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EFFECT OF FUNCTIONALIZED POLYMER MODIFIERS ON STRUCTURE AND MECHANICAL PROPERTIES OF DEGRADED LOW-DENSITY POLYETHYLENE

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This paper investigates the influence of functionalized polymer additives – sulfochlorinated atactic polypropylene (SCAPP) and chlorinated atactic polypropylene (CAPP) – on the structural, mechanical, and rheological properties of composite materials based on recycled low-density polyethylene (RLDPE). Waste polyethylene was collected from the Gazakh and Aran regions of Azerbaijan, and the additive content ranged from 5 to 20 weight mass. The composites were prepared by melt blending in a laboratory twin-screw extruder at temperatures of 170–180°C. The results show that the incorporation of functional additives improves phase compatibility, enhances thermal stability, and increases the mechanical strength of the material. Rheological analysis revealed that the melt flow index (MFI) of RLDPE grows with increasing temperature and applied load, but decreases with increasing content of the second component in binary mixtures with CAPP or SCAPP. Three-dimensional plots constructed at 130°C, 150°C, and 170°C confirm this relationship. The optimal SCAPP content provides improved melt flow behavior in the range of 150–170°C, indicating enhanced processability of RLDPE. The highest MFI values were observed at 170°C, which is associated with reduced melt viscosity. Mechanical testing showed that the addition of 5–10 weight mass CAPP or SCAPP raises the tensile strength and elongation at break, while an additive content of 15 weight mass ensures optimal mechanical stability. Modification with CAPP improves the properties of RLDPE by approximately 80–86%, whereas SCAPP exhibits a slightly lower effect due to the presence of sulfur-containing groups. Furthermore, the addition of 5–7 weight mass CAPP to binary systems containing mineral fillers such as sludge and zeolite enhances both mechanical and thermal properties while maintaining an effective viscosity of 9–11 Pa·s.

Keywords: **polyethylene, sulfochlorinated atactic polypropylenes, chlorinated atactic polypropylenes, composite materials**

INTRODUCTION

The rapid development of modern industry is accompanied by the accumulation of significant amounts of solid waste, among which polymeric materials such as polyethylene, polypropylene, and various elastomers occupy a prominent place. Their accumulation poses serious environmental challenges due to their high resistance to biodegradation. One of the most effective approaches to mitigating these impacts is the recycling and reprocessing of polymer waste into new composite materials [1–5].

The development of polymer composites based on polyolefin waste contributes to the conservation of primary resources while simultaneously addressing environmental concerns. The incorporation of modifying additives containing functional groups can improve compatibility between the components and enhance the physicomechanical properties of the resulting materials [6–11]. The addition of compatibilizers such as CAPP and SCAPP improves interfacial adhesion between phases in composite systems.

The aim of this study is to develop composite materials based on recycled polymers with improved performance, as well as to investigate the effect of CAPP and SCAPP on the structural and mechanical properties of RLDPE-based systems. These additives possess amphiphilic characteristics, enabling improved interaction between polymer phases and the formation of more stable interfacial structures.

EXPERIMENTAL PART

Materials

Recycled low-density polyethylene (RLDPE) waste was collected from sewage service facilities in the Gazakh and Aran regions of Azerbaijan. The effect of CAPP and SCAPP on the RLDPE samples that had been in service for 1 and 5 years was investigated. The content of these functional additives in the compositions ranged from 5 to 20 weight mass, which made it possible to investigate the influence of their concentration on the structure and properties of the resulting materials.

Preparation of composite mixtures

The compositions were prepared by melt blending in a laboratory twin-screw extruder at 170–180°C (Tables 1 and 2). The screw speed was maintained at 40–60 rpm. Prior to processing, all the components were dried for 2 h to prevent moisture-induced defects such as porosity [12, 13]. The extrudates were cooled in a water bath and pelletized. The test specimens and films (1–1.2 mm thick) were produced using flat-die extrusion.

