

Extrusion Processing of Polypropylene/Ethylene–Octene Copolymer Recycled Composite Material

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Abstract—Polymer mixtures based on recycled polypropylene with the addition of an ethylene–octene copolymer underwent extrusion processing to improve its physical and mechanical properties. Experimental thermodynamic and structural parameters of the composite material and its physical and mechanical properties were obtained. An increase in relative elongation at break of the composite materials prepared with an extrusion method as strands and films is due to the plasticization of recycled polypropylene with an ethylene–octene copolymer and a decrease in degree of crystallinity in the range of compositions studied. The possibility of practical use of recycled polypropylene as a part of composite materials for light industry and long products (pipes and film packaging) is shown.

Keywords: recycled polypropylene, ethylene–octene copolymer, extrusion, composite material, thermodynamic parameters, elongation at break

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The relevance of this work from the scientific and practical points of view is due to the need to improve the physical and mechanical properties of recycled polypropylene via creation of new polymer-composite materials based on its mixtures with thermoplastic elastomers, including dispersion-filled ones.

Recycled polypropylene obtained from sorted industrial polypropylene waste and from municipal solid waste has a number of disadvantages that limit the possibility of its practical reuse [1–3]: low relative elongation values and stress at break and low hardness, impact strength, and other properties compared to starting polypropylene. The formulation of composite materials based on recycled polypropylene and ethylene–octene copolymer to improve strength properties and the use of new compositions for these purposes using thermoplastic elastomers and highly dispersed fillers are important tasks.

The formulation will allow the range to be expanded of new composite polymeric and hybrid materials and their composites with various properties for extrusion processing to reuse secondary polymers [4–6].

It is known that polyolefins, for example, polypropylene (PP) and recycled polypropylene (RPP), are poorly compatible with polymers of different chemical nature [7, 8]. This paper proposes the development of a means to modify the sorted recycled polypropylene and the selection of components as modifiers to

increase the compatibility for extrusion processing into composite materials. As a modifier for polyolefins, a thermoplastic elastomer (TPE) of polyolefin type was used—an ethylene–octene copolymer, which can be processed with an extrusion method similar to that for thermoplastic materials, which include RPP, in contrast to conventional vulcanized rubbers [9–11].

The melting and curing processes of RPP and polyolefin-type TPEs is reversible, and, therefore, both waste from the industrial polymer production of PP and components of municipal solid waste (MSW) are suitable for recycling. It is important in choosing the type of TPE of POE SOLUMER 875L ethylene–octene copolymer as a modification component that they can be processed with the same methods (for example, extrusion) as the RTP thermoplastic. Information is available on the morphological features of films obtained from a mixture of PP and an ethylene–octene copolymer [12–15].

The aim of this work is to obtain multipurpose composite materials with extrusion processing of polymer mixtures of RPP with thermoplastic POE Solumer 875L ethylene–octene copolymer and to study the influence of a composition on the physico-mechanical and thermodynamic properties of polymer-composite materials.

The following materials were used in this work: a recycled polypropylene (ETM, Kostroma) with a density of 0.97 g/cm³; POE Solumer 875L ultra-low-den-

sity polyolefin thermoplastic ethylene–octene copolymer produced in the form of granules with a Nexlene technology (SK Global) with a density of 0.87 g/cm^3 ; MFI of 5.0 g/10 min , tensile strength of 6.1 MPa , and elongation at break over 1000% ; and composite materials based on a mixture of RPP and POE Solumer 875L.

Composite film materials were prepared from RPP and POE Solumer 875L polyolefin thermoplastic elastomer in different concentration ratios in laboratory extruders (Brabender, Russia) and Mashplast (Russia) at Moscow Polytechnic University. For this purpose, the recycled polyolefin and POE Solumer 875L were mixed, after which the resulting extrudate was loaded into the extruder and processed into a rod (strand) at temperatures at the outlet of extruder from 160 to 190°C . The resulting strands were cooled and crushed on a granulator to obtain granules from 2 to 4 mm in size, with the finished composite polymer films then being obtained on a laboratory flat-slot extruder (Mashplast).

The melt flow index of polymer components and their mixtures was found on an IIRT-5 capillary viscometer (TOCHMASHPRIBOR, Russia) at a mass ratio of RPP : POE Solumer 875L of $95 : 5$ and $90 : 10$ at 190°C and a load of 2.16 kg .

