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Please cite this article as: Soykan U, Ozturk Sen B, Cetin S, Yahsi U, Tav C, A detailed survey for determination of the grafted semifluorinated acrylic compound effect on thermal, microstructural, free volume, mechanical and morphological features of HDPE, *Journal of Fluorine Chemistry* (2020), doi: https://doi.org/10.1016/j.jfluchem.2020.109511

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A detailed survey for determination of the grafted semifluorinated acrylic compound effect on thermal, microstructural, free volume, mechanical and morphological features of HDPE

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This graphical abstract shows the dependence of the ultimate strengths, Young's modulus and impact strength on the percentage of side chain flouroalkyl acrylate polymer content in graft coproducts.

Highlights

• Side chain graft copolymerization of the fluoroalky acrylate onto HDPE was performed with high yield.

- Impressive mechanical reinforcement was obtained by using the flouroalkyl acrylate including perfluorinated pendant units.
- The grafting onto HDPE caused the linearly increament in the free volumes in consistence with the percent poly(ABCF13).
- Significant changes in *a* and *b* unit cell parameters as well as particle size of HDPE crystals with grafting were recorded.
- The graft copolymerization brought about the significant increments in the melting temperature of HDPE crystalline domains.

ABSTRACT

This study mainly aims to investigate the role of grafted semifluorinated acrylic compound in the crucial characteristic properties of high density polyethylene (HDPE). Graft copolymerization of the semifluorinated acrylic compound, 3,3,4,4,5,5,6,6,7,7,8,8,8dodecafluoro-5-methyloctyl-4-(acryloyloxy) benzoate (ABCF13) onto HDPE within the different content levels of ABCF13 (5, 10, 15, 20, 30 and 40%) was performed by bulk-melt polymerization method. The changes in the thermal, microstructural and free volume characteristics of graft coproducts with extent of grafting were investigated in detail by means of DSC, powder X-ray diffraction and PALS techniques, respectively. The experimental findings showed that the melting temperature of crystalline domains and crystallinity of HDPE reached the maxima at the 15% and 40% ABCF13 contents, respectively. The grafting of ABCF13 onto HDPE also gave rise to significant expansion and contraction in lateral dimensions of orthorhombic unit cell parameters in the crystalline domains of HDPE. Moreover, PALS analyses depicted that the size of the free volumes increased almost linearly with the grafting percentage. As for mechanical behaviours of the graft products, remarkable improvements were achieved in especially tensile strength (from 18.75 MPa to 43.75 MPa) and impact strength (from 19.30 Mpa to 38.72 MPa). The morphological properties of the

fractured surfaces obtained from tensile and impact tests of products were also examined by SEM analysis. The samples possessed completely homogeneous structure without any phase separation. A gradual transition from ductile behaviour to brittle nature was observed as the grafting level increased in the products .

Keywords: High density polyethylene, semi-fluorinated acrylic compound, grafting, mechanical reinforcement, unit cell parameters, free volume.

1. Introduction

The most common way to upgrade the crucial some characteristics of thermoplastics (TPs) is the preparation of their blends formed by combining with rigid-rod like polymers such as liquid crystalline polymers. In many studies, the rigid-rod like polymers, exhibiting relatively considerable larger mechanical performance thanks to their stiff molecular backbones with the ability of high orientation, have been blended with TPs so as to obtain reinforced composite like materials [1-3]. In order to achieve effective mechanical improvements in these blends, it is required that the dispersed polymers having rigid backbone in the molecular structure act as fibrils in the TPs matrix. The fibrillar structure of the rigid-rod like polymer component strengthen the TPs matrix like in the fiber-reinforced polymer composites due to the fact that these fibrils forming under the proper processing conditions possess the relatively larger load carrying capacity[4, 5].