TABLE 1. **Composition of RLDPE and CAPP binary mixture (weight mass)**

Components	1	2	3	4	5
RLDPE	100	100	100	100	100
CAPP	-	5	10	15	20
total	100	105	110	115	120

TABLE 2. **Composition of RLDPE and SCAPP binary mixture (weight mass)**

Components	1	2	3	4	5
RLDPE	100	100	100	100	100
SCAPP	-	5	10	15	20
total	100	105	110	115	120

METHOD OF ANALYSIS

Extraction procedure

For characterization, the prepared samples were subjected to sequential solvent extraction in order to remove low-molecular-weight fractions and any unreacted additives. The extraction was carried out in two stages utilizing acetone and toluene as solvents. In the first stage, the samples were extracted with acetone for 6 h by means of a Soxhlet apparatus to remove residual impurities, plasticizers, and other low-molecular-weight components. After acetone extraction, the samples were dried in a vacuum oven at 60°C until a constant weight was attained. In the second stage, the dried samples were extracted with toluene for 8 h to dissolve and remove soluble polymer fractions and unbound modifier molecules. After extraction, the samples were again dried under vacuum at 60°C to a constant weight. The purified samples were subsequently employed for further analysis.

FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups and confirm the chemical structure of the samples. All the measurements were carried out utilizing a compact high-precision FTIR spectrophotometer (ALPHA II, Bruker, Germany).

Rheological measurements

Rheological measurements were performed by means of a melt flow index apparatus at temperatures of 130°C, 150°C and 170°C. The experiments were conducted under applied loads of 11.75 kg, 20.85 kg, 26.15 kg and 32.95 kg. Prior to the measurements, the samples were conditioned at the test temperature to ensure thermal equilibrium. The melt flow behavior was evaluated by recording the viscosity as a function of the temperature and composition. The obtained data were presented as three-dimensional plots illustrating the dependence of the melt viscosity on the temperature and composition.

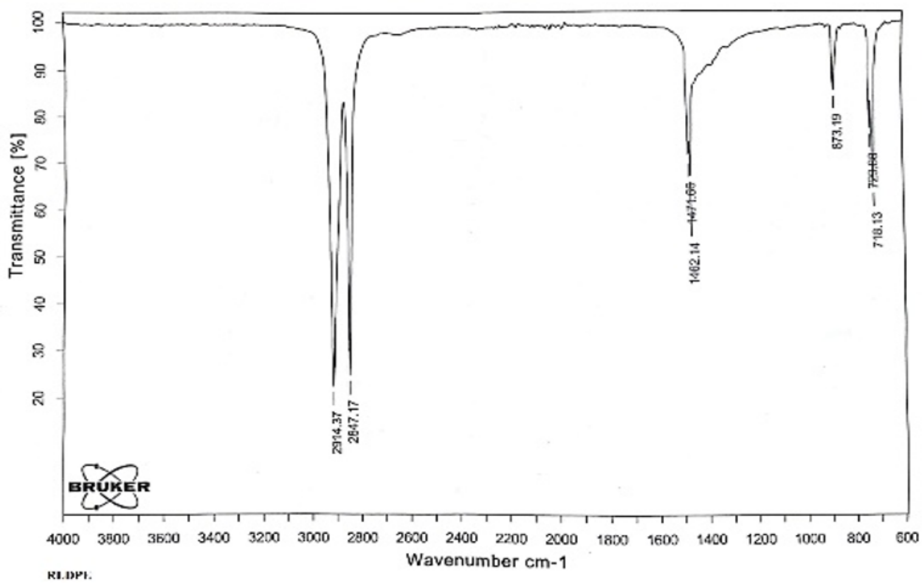
RESULTS AND DISCUSSION

The samples were extracted first with acetone, then with toluene (each separately) for 18 h and the gel fraction was determined (Table 3).