Tensile mechanical properties of the samples were studied on an RM-50 testing machine (Mashplast) equipped with a computer interface with the StretchTest software (Russia). The tensile stress at break and elongation at break of the composite films were measured at a temperature of $23 \pm 2^\circ\text{C}$ and a relative humidity of $50 \pm 5\%$ according to GOST (State Standard) 14236–81. The limit of a permissible load measurement error was no more than $\pm 1\%$. The limit deviations along the sample width were $\pm 0.2 \text{ mm}$. The mean value was found from three to five measurements. The tests were performed at a strain rate of samples of 100 mm/min . Film samples for testing were obtained on a punching device, and the shape of the samples corresponded to type 1B (ENISO 527-3).

The chemical structure of the film composites was studied with a Fourier IR spectroscopy on an FSM-1201 spectrometer with an MNPVO attachment (Germany) and a resolution of 1.0 cm^{-1} (the spectral range of wavenumbers was $375\text{--}4900 \text{ cm}^{-1}$).

The microstructure of polymer films was visualized with a fluorescence microscopy on a Biomed-4 PR LYUM direct epifluorescence microscope with $4\times$, $10\times$, and $20\times$ objectives equipped with a digital camera. A Ximea MD061CU-SY CCD color scientific camera was connected to the lens output used to record reverse fluorescence and images of polymer films in transmitted light.

The degree of crystallinity and the temperature stability of the samples were found with a differential scanning calorimetry (DSC) combined with synchronous TGA determination on a DSC 214 Polyma NETZSCH-Gerätebau GmbH calorimeter (Ger-

many) in the temperature range from 20 to 190°C at a scanning rate of $10^\circ/\text{min}$ and sample weight of $10 \pm 1 \text{ mg}$. The temperature scale and the enthalpy of melting were calibrated on a standard indium sample (melting point $T_m = 156.6^\circ\text{C}$ and specific heat of melting $\Delta H = 28.44 \text{ J/g}$).

Polypropylene, a nonpolar polyolefin, is used in many light industries from food packaging to structural parts and molded products. Polypropylene has one significant disadvantage, despite its various advantages (high barrier properties, rigidity, strength, and transparency): it is not a bioutilizable material. Taking this fact into account, one of the options for utilization of polypropylene is recycling. Recycling will expand the scope of recycled polypropylene and decrease the burden on the environmental situation in the country.

Taking these facts into account, it is of interest to use the recycled polypropylene not only as an individual polymer to produce products from it, but to use the recycled polypropylene in combination with any other polymers or fillers as modifiers. It would provide the compatibility of polymers in a mixture, influence the formation of new technological properties, and make joint recycling possible.

One promising means of expanding the range of using recycled polypropylene in mixed compositions is the use of thermoplastic polyolefin elastomers. One such thermoplastic elastomer is a POE Solumer 875L polyolefin elastomer that can be used not only as an individual thermoplastic elastomer material, but also as a modifier.

The products made of POE Solumer 875L polyolefin elastomer possess good elasticity, ductility, high strength, and puncture resistance; withstand sharp temperature changes; and are resistant to ultraviolet radiation. POE Solumer 875L polyolefin elastomer, which possesses properties that are similar to those of thermoplastic polymer including recycled polypropylene, can be processed on the same extrusion equipment as RPP.

A composite material obtained from recycled polypropylene and 875L POE Solumer thermoplastic elastomer will have new properties in this regard, among which high physical and mechanical properties can be distinguished. This composite material can be used to produce cables, seals, and hoses; in the shoe industry; as linings and soles for shoes; for constructing bags in the packaging industry; and bags for the disposal of municipal solid waste (MSW). This will expand the scope of its application, making this material important from scientific and practical points of view.

Rheological properties, in particular, the melt-flow index (Table 1), were found to select the extrusion production modes for composite samples. The data show that the melt viscosity of the composite material based on RPP : POE Solumer at a ratio of $90 : 10$ increases, while the MFI decreases, compared

Table 1. MFIs of starting components and compositions based on their mixture

#	Compositions	MFI, g/10 min
1	Recycled PP	6.0 ± 0.2
2	POE Solumer 875L	5.0 ± 0.1
3	RPP : POE Solumer 875L 90 : 10	5.4 ± 0.1

to those of a starting RPP. The MFI of the composite sample, however, increases in comparison with starting POE Solumer. This, in turn, confirms the compatibility of affinity of the components, which has a positive influence on the performance of extrusion equipment to produce such compositions.

Extrusion technology was used to process RPP and its mixtures with an ethylene–octene copolymer. The granules of recycled polyolefin were mixed with those of 875L POE Solumer thermoplastic elastomer at different concentration ratios, where the proportion of POE Solumer in the film compositions was from 0 to 10 wt %, respectively. The mixed extrudate was obtained in the form of strands on a twin-screw extruder under the temperature conditions given in Table 2.