It is known that the fluorine-containing polymers have continuously growing role in the materials science due to their superior properties. The substituting fluorine for hydrogen in a number of fully or partially fluorinated polymer molecules cause three main useful corridors: (I) increase in thermal stability and reduction in flammability (II) lower surface energy, supporting anti-adhesiveness, lower friction coefficient, self-lubricating and (III) impressive optical and electrical properties [6]. Despite of these advantages, the practical usage of fluorine containing polymers in the TPs blends are highly restricted due to the serious compatibility trouble between components, which resulting in phase separation in the polymer matrix. It is well known the fact that fully or partially miscible systems in the blends gain better properties to the polymer matrix compared with totally immiscible systems [7,8]. Thus, in order to ensure homogeneity without any phase separation, the certain amount of the compatibilizing agents such as catalyst [9], modified graft [10,11], block [12], liquid crystal [13] or any polymer [14] are used in the matrix of thermoplastic polymer/TPs blends. In addition to that, the another effective way to obtain fluorine-containing polymer/TPs blend having

desired and improved properties is the designing of copolymers cooperated with more fluorinated groups or grafting of the modified partially (or fully) fluorinated monomers onto thermoplastics [15-17]. With this aspect, since fluorooalkyl acrylates (FAs) possesses the rigid perfluorinated pendant unit in the helix structure, self-organization ability in the matrix, remarkable low surface energy caused by the fluorine atoms, chain sliding effect and tendency to show smectic phase due to the fluorinated groups, the designed FAs could serve as the component of the thermoplastic polymer blends to achieve the improvements in the polymers [18-21]. In a way that supports this approach, in terms of mechanical characters, the presence of the rigid-rod like groups like mesogenic groups in the molecular structure of one component of thermoplastic polymer blends brings about more arranged and organized structures with considerable orientations and molecular extensions, which resulting in mechanical reinforcements [2,22]. In accord with that, in our previous work, the considerable improvement in the mechanical characteristics of HDPE was obtained due to the increasing of chain orientations of HDPE chains in the matrix, which resulted from the presence of sidechain bonded acrylate units having rigid-rod like molecular structure [23]. The presence of liquid crystalline polymer (LCP) with rigid molecular backbone in the PP matrix raised to improvement in the fibrillation with the use of silica fillers. This dual reinforcements observed in the LCP/SiO2/PP system resulted in the relatively higher yield strength and modulus [24].

On the other hand, the free volume indubitably effects the mechanical properties of the polymers [25,26]. The free-volume and mechanical properties of the polymers possess the anti-correlated relationship due to the fact that the formation of excess amount of holes in matrix damages the microscopic structure of polymers [27]. That is, the molecular motions and mobility of polymer chains in the bulk state are directly related to the presence of the holes, spaces and places where there exist voids and vacancies [28]. As the molecules in matrix are in motion into the holes, the molecules exchange the place with the holes and the more holes can be needed for this movement of the polymer chains [29]. Therefore, the critical free volume must exist in polymer matrix for supplying the optimum molecular motion of the polymeric segments. Burgess et al. reported that the addition of the small caffeine molecule into PET, which results in filling of holes in the matrix, gave rise to the chain motions restrictions and the reduction in the free volume in the film samples compared to neat PET [30]. Kumar et al. studied the relation between free volume and the physico- mechanical behaviour of polyurethane (PU)/polyacrylonitrile (PAN) polymer networks. The obtained results showed that the maximum tensile strength was achieved with the 70/30 PU/PAN mixture at which the lowest free volume and percent elongation were

found. That is, the mechanical characters of the PU/PAN blends affected positively from the decrement in the free volume due to the better interpenetration, higher degree of physical entanglement and hydrogen- bond formation between PU and PAN[31].

Although the fluorine-containing polymers possess superior properties, there existed any studies in the literature, showing how the mechanical, thermal and microstructural properties of graft copolymers bearing fluorine-containing polymers bonded as side chain were effected from the free volume change. To fill this gap, this current work focused on the examination of the crucial properties of HDPE graft copolymers formed by using the fluorooalkyl acrylate molecule bearing perfluorinated pendant units. By considering stiff molecular backbone, the larger lateral polarity effect, self orientation properties, chain sliding effect, tendency to show smectic phase and ability to increase free volume of this semifluorinated acrylic compound, the main characteristic properties of HDPE were improved via grafting of semifluorinated acrylic compound onto it.

2. Experimental

2.1. Materials

For the synthesis of the monomer (ABCF13), the major chemicals, acryloyl chloride (AC), *p*-hydroxybenzoic acid (HBA), thionyl chloride (Merck), 3,3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-1-octanol (F13) (Alfa Aesar, 97%) were used as received from companies without any further purifications. Dichloromethane (Merck A.G.), dimethyl sulfoxide (VWR International), Ethyl acetate (Sigma Aldrich), benzoly peroxide (BP) (Merck) and triethylamine (TEA) (Merck) were also used as received. All the other reagents and solvents were analytical grade and used as received without any further purifications.