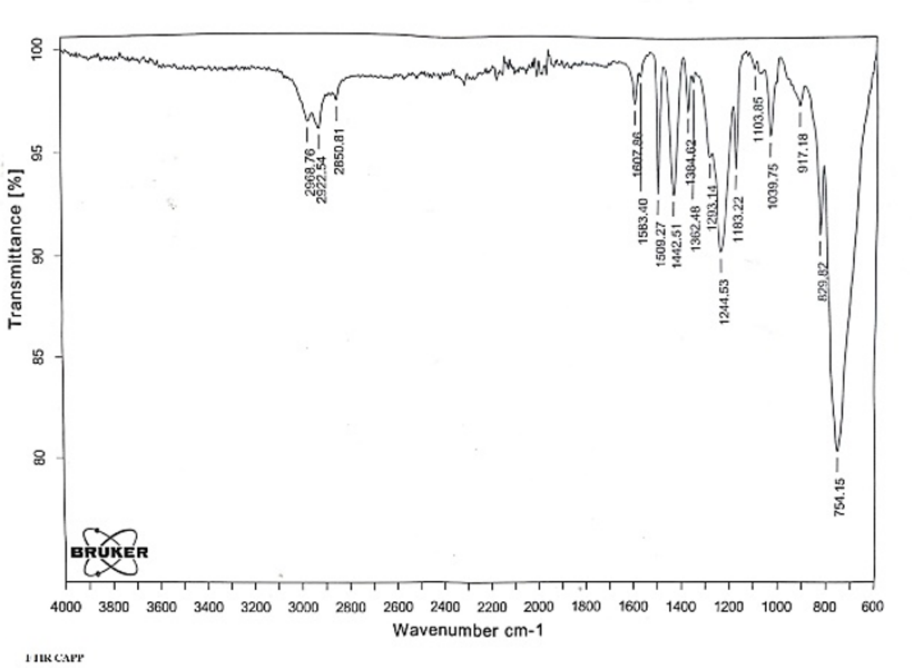
TABLE 3. **Gel fraction after extraction**

Samples (RLDPE and CAPP)	Amount of gel, %	Samples RLDPE SCAPP	Amount of gel, %
1	99.6	1	99.7
2	98.9	3	98.6
3	98.8	4	98.2
4	98.0	5	98.0
5	97.7	6	97.5

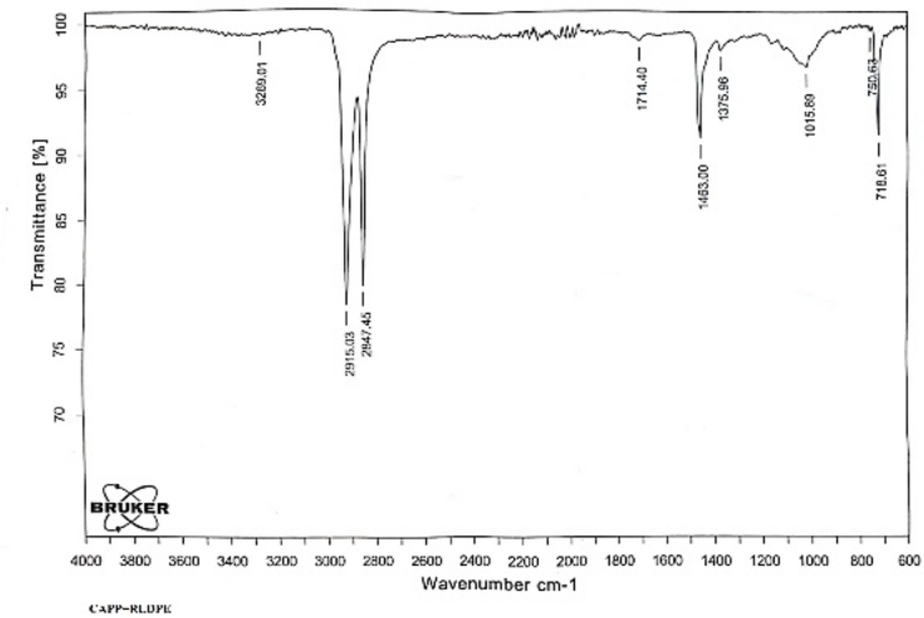
FTIR spectroscopy was performed to characterize the structural features of the initial polymer components used in composite fabrication: RLDPE, CAPP and SCAPP (Figure 1). The spectral data provide critical insights into the macromolecular backbone integrity and the degree of functionalization achieved during chemical modification [13].