The diameter of extruder screws is 16 mm. The rotational rate of the screws was from 60 to 80 rpm. The strands were cut into granules about 2 mm in size at a knife-rotation rate from 140 to 160 rpm.

The granules obtained on a twin-screw extruder were then loaded into a laboratory single-screw extruder with a screw diameter of 12 mm and extruded through a flat die with a width of 130 mm. In this case, a barrier screw was used. It provided good homogenization of mixtures based on RPP and 875L POE Solumer and high quality of the resulting composite polymer films during the extrusion process. The rotation frequency of the screw varied from 70 to 90 rpm.

The mass coming out of the head was received on cooled take-up rolls, stretched on a stretching device, and wound into rolls to obtain a composite film material. At the same time, laboratory samples have a uniform glossy surface without the formation of local holes or nonmelted thermoplastic agglomerates, which, in turn, indicates good homogenization of compositions based on RPP and POE Solumer. The edges of the samples are even and smooth.

When considering composite films as an option for producing packaging intended for municipal solid waste and for molding and structural parts, it is important to take into account the operational properties of a material. For this purpose, their mechanical properties were found: tensile stress at break δ and elongation at break ϵ (Table 3).

The test results indicate that the breaking tensile stress of recycled polypropylene is less than that of starting polypropylene, and the relative elongation at break is higher; both indicators of physical and mechanical properties change by 100%. It is known that the degree of crystallinity in polypropylene is 75–85% and decreases to 30–40% after repeated processing, so that the amorphous phase of the polymer and the deformation properties of the material increase, which is confirmed by the values obtained.

The incorporation of TEP into polymer matrix of RPP influences both the strength and the deformation properties of the finished composites. When 5 wt % of 875L POE Solumer is introduced into the composition, the breaking tensile stress and the elongation at break increase. When 10 wt % of 875L POE Solumer is introduced into the composition, the breaking stress at tension decreases, and the relative elongation at break increases. This is due to the fact that the introduction of higher amount of 875L POE Solumer influences the formation of fewer energy bonds between the components. We assume that TEP macromolecules interact with a polymer matrix and cross

Table 2. Temperature ranges to produce composite films

Composition	Temperature in zones of cylinder, °C				
	1 zone	2 zone	3 zone	4 zone	5 zone
RPP : POE Solumer 875L	160	175	185	190	190

Table 3. Physical and mechanical testing results of films

#	Material	σ , MPa, ($\Delta \pm 0.2$)	ϵ , %, ($\Delta \pm 5$)
1	Starting PP	28	240
2	Recycled PP	13	476
3	POE Solumer 875L	4.5	900
4	RPP : POE Solumer 875L 95 : 5	15	511
5	RPP : POE Solumer 875L 90 : 10	10	653

linking of the components proceeds to form a “network in network” structure.

It should also be noted that the macromolecules begin to orientate during stretching, so that relative elongation of the composite material at break increases by 1.4 times in comparison with RPP.

The experiments showed that the physical and mechanical properties of RPP and its composite material decrease during storage. This is probably due to the fact that polypropylene is partially destroyed during the extrusion process, which influences the change in the supramolecular structure of the composite material.

The temperature stability, the degree of crystallinity, and the intensity of heat fluxes of RPP and composite films based on HTPP : 875L POE Solumer were found with a DSC equipped with a synchronous TGA to confirm the hypotheses. Figures 1–3 show the TGA and DSC curves.

The synchronous TGA/DSC analysis data of ethylene–octene copolymer samples and its mixtures based on RPP indicate that the introduction of ethylene–octene copolymer into RPP within concentration range does not change significantly the thermal stability of the polymer–composite material.

Two crystalline phases are also characteristic of these compositions (Fig. 3): the secondary polyolefin, the melting peak of which appears at 164–170°C, which corresponds to the melting temperature of polypropylene, and the second component of the system (875L POE Solumer), the melting peak of which corresponds to a temperature of about 125°C. In this case, the total degree of crystallinity of the composition is about 30%, which is consistent with the physico-mechanical properties of these compositions.

Fourier transform IR spectra of a starting RPP and its mixtures with 875L POE Solumer ethylene–styrene copolymer were studied to confirm the choice of compositions that provide the compatibility of components in polymer mixtures and to substantiate the formulation of new composite materials.