Granular high density polyethylene (HDPE) (coded as S 0464) supplied from Turkish Petrochemical Industry (PETKIM) was used to prepare powder form of HDPE. With this purpose, HDPE granules were dissolved in boiling xylene at 138-139 °C by refluxing for 3-4 days. The polymer was precipitated adding ethanol, collected by filtering and dried in vacuum at 50 °C. The polymer was then ground by cooling in liquid nitrogen to obtain HDPE in powder form. The obtained powder HDPE was used in the graft copolymerization experiments.

2.2. Synthesis of the monomer, ABCF13

The synthesis of the monomer, ABCF13, was accomplished in three stages: (I) preparation of p-acryloyloxybenzoic acid, ABA, (II) preparation of p-acryloyloxybenzoyl chloride, ABC and (III) preparation of ABCF13. The syntheses of both p-acryloyloxybenzoic acid (ABA) and p-acryloyloxybenzoyl chloride (ABC) were announced in our previous work [32,33]. The monomer was prepared by the condensation reaction between 3,3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-1-octanol (DFO) and ABC. Typically, 4.75 mmol of DFO and 4.75 mmol of triethylamine was dissolved in 100 mL of EtOAc in a flask equipped with a magnetic stirrer. 4.75 mmol of ABC dissolved in 100 mL of EtOAc was added dropwise at room temperature by stirring the mixture simultaneously. After the reaction was completed, triethylamine hydrochloride salt formed during the reaction was extracted from the product by successive washings (3-4 times) with water. The product was then dissolved in EtOAc. The remaining water in the solution was removed by adding Na₂SO₄ as drying agent and then by filtering off. Finally, the solvent was evaporated and the product was purified by repeated recrystallizations from methanol, and dried in vacuum at the room temperature. The reaction yield was founded to be 81%. FTIR, DSC, ¹H-NMR, High Resolution Mass Spectroscopy (HRMS) and elemental analysis techniques were used for the chemical characterization of the monomer synthesized. The plain reaction steps for the synthesis of ABCF13 was displayed in Fig. 1. White solid: 81% yield. melting point; 44°C with respect to DSC. ¹H-NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 2.60-4.62 (4H, -CH₂), 6.06-6.32-6.60 (3H, -CH), 7.22-8.08 (4H, ArH). IR (KBr) (v max, cm⁻¹) 2976 (-CH₃), 1739 and 1716 (-C=O), 1635 and 1508 (C=C), 1284-1122 (-C-F and -C-O-C) and 908-765 (C-H). Elemental analysis calcd. for C₁₈H₁₁F₁₃O₄; C, 40.17; H, 2.06. Found: C, 40.67; H, 2.14. HRMS: *m/z* (ESI-TOF, $[M + H]^+$) calcd. for $C_{18}H_{12}F_{13}O_4$: 539.0528. Found: 539.0527.

2.3. Homo and Graft Polymerization of ABCF13

Homopolymerization of the monomer, ABCF13, was conducted by bulk-melt polymerization method. 10.00 g of ABCF13 and 0.20 g of benzoyl peroxide (BPO, 2% weight of monomer) were mixed in mortar and by grinded by hand for the homogeneity. This mixture was put into the glass ampule, and vacuumed for 30 minutes. Then, for the polymerization, the mixture in the vacuum tube was annealed at constant temperature of 140 °C for an hour. After the reaction, the obtained product, poly(ABCF13) was washed repeatedly with DCM (3×100 mL) to remove monomer residual, low molecular weight products and undesired compound formed during the homopolymerization. After the washing, poly(ABCF13) was dried under the vacuum for 6-8 hours. The yield of the reaction was found

to be 96%. In addition to that, graft copolymerizations of ABCF13 onto HDPE were also carried out with the use of the same polymerization technique. 20 g of individually six mixtures, which were composed of HDPE powder (19, 18, 17, 16, 14 and 12 g), ABCF13 monomer in fine powder form (1, 2, 3, 4, 6 and 8 g) and benzoyl peroxide (BPO) initiator (2% with respect to weight of ABCF13 presenting in the each mixture), were prepared by hand grinding in mortar. After these homogeneous mixtures were vacuumed for 30 minutes in the vacuum ampules, they were heated to 140 °C at which kept constant for an hour for graft copolymerizations. The obtained products were then washed extensively with acetone and methanol (3×100mL for each one) to remove monomer residuals, oligomeric ungrafted polymer products formed during the polymerization. Despite these washing, the obtained products included both graft copolymer and ungrafted homopolymer units. Thus, the products were also washed several times with the hot DMSO and DMF solvents to get away the homopolymers existing in the poly(ABCF13)-g-HDPE matrix so as to determine the percentage of grafting. The founded results were reported as the averages values of the five experiments with the standard deviations. The degrees of grafting were calculated as 88.5, 90.7, 92.4, 93.6, 94.8 and 95.9% for the products containing 5, 10, 15, 20, 30 and 40% ABCF13, respectively. The possible graft copolymerization reaction between HDPE and ABCF13 was depicted in Fig. 2.