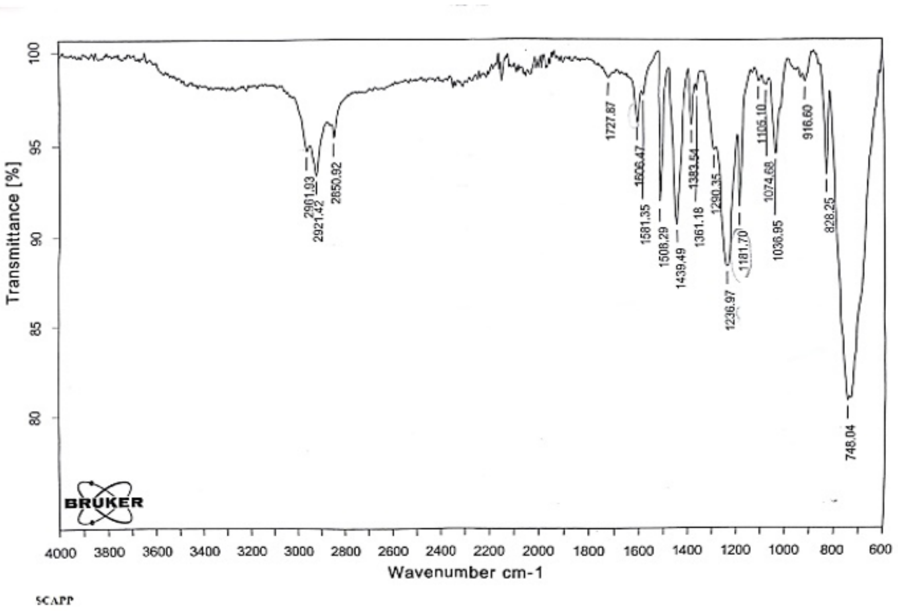
a) RLDPE



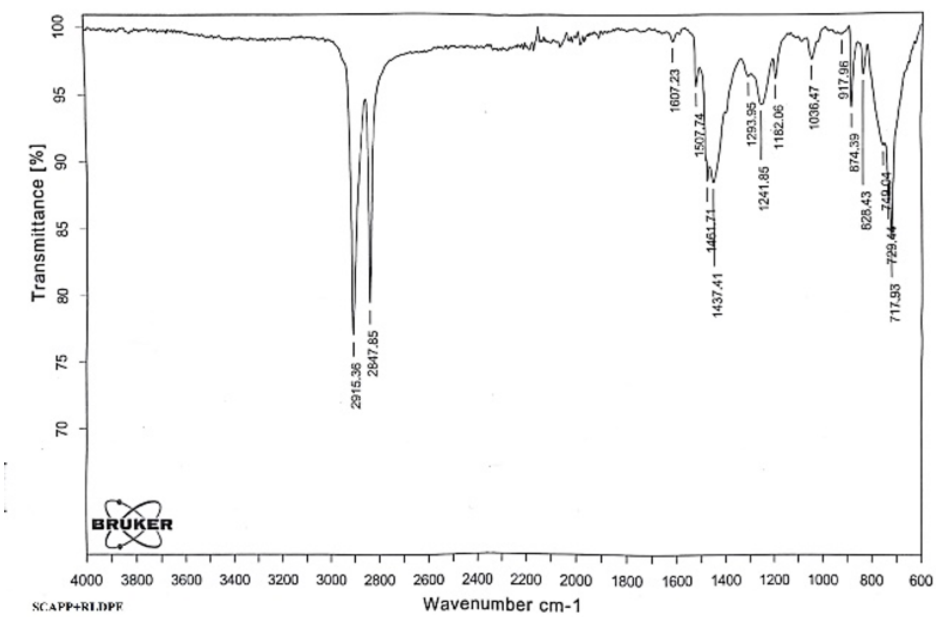
b) CAPP



c) CAPP-RLDPE



d) SCAPP



e) SCAPP-RLDPE

Fig. 1. FTIR spectra of RLDPE, CAPP, SCAPP, and their composites

The FTIR spectrum of RLDPE (Figure 1a) exhibits characteristic absorption bands at 2914 and 2847 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of –CH_2– groups. The deformation vibration at 1462 cm^{-1}, along with the rocking bands at 718 and 729 cm^{-1}, confirms the preservation of the polyethylene backbone and the presence of crystalline domains. The weak band near 873 cm^{-1} indicates the formation of vinyl or vinylidene groups, suggesting thermo-oxidative degradation accompanied by chain scission. Notably, the absence of strong carbonyl (≈1700–1750 cm^{-1}) and hydroxyl (≈3200–3600 cm^{-1}) bands implies that oxidation remains limited, likely occurring at an early stage or surface level [14, 15].