Fourier transform IR spectra of RPP were explained based on characteristic frequencies of stretching vibrations of a CH group, the symmetric deformation vibration of a CH group (band at 1435 cm^{-1}), the antisymmetric deformation vibration of a CH_3 group (1435 and 1640 cm^{-1}), and symmetric deformation vibration of a CH_3 group (band at 1378 cm^{-1}). The absorption bands within 3000 cm^{-1} of the RPP samples indicates that there are amide-type additives, for example, dyes, in the mixture. This was concluded from the comparison of absorption bands in raw RPP samples from different manufacturers: absorption bands, for example, of Balen RPP at 1462 ($-\text{CH}_2-$), 2960 and 2880 (CH_3-), and 860 cm^{-1} ($\text{RRC}=\text{CH}_2$). We found that an amount of peroxide

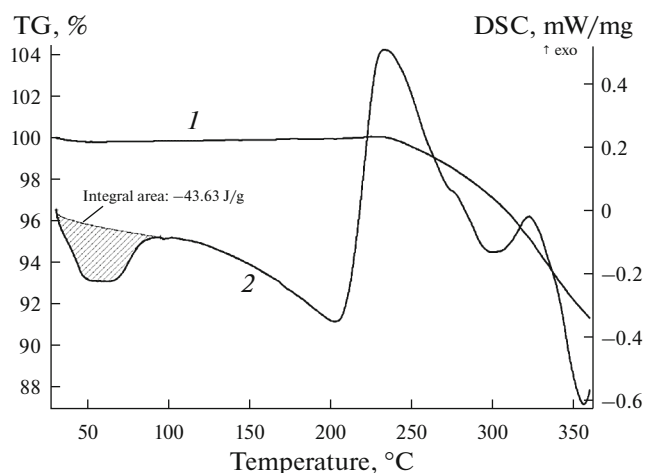


Fig. 1. (1) TGA and (2) DSC curves of ethylene–octene copolymer within 20–350°C.

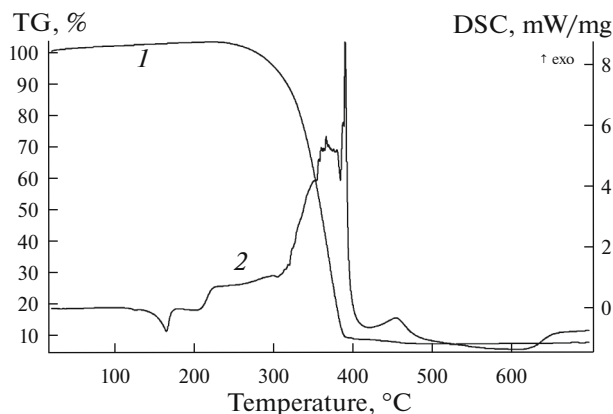


Fig. 2. (1) TGA and (2) DSC curves for RPP.

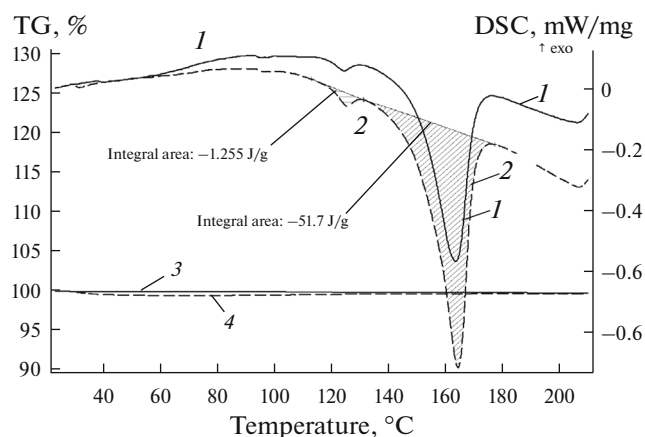


Fig. 3. TGA/DSC curves of RPP : POE Solumer compositions of various compositions: (1) 90 : 10 and (2) 95 : 5 wt %. Temperature range was 20–200°C.

and hydroperoxide groups in the samples is insignificant.

Analysis of Fourier transform IR spectra for RPP mixtures with 5–10 wt % of 875L POE Solumer ethylene–octene copolymer indicates that there is no shift in the position of characteristic absorption bands of CH_2 groups, which confirms that there is no a significant chemical or other interaction between these components of mixtures. These spectral results of the samples of the mixtures and their starting components, therefore, indicate that there are no chemical or other strong interactions between the starting RPP components and TPE in the polymer mixtures studied.