2.4. Instruments

FTIR analyses of the obtained products were carried out by a Shimadzu 8400 S FTIR spectrophotometer in the region ranging from 400 to 4000 cm⁻¹. KBr pellets containing roughly 3 mg of sample in 100 mg spectroscopic grade KBr were prepared for obtaining FTIR spectra. ¹H-NMR spectra of the synthesized ABCF13 monomer was recorded in deuterium chloroform (CDCl₃) with a frequency of 400 MHz. The chemical shifts are reported in ppm (parts per million) by using tetramethylsilane (TMS) as an internal reference. The thermal analysis of the products obtained was carried out by Shimadzu TA-60 WS Differential Scanning Calorimeter under nitrogen atmosphere with a heating rate of 10 °C/min and the amount of sample changed between 5-15 mg. High resolution accurate mass spectral measurement (HRMS) was carried out by using Waters SynaptTM G1 ESI-TOF High Definition Mass Spectrometer (Manchester, UK). In order to determine the percentage of C and H atoms in ABCF13 molecule, elemental analysis of ABCF13 was done with the use of LECO CHNS-932 Elemental Analyser (USA). Rigaku Multiflex powder X-ray diffractometer system with CuKα target giving a monochromatic beam ($\lambda = 1.54^\circ$) was performed at 5°/min

scan speed and 0.02° step increment at the room temperature condition for the XRD analyses of the coproducts. The XRD patterns obtained enabled us to determine the lattice constant and grain size parameters. The dogbone shaped samples of the graft products (with the thickness of 2.1 mm, width of 7.4 mm and gauge length of 80 mm) were prepared at 220 °C by using DACA Instruments Microinjector. The tensile properties of the prepared dogbone samples were measured with the use of LLYOD LR30K Mechanical Tester with load cell of 5 kN at crosshead speed of 50 mm/min according to the standard of ASTM D- 638. The stress strain curve obtained from the software of the instrument give directly the tensile strengths and moduli. The minimum four samples were analyzed for each composition. The Izod impact strengths of the unnotched samples $(3 \times 6 \times 130 \text{ mm}^3)$ were carried out by using Coesfeld Material Test Pendulum Impact Tester at room temperature according to ASTM standard of D256. The free volume characteristics of neat HDPE and coproducts were investigated by means of PALS experiments. Fast-fast conventional coincidence system was utilized in order to measure the time elapsed between emissions belonging to the β^+ generated from ²²Na (known as the birth signal of positron with 1.274 MeV photon energy) and gamma annihilation (known as the dead signal with 0.511 MeV photon energy). The ²²Na source was made ready with deposition and evaporation of the 25µCi of ²²NaCI aqueous solution on a thin aluminum foil (5 µm thick) inserted between two pieces whose surface areas were 0.5x0.5 cm² and whose thicknesses were 1 mm. The lifetime spectra of the all samples were resolved by means of RESOLUTION and PATHFIT programs to obtain intensities and lifetime, the spectroscopic data yielded from MCA were analyzed by using the code of LT 92 3. The plastic scintillators adhered to Hamamatsu 2059 photomultiplier tubes (PMTs) based by 265 Ortec operated at negative 2000 Volts has been employed for γ ray detection. For windows settings of 1274 keV and 522 keV, and timing signals, two constant fraction differential discriminators (Ortec CFDD 583B) were used. A time to Amplitude Converter, TAC, was used to convert pulses of different heights to a time-to-pulse-height signal. The converted signals were fed to a multichannel analyzer (Ortec Model 919E Ethernim MCA). The system used for the measurements possessed roundly 400 ps (FWHM) resolution and a million counts were detected for each lifetime spectrum of the samples. Morphological examinations of the tensile and impact fractured surfaces of graft coproducts were recorded with the aid of JEOL 6390-LV scanning electron microscope, operated at 20 kV with a resolution power of 3 nm.

