peaks move to lower temperature and become more unsymmetrical after ageing, which confirms the occurrence of destruction processes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{DSC second melting thermograms of TW blends modified with 7, 10 and 15 wt\% EPDM before and after artificial ageing.}
\end{figure}
The ageing effects are less pronounced than in the virgin material and one possible explanation is the presence of antioxidants. Technological blends show normal behavior corresponding to immiscible blends in the melting and cooling processes. The melt in all cases appear as two clear peaks of crystallization corresponding to the different components of the blend: LDPE and iPP after ageing processes.

The PWB second melting curves before ageing show multiple melting peaks. Based on the comments discussed in the DSC results above for LDPE$_{PW}$, it can be said that the blend PWB contains different kinds of PEs – LDPE or LLDPE, HDPE with a heterogeneous distribution corresponding on a Ziegler-Natta catalyst (indicate the position of the peak). The iPP has different polymorphs as a result of multiple phase transitions. The present results show the formation of significant amount of the $\beta$ polymorph: the peak at about 146°C is clearly seen, and it is higher than the other peak for PP$_{PW}$. This tendency is kept in the blends containing EPDM. The ternary peak of the first melting LDPE$_{PW}$ is transformed into two separate peaks – one for LDPE and another for HDPE. Both the peaks keep their location in the second melting curves of the blends, showing the stability of the PE phase during blending and ageing. After artificial ageing, decrement in the quantity of the $\beta$ polymorph of PP$_{PW}$ can be noticed in the blends and not recrystallization processes have places. The melting peaks of PP$_{PW}$ shift to the left, and the melting thermograms become smaller with different

Figure 6. DSC cooling thermograms of TW blends modified with 7, 10 and 15 wt% EPDM before and after artificial ageing.
shapes and features, which results from the different phase transformations. Observing Figures 7 and 8, it can be concluded that the effect of EPDM in proving the stability is not so clear in the case of the postconsumer waste.

**Mechanical properties**

The irreversible ageing effects are connected with the melt flow, molecular weight and viscosity of the polymers. They have big influence on mechanical properties. The effects of weathering can vary from a complete loss of tensile strength and reduction of ductility (strain) to slight surface degradation. The last re-extrusion most often tend to improve the mechanical properties of a material.\(^{35}\) Reduction in molecular weight (chain scission) leads to shorter polymer chains and decreases all mechanical properties, but increase in molecular weight (cross-linking) leads to stiffer materials and increase in impact strength.\(^{22}\) Sometimes the hardness and stiffness of the aged thermoplastic elastomers are higher than that of the unaged, because of increased cross-link density in their structural and molecular reorganization.\(^{36}\)

For the mixed waste materials, it is expected that there will be considerable variability in the test results because the source materials are with unknown history.\(^{22}\)

The presence of a small amount of foreign material in PP may considerably change the crystallization temperature and type, size and density of spherulites. Pigments and
additives can have quite a dramatic effect on the rate of crystallization during processing. Some pigments act as nucleating agents or as antinucleating ones. Although the overall degree of crystallinity can be higher than expected, the fine crystal structure can lead to brittle material.

The tensile properties of the blends from virgin materials before and after natural ageing are shown in Figure 9. Before ageing, the tensile strength decreases and deformation enhances with increasing the modifier content. The natural ageing deteriorates the mechanical properties of the blends. Our observation established that the virgin samples after ageing have lost their continuity and they crumble, because they have no strength. There is one exception – the blends with 15% EPDM (15VR), for which after ageing a slight positive effect of the mechanic performance is observed. The deteriorated mechanical properties of the natural ageing blends are in accordance with the changes in their microstructure after ageing established by DSC.

The tensile strength of the recycled TW blends before and after accelerated ageing is presented in Figure 10. As a whole the extent of ageing deterioration process on the mechanical properties is smaller for the technological blends than for the virgin ones. The tensile strength does not exhibit significant change because of ageing.