In fact, there is a simple additivity of the spectral manifestations of the properties of the components, i.e., the bands that are most characteristic of the studied thermoplastic elastomer POE Solumer 875L in mixtures with RPP also do not change their position or shape, but only demonstrate an increase in their intensity. Therefore, the ethylene–octene copolymer provides a physical modification of the RPP, and there are no chemical or any other types of strong interactions.

Samples with a size of 20×20 mm that were cut out from polymer and composite polymer–film sheets obtained with the extrusion method and washed with absolute ethanol (HPLC grade 99.8%, Acros Organics) and, then, with deionized water (Sigma) were used to study structural properties with fluorescence. After drying, a polymer–film sample was placed on a 1-mm glass slide; the sample on the glass was then placed on a microscope stage for visualization. The excitation light was the radiation of a high-pressure mercury lamp within 400–430 nm, which was cut out with a fluorescent cube, for optimal excitation of fluorescence and maximum contrast of the resulting images. The sample was then viewed through an objective. The reverse fluorescence was observed with the same objective, and then it was recorded within 450–700 nm with a color digital camera after passing through the fluorescent cube. The following objectives were used: $4 \times 0.13\text{NA}$ Plan (Biomed), $10 \times 0.3\text{NA}$ Plan-Neofluar (Carl Zeiss), and $20 \times 0.5\text{NA}$ Plan-Neofluar (Carl Zeiss).

Experimental optical studies of the fluorescence of samples of RPP, 875L POE Solumer, and their composite material indicate that the samples of polymer films mainly had blue–green fluorescence from 470 to 570 nm under excitation of fluorescence in the violet spectral range. In this case, individual inclusions in the films had red fluorescence within 600–650 nm. The fluorescent images of the samples and their transmission images indicate that the sample of pure 875L POE Solumer had the weakest fluorescence, for which only a weak blue–green fluorescence of inclusions up to $100 \mu\text{m}$ in size was observed. The RPP samples had a significantly stronger fluorescence, and the bright background fluorescence was combined with an even clearer

fluorescence of individual inclusions in them, which were also visible in the images in transmitted light.

The fluorescent images of RPP show a large number of inclusions up to $20 \mu\text{m}$ in size, which have bright fluorescence. When 875L POE Solumer ethylene–octene copolymer was added to RPP with a concentration of 5 and 10 wt %, there was a significant increase in the uniformity of the distribution of fine fluorescent particles with $1\text{--}5 \mu\text{m}$ in size. The addition of 875L POE Solumer to RPP, therefore, significantly changes the internal structure of the system and leads to the formation of polymer compositions with a less clear anisotropy of properties over their volume, which provides more uniform distribution of particles of up to $5 \mu\text{m}$ in size to have a positive effect on the physical properties.

CONCLUSIONS

Studies were performed to create composite film materials based on mixtures of RPP and polyolefin thermoplastic elastomer (875L POE Solumer ethylene–octene copolymer) at RPP : POE Solumer concentration ratios of 95 : 5 and 90 : 10 wt %.

Optimal temperature–concentration regimes to obtain composite material samples based on recycled polypropylene RPP : 875L POE Solumer via extrusion processing were selected. There was positive compatibility of components to create composite materials based on them.

The MFIs of components and compositions were measured, and the affinity of the polymer components of the system was found, which positively influences the productivity of extrusion processing.

The physicochemical properties of composite materials were determined. We found that the compatibility of RPP and ethylene–octene copolymer (875L POE Solumer) in the range of compositions of up to 10 wt % is due to a change in the amorphous–crystalline state of the system and proceeds without chemical modification of RPP structure or any other strong interactions.

Optical properties of film composite materials in the range of compositions of polymer mixtures were described with fluorescence microscopy. There was an increase in fluorescence from images of RPP to RPP : 875 L POE Solumer mixtures with an amount of ethylene–octene copolymer of 5 and 10 wt %.

There was a change in number and size of fluorescent particles from RPP to mixed polymer–composite materials, and there was an increase in the uniformity of their distribution in the volume, which indicates a more homogeneous structure of composite materials compared to that of RPP.

Physicomechanical properties of composite–film samples were assessed quantitatively. We found that the introduction of 875L POE Solumer thermoplastic additives into the polymer matrix of thermoplastic

RPP has a significant effect on the deformation properties of finished composite materials. Indeed, the deformation properties of the composite material increase by 36% compared to RPP the introduction of 10 wt % of 875L POE Solumer due to a change in supramolecular structure of the material caused by a decrease in degree of crystallinity of the system. This probably leads to cross linking of polyolefin thermoplastic elastomer with secondary PP, which influences this indicator.

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