For the CAPP sample (Figure 1b), the characteristic stretching vibrations of $–CH_3$ and $–CH_2–$ groups are identified at 2968, 2922, and 2850 cm^{-1}, confirming that the aliphatic hydrocarbon skeleton remains largely intact post-chlorination. The deformation bands in the 1450–1360 cm^{-1} region align with the standard atactic polypropylene structure. The successful covalent incorporation of the chlorine atoms is substantiated by the emergence of new absorption bands in the fingerprint region (800–600 cm^{-1}), corresponding to C–Cl stretching vibrations. Minor peaks near 1600 cm^{-1} likely reflect localized unsaturation or structural irregularities induced by the chlorination process.

The FTIR spectrum of SCAPP (Figure 1c) reveals more pronounced chemical transformations. Alongside the typical hydrocarbon bands at 2961, 2921, and 2850 cm^{-1}, distinct absorption at 1727 cm^{-1} indicates the presence of carbonyl groups formed under oxidative conditions. The bands at 1361, 1290, 1236, and 1181 cm^{-1} are characteristic of S=O and C–S vibrations, providing clear evidence of sulfonyl ($–SO_2–$) group incorporation. Additional peaks at 1105–1036 cm^{-1} further support the presence of oxygen- and sulfur-containing functionalities. The weak absorptions at 916 and 828 cm^{-1} suggest the formation of unsaturated structures, likely owing to concurrent degradation processes.

For the CAPP/RLDPE composite (Figure 1d), the spectrum shows prominent absorption bands at 2915 and 2847 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of $–CH_2–$ groups, confirming the dominance of the polyethylene phase in the composite. The band at 1463 cm^{-1} is assigned to $–CH_2–$ bending vibrations, while the peak at 1376 cm^{-1} is associated with $–CH_3$ deformation, indicating the contribution of the polypropylene component. The weak absorption near 1714 cm^{-1} suggests the presence of carbonyl (C=O) groups, likely formed due to slight thermo-oxidative degradation of recycled polyethylene during processing. The band observed at 1015 cm^{-1} may be attributed to C–C or C–O stretching vibrations influenced by the presence of chlorine-containing groups from CAPP. Additionally, the peaks at 718–750 cm^{-1} correspond to the rocking vibrations of long $–(CH_2)n–$ sequences, indicating the preservation of crystalline domains within the polyethylene phase.

In the case of the SCAPP/RLDPE composite (Figure 1e), more pronounced structural modifications are observed. Along with the typical $–CH_2–$ stretching bands at ~2915 and 2847 cm^{-1}, additional absorption features appear in the fingerprint region. The presence of bands in the 1200–1150 cm^{-1} region is attributed to S=O stretching vibrations, confirming the incorporation of sulfonyl ($–SO_2–$) groups from sulfochlorinated polypropylene. The peaks around 1030–1060 cm^{-1} further support the presence of oxygen- and sulfur-containing functionalities.

Compared to the CAPP-based composite, the SCAPP/RLDPE system exhibits increased intensity in polar functional group regions, indicating a higher degree of functionalization. This suggests enhanced interfacial interactions between the modified polypropylene phase and the polyethylene matrix. The weak carbonyl band near ~1710–1730 cm^{-1} also indicates minor oxidative processes but does not dominate the spectrum.

The rheological properties of the obtained compositions were subsequently investigated. To determine the melt-flow index of the alloy based on modified RLDPE containing the functional polymers CAPP or SCAPP, measurements were conducted under stresses generated by different temperatures (130°C, 150°C and 170°C) and various loads (11.75kg, 20.85kg, 25.35 kg and 31.30kg). Under these conditions, plots were constructed illustrating the dependence of the volumetric flow rate of RLDPE alloys, as well as binary RLDPE /CAPP and RLDPE /SCAPP blends, on the content of CAPP (or SCAPP) in the mixture [16].

Three-dimensional surface plots for the three temperatures – 130°C, 150°C, and 170°C – are presented in Figure 2. These plots illustrate the dependence of the melt flow index (MFI) of RLDPE composites containing SCAPP and CAPP on the applied load and temperature [17, 18]. The graphs were constructed based on the results obtained from the displacement–stress dependence analyses of composite materials produced from RLDPE in binary mixtures.