The impact strength values of binary and ternary blends with different quantity of EPDM before and after accelerated ageing are shown in Figures 11 and 12. The impact
properties of the binary VR and TW blends are reasonably poor, because of the weak PE/PP interspherulitic boundaries. The toughness of the ternary blends increases with EPDM addition because the compatibilizer is localized at the interphase boundaries and enhances the stress transfer, contributing to particle size reduction. The impact strength of modified recycled blends is higher than that of the corresponding virgin blends; and after accelerated ageing, the impact strength of the modified virgin blends decreases significantly (Figure 11) in comparison with the corresponding recycled blends (Figure 12). Insignificant reduction in mechanical properties observed in the recycled samples is due to the addition of antioxidants. Moreover, TWag becomes more tough than before ageing and the ageing effect in this case is in fact annealing positive effect which results in better crystal structure. In the future more detailed experiments have to be performed on the TWag to explain this interesting phenomenon.

**SEM micrographs**

SEM observation of blend morphology before (images on the left) and after artificial ageing (images on the right) is essential for understanding the destruction processes (Figures 13 and 14). The obvious effect of weathering is a slight discoloration of the pigment resulting in a chalky surface or whitening of the coloration. During photodegradation, the molecules that were located near the exposed surface become heavily degraded, broken into smaller fragments and cross-links also introduced.19 We have surface degradation; predominantly the surface layer is degraded upon ageing. After ageing, debonding between filler and matrix is expected to occur, which can be more pronounced at higher strains, higher filler contents

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**Figure 9.** Tensile strength and strain at maximum stress of polymer blends VR vs. EPDM content before and after natural ageing.
Figure 10. Tensile strength and strain at maximum stress of polymer blends TW vs. EPDM content before and after natural ageing.

Figure 11. Impact strength of polymer blends VR vs. EPDM content before and after accelerated ageing.
and longer test times. After ageing, an additional factor could be chemical breakdown of the matrix especially due to impurities in the filler.

After natural ageing, separated phases and a lot of crazes in the blend without modifier can be clearly seen in Figure 13(b) for the VR blend. After ageing, both the crack initiation and propagation are accelerated. PP globules and a lot of holes in the result of got out globules are formed during the ageing. The boundaries between the three components in the blend modified with 12.5 wt% EPDM are not clearly discernible before natural ageing (Figure 13(c)). After ageing, separated rubber domains have appeared as a result of shrinkage of the main LDPE and PP phases (Figure 13(d)). EPDM delayed the formation of crazes and stopped the growth of microcracks. This effect is best observed at 15% EPDM (Figure 13(f)), which confirms the mechanical properties and DSC data.

There is no visible difference between the unmodified and modified blends from technological and postconsumer wastes after accelerated ageing in the chamber (Figure 14). Recyclate blends are more potent and separation of phases and crazes are not observed in the examined fracture surfaces inside in the sample.

**Conclusions**

DSC thermograms and mechanical tests made before and after ageing show greater destruction in the blends from VR than those from recycled material. This can be explained due to the absence of antiageing additives in the neat blends.
The impact EPDM modifier improves the stability of LDPE/PP blends against natural and accelerated ageing. The tensile and impact strength of the aged blends enhance with increasing of the modifier content.

The impact modifier has significant effect on recrystallization of PP in the blends during ageing and decreases the formation of the imperfect β polymorph. The reduction in the crystallinity degree of PP in the blends containing EPDM is lower in comparison to the blends without modifier.

Figure 13. SEM micrographs of blends before and after natural ageing—VR (a and b); 12.5VR (c and d) and 15VR (e and f).
After ageing, SEM micrographs show the presence of phase boundaries and a lot of holes in the blends without a modifier. EPDM improves the compatibility between both polymers and prevents the formation of crazes.

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**Figure 14.** SEM micrographs of recycled blends after accelerated ageing—TW (a); 15TW (b); PW (c) and 15PW (d). TW: technological waste; PW: postconsumer wastes; SEM: scanning electron microscopy.