3.Results and Discussions

3.1. Graft Polymerization of ABCF13 onto HDPE

The extent of grafting belonging to products were determined by gravimetric calculations. Prior to discussions on the graft copolymerization, it was to be stated that the solubility test for the poly(ABCF13) were done by using the various polar solvents such as DMSO, DMF, 2,2,2-trifluoroethanol, benzotrifluoride, N-methylpyrrolidone, 1,4-dioxane, methanol and acetone. As a result of solubility test, it was found that hot DMSO and DMF were suitable for the dissolving of the non-grafted fluorinated polyacrylate (or the homopolymers). Thus, hot DMSO and DMF were used to remove homopolymers from the graft coproducts. After the extensively washing of the coproducts, the obtained gravimetrically findings were presented in Table 1. The obtained results showed that the percentage of grafted poly(ABCF13) in the products increased consistently with the increasing of the content of ABCF13 monomer in the reaction mixture. Whereas the minimum grafting percentage was found to be 88.5% at 5% ABCF13, the maxima, 95.9% was achieved at the product containing 40% ABCF13. This was probably due to the increase in the initiator content increasing with respect to the percentage of monomers in the reaction mixtures. Namely, the amount of initiators in the mixtures were 2% of the weight of the monomers. Thus, the increment in the initiator concentration in the reaction medium gave rise to the formation of higher number of radicals in the medium, which resulted in the raising of the percent grafting in the copolymers.

The molecular characterizations of HDPE, poly(ABCF13) and the copolymer containing 8.29% grafted units were performed by means of FTIR analysis and the obtained spectrums were depicted in Fig 2. The characteristics absorption bands of neat HDPE were recorded as C-H stretching at 2918 and 2848 cm⁻¹, C-H bending at 1471 and 1462 cm⁻¹, and C-C bending at 729 and 717 cm⁻¹. As for poly(ABCF13), the moderate IR bands detected at 3128 and 3078 cm⁻¹ were corresponding to C-H stretching vibrations of aromatic phenyl group. The other moderate absorption peaks observed at 2966 and 2931 cm⁻¹ were due to the stretching vibrations of -CH₂ groups. The strong bands detected at about 1759 and 1728 cm⁻¹ were assigned to the stretching vibrations of C=O bonds in ester groups. The absorption band detected at 1608 cm⁻¹ was directly related to the stretching vibrations of C=C bonds in phenyl groups. Moreover, the strong absorption band observed at about 1207 cm⁻¹ was due to C-O

stretching vibrations. The broad and strong bands observed in the range of 1118-1280 cm⁻¹ were corresponding to the stretching vibrations of C-F bonds presenting in the molecular structure. As seen in the Fig. 2c, all the characteristics absorption bands belonging to both HDPE and poly(ABCF13) were also detected in the coproduct containing 8.29% grafted poly(ABCF13) by observing little vibration shift. This may be seen as directly experimental evidence that graft copolymerization of ABCF13 onto HDPE taken place with the formation of chemical bonds.

3.1. DSC Analyses of the Products

The effect of the graft copolymerization of ABCF13 onto HDPE on the thermal properties of the coproducts was comprehensively investigated by DSC analyses. The thermograms of products containing varying content of poly(ABCF13) were presented in Fig. 3. The endothermic heat flows attributed to the crystalline melting were merely that show the melting of HDPE crystalline domains, recorded between 130.80 °C and 134.21 °C. On the other hand, the more prominent exothermic heat flows were observed at around 220 °C with the products containing 13.96 and 19.18% poly(ABCF13). This presumably arose from some reorganizations in the poly(ABCF13) units in the matrix.

The dependence of melting temperature of HDPE crystalline domains on poly(ABCF13) content in the products was graphically displayed in Fig. 4a. The melting temperature initially increased with the content and reached the maximum 134.21 °C at 13.96% poly(ABCF13) which was followed by a sharp decrease reducing to comparable values with that of pure HDPE. In general, high melting points are associated with highly regular structures, close packing capability, rigid molecules, strong interchain attraction, or several combinations of these factors. Melting temperature is also directly related to crystallization process, affected by nucleation and miscibility of the components in polymer combinations [34]. The initial increases in the melting temperatures of HDPE domains observed at products containing lower content from 14% poly(ABCF13) are believed to arose from the improvements in the packing order of the chains due to the attractive interactions between the polar groups belonging to graft units. The decreasing after the maxima presumably resulted from that the assisting function of the graft units making more ordered packing of HDPE chains might be lost with the increasing of poly(ABCF13) percentage in the products. That is, at low percentages, the graft units with polar groups contributed the ordering and packing of HDPE chains, at high contents, the interaction between side chain bonded grafted poly(ABCF13) units probably became more dominant. This may caused the

increasing of irregularity in the HDPE matrix, which resulted in the decreaments in the crystalline melting temperatures of HDPE domains.

In addition, the heat of fusion values (ΔH_f) of HDPE crystalline domains in the coproducts were determined directly by using software of the DSC instrument from the endotherms of the thermograms, and percent crystallinities (X_c%) in HDPE matrices were calculated by using following equation:

$$X_{\rm C}\% = \frac{\Delta H_{\rm f}}{\Delta H_{\rm f}^{0}} \times 100 \tag{1}$$

where, ΔH_f and ΔH_f° designate heat of fusion (specific enthalpy of melting) of HDPE crystalline domains in the matrix of the coproducts and heat of fusion of 100% crystalline HDPE (290 J/g). Percent crystallinity properties of the products were considerably affected from poly(ABCF13) content existing in the matrix, as shown in Fig 4.b. The results showed that the degree of crystallinities of all products were larger compared to that of neat HDPE. The percent crystallinity of HDPE domain increased initially with the increasing of poly(ABCF13) content and reached to 65.83% at the product containing 9.15% poly(ABCF13), which was followed by decreasing trend until to 19.18% poly(ABCF13) content. This decreasing trend may be derived from the weakening of spatial ordering effects assisted by poly(ABCF13) and increment in defects stemming from regional irregular crystallization at 13.96 and 19.18% poly(ABCF13) products. Up to 20% poly(ABF13), the increasing trend was observed again and the percent crystallinity reached the maximum value, 69.71% with 39.18% poly(ABCF13) product. The larger degree of crystallinity means the existence of higher orderly arranged polymer chains in the crystalline region of solid polymers. That is, at high contents, the poly(ABCF13) bearing rigid and stiff segments in its molecular structure may contribute to the arrangement of the HDPE chains, which end up larger percent crystallinity of HDPE domains. Moreover, the increasing of poly(ABCF13) content in polymer matrix may create the additional co-crystallization effects, which result in increment in the percent crystallinity at high contents [35].

3.2.XRD Analysis of the Products

The products were also analyzed by XRD in order to unfold the effect of the extent of grafting on the microstructural properties of the coproducts. The crystal cell parameters (a, b and c) were estimated from the XRD patterns by means of the least square method using

Miller indices $(h \ k \ l)$ and d values. The crystal sizes (grain sizes) of the each graft products were calculated from the patterns by using the formulas;

$$d = \frac{0.941\,\lambda}{B\,\cos\theta_B}\tag{2}$$

where *d* represents the thickness of the crystal, λ is the wavelength of the XRD source, B designates the full width at half maximum (FWHM) of the Bragg peak and θ denotes the Bragg angle. *B* value is calculated from;

$$B^2 = B_m^2 - B_s^2$$
(3)

where B_s exhibits the half-width of the standard material in radians and B_m depicts the difference between the angles at FWHM of the corresponding peak.

The diffraction patterns of the products with Braggle's angle (20) varying from 10° to 60° displayed the reflections corresponding merely to HDPE crystalline characteristics since the poly(ABCF13) had completely amorphous character. The formed patterns were corresponding to the crystallographic planes belonging to the orthorhombic form of HDPE in Fig. 5. That is, the microstructure of HDPE, the crystalline packing of the chains in orthorhombic system has been preserved throughout the graft copolymerization. The lateral dimensions of orthorhombic unit cell, on the other hand, were observed to be considerably affected by poly(ABCF13) content in the products. At relatively lower percentages significant expansions and at higher contents remarkable contractions in the unit cell parameters were recorded. The presence of the expansions and contractions were also evidently revealed by shifts of the reflections in the patterns to the left or right, as seen in Fig 5. At high content of poly(ABCF13), the broadening pattern with the shoulder forming at about 18^0 may be a sign of the formation of the amorphous structures in the HDPE matrix [34].

The dependence of the unit cell dimensions (*a*, *b* and *c* parameters) and *ab* basal area of the unit cells on the percentage of poly(ABCF13) in the products were presented in Fig.6. Both parameters, *a* and *b* increased initially with the contents and the maxima, 7.420 Å in the parameter *a* (0.84% increase) and 4.957 Å in the parameter *b* (0.98% increase) were recorded with the product involving 13.96% poly(ABCF13). The maxima were then followed by contractions in *a* and *b* unit cell parameters. The minimum 7.329 Å in the parameter *a* (0.39% decrease) and 4.897 Å in *b* (0.24% decrease) were measured at 39.18% poly(ABCF13). The lateral enlargements in the unit cell dimensions of oriented and branched polyethylene dependent on type, distribution and content of the branches[36, 37]. It is also known that the branches existing in the crystalline regions of HDPE compelled the chains to expand laterally[23]. Additionally, branch rejection was also announced to have possible contribution to the structural changes[38]. Accordingly, at relatively lower contents in the coproducts, up

to about 14% poly(ABCF13), the grafted polar units probably forced the HDPE chains apart laterally to expanded lateral dimensions, and thus led to the formation of the enlarged *ab* basal area. In addition, that fully fluorinated segments of the grafted poly(ABCF13) units had the helical conformation structure forming by twisting of each CF₂-CF₂ bond caused that the lateral repulsions of fluorinated pendant units in the matrix occurred more effectively as the three dimensions, which resulted in the increasing of a and b unit cell parameters. On the other hand, the contraction trends in a and b dimensions after the maxima probably arose from the compressing effect of the graft units. That is, at further percentages beyond about 14% poly(ABCF13), the accumulation of the graft units with the interactions between the polar groups might have created a squeezing effect on the packing of HDPE chains in the crystalline ordering and arrangements. This effect accordingly resulted in packing of the HDPE chains in the unit cells with relatively smaller dimensions and smaller *ab* basal areas. In the coproduct involving 39.18% poly(ABCF13), 0.39% decrease in the parameter a and 0.24% decrease in b were recorded when comparing to the dimensions of virgin HDPE. Furthermore, the shifting of reflections toward right side in the XRD patterns with the increasing of poly(ABC13) content (Fig. 5) showed evidently the reason of the decrement in a and b unit cell parameters. On the other hand, since the axis of unit cell parameter c was the parallel with the axis of HDPE chains, the parameter c was found to be almost not affected by the graft copolymerization.

In addition to the dimensional variations in the unit cells with the content, the variation of size of the HDPE crystals (grain size) with the percentage of poly(ABCF13) in the products was also studied by XRD measurements and the results obtained were presented in Fig. 7. The trend in the grain size of the products was dissimilar from that seen in a, b and c cell parameters. The size increased initially with the percentage, and reached the maximum value, 19.42 nm (18.3% increase comparing to virgin HDPE), in the sample involving 9.15% poly(ABCF13). The maximum was then followed by a consistent shrinkage with the increase in the content. The minimum size, 14.25 nm (13.2% decrease) was recorded with the sample involving 39.18% poly(ABCF13). The initial rise in the crystal size could be explained by contribution of two factors: (I) the initial increase in the conformational freedom of HDPE chains arising from the increase in the free volume and (II) the enlargement in the basal area (axb) of the unit cells. The initial increase in the conformational freedom probably conduced to the packing of the chains to relatively larger sized crystals in their growth. The enlargements in the basal area of the unit cells might have additionally resulted in the growth of the crystals to larger sizes. The formation of the similar trends in both the basal area and the size of the grains evidently supported the contribution of the basal area. In fact, a larger

size might be normally expected when the crystals grow on the unit cells with larger basal area. The decrease trend in the size after the maximum, on the other hand, might have arisen from the decrease in the free volume fraction and, with the same line of reasoning, the decrease in the basal area of the unit cells. The accumulation of the graft units with the presumable rigid, rod-like characteristics of the fluorinated segments, besides leading to consistent decrease in the free volume fraction, might have had a blocking role on the growth of the crystals to larger sizes.

3.3. PALS Analysis of the Products

Both neat HDPE and the graft coproducts were meticulously analyzed by Positron Annihilation Lifetime Spectroscopy (PALS) so as to unfold the influence of the graft copolymerization of ABCF13 on the free volume characteristics of the HDPE. The lifetime spectra obtained by measurement of lifetimes of