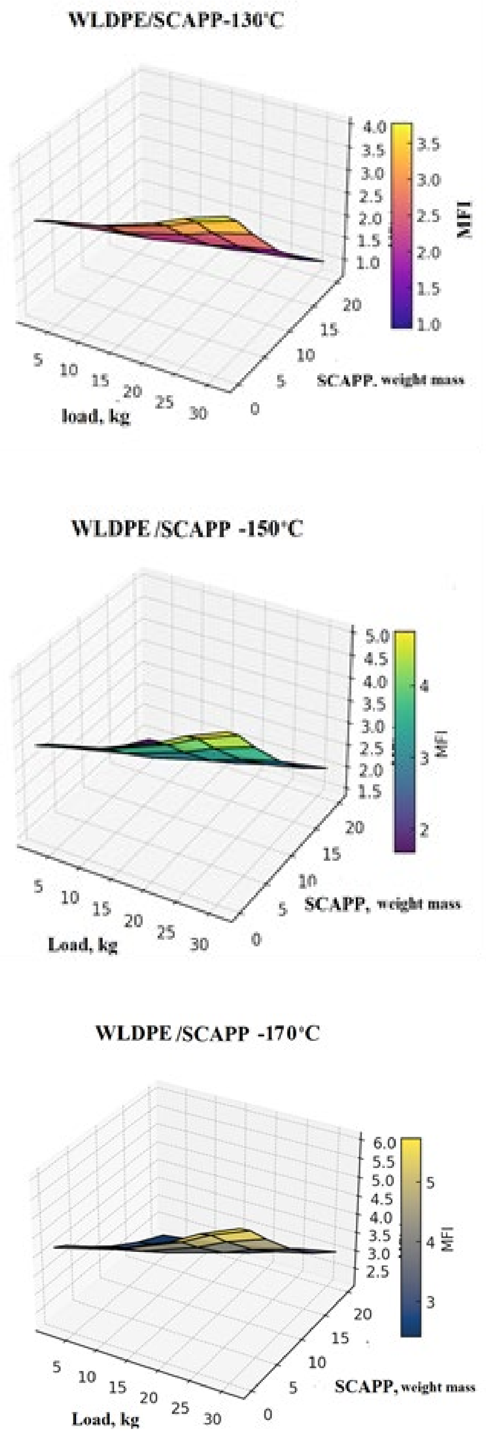


Fig. 2. 130°C, 150°C and 170°C — 3D surface plates of prepared composites

As can be seen from the graphs, at 130°C the results show that an increment in load gradually raises the MFI value. At the same time, an increase in the content of the second component in the binary blend leads to a decreasing trend in MFI. Therefore, under conditions of both high load and low SCAPP (CAPP) content, the MFI reaches its maximum value. At 150°C, the MFI values are higher compared to the previous temperature, which indicates an intensification of the melt flowability of RLDPE with increasing temperature. Although an increment in load elevates the MFI, an increase in the SCAPP (CAPP) content leads to its reduction. The maximum MFI is observed under the combination of high load and low SCAPP (CAPP) concentration. At 170°C, the highest MFI values are obtained. The influence of load and SCAPP (CAPP) content remains consistent with the trends observed at lower temperatures: increased load enhances MFI, whereas a higher SCAPP (CAPP) content reduces it. The surface plot appears smoother and is characterized by higher MFI values, further confirming the significant effect of temperature on the melt flowability of the polymer. Thus, the graph clearly demonstrates that the MFI of the composites prepared on the basis of RLDPE with CAPP or SCAPP depends on the applied load, temperature, and modifier content. As the temperature and load grow, the MFI rises, whereas an increment in modifier concentration results in a decrease in MFI. This indicates that the MFI of the composite material can be regulated depending on the processing conditions. At 170°C, the viscosity of the polymer is at its lowest, resulting in a smoother surface plot and higher MFI values.

Based on the results of the conducted research, the influence of different types (CAPP or SCAPP) and amounts of additives on the mechanical and rheological properties of the polyethylene-based systems was determined. The addition of 5 weight mass CAPP leads to a rise in the stress at break (σq), indicating a moderate level of strength. This suggests that modification with CAPP induces a certain degree of structural reinforcement. When the same amount (5 weight mass) of SCAPP is introduced, the stress at break (σq) becomes slightly higher, although the overall values remain at a moderate level, demonstrating that SCAPP exhibits somewhat stronger activity. When the additive concentration is increased to 10 weight mass, modification with CAPP results in a further rise in σq, and the elongation at break (Lq) also grows. This composition can be considered close to optimal. The use of 10 weight mass SCAPP shows a stabilization tendency within the system, accompanied by an increase in Lq. When the amount of additive is increased to 20 weight mass, modification with CAPP yields σq values approaching their maximum, indicating high material strength. In contrast, the introduction of 20 weight mass SCAPP results in a slight decrease in mechanical performance and stabilization within the system.

The analysis of the obtained results shows that in binary blends, the addition of CAPP up to 15 weight mass leads to an improvement of 80–86% in the fundamental properties of RLDPE. The presence of 0.3–0.35 weight mass sulfur in SCAPP causes its interaction with the RLDPE macromolecules at elevated temperatures (180°C). As a result, the property enhancements achieved by SCAPP modification are slightly lower than those obtained with CAPP. In both cases, however, improvement in the properties of RLDPE is observed. This enhancement is attributed to the growth in the amount of the elastic polymer phase within the system. It is assumed that the functional –Cl and $–SO_2Cl$ groups present in CAPP and SCAPP not only raise the proportion of the elastic phase in the blends but also contribute to better wetting and normalization of the dispersion of filler particles.

Taking these findings into account, composite materials based on RLDPE +CAPP+sludge and RLDPE +CAPP+zeolite were prepared at the optimal amounts of XAPP and SXAPP (15 weight mass), then their main physicomechanical and technological properties were investigated (Table 4) [19].

TABLE 4. **Physicomechanical and technological properties of RLDPE+CAPP+sludge and RLDPE +CAPP+zeolite composites containing 15 weight mass CAPP and SCAPP**

Row	Composition and properties of composition based on RLDPE	Compositions and characteristics				
		RLDPE	Composites based on RLDPE			
			1	2	3	4
1	CAPP content, weight mass	-	15.0	15.0	-	-
2	SCAPP content, weight mass	-	-	-	15.0	15.0
3	Sludge content, weight mass	-	5		5	
4	Zeolite content, weight mass	-		7		7
5	σq, MPa	4.8	13,1	14.1	13.8	14.2
6	Lq, %	116	221	195	205	185
7	MFI, g/ 10 min	0.28	0.68	0.67	0.63	0,55
8	Effective viscosity at 160 °C, Pa·s	12.5	9.1	10.0	9.2	11.0

As seen in the table, the addition of CAPP and SCAPP increases the tensile strength and elongation at break of the composites filled with either sludge or zeolite, while in the RLDPE+CAPP-based composites, it maintains effective viscosity at the desired level of 9.1–10 Pa·s. Considering the fillers and compatibilizing additives, for recycled LDPE, using 5–7 weight mass fillers and 10–15 weight mass functional compatibilizers allows the processing of composite materials with suitable properties for fabrication and service, thereby reducing the consumption of virgin polymer raw materials.

For this reason, producing filled composites based on recycled polymers and studying the influence of various fillers and functional compatibilizers on their properties has both scientific and practical significance.

The obtained results demonstrate that, in RLDPE-based composites, the addition of 5–7 weight mass selected mineral fillers such as sludge and zeolite improves the tensile strength, density, and thermal stability, while also allowing the elongation at break, elasticity, relaxation modulus, viscosity, and melt flow properties to be maintained at the required levels. Exceeding the recommended filler content increases brittleness during service, especially in RLDPE, potentially rendering the composite unsuitable.

Considering various factors, the incorporation of fillers together with a functional compatibilizer improves the distribution of the filler as an insoluble phase (28.6%) within the solid matrix, enhancing adsorption and chemical interaction between the polymer and filler. As a result, the properties of RLDPE-based composites approach those of the virgin polymer, providing technological and physicochemical characteristics suitable for practical applications.

CONCLUSIONS

The introduction of CAPP and SCAPP into recycled polyethylene resulted in a noticeable modification of the structure and properties of the resulting materials. Increasing the concentration of the functional additives led to a decrease in the degree of crystallinity and an increment in elongation at break, indicating a plasticizing effect of CAPP and SCAPP. The samples containing 6 weight mass SCAPP exhibited an optimal combination of strength and elasticity, making them suitable for the production of film packaging.

Thus, the conducted experimental studies confirm the effectiveness of using functionalized polymers CAPP and SCAPP as compatibilizers during the processing of recycled polyethylene, contributing to improvement of both the structure and the operational properties of the resulting composite materials.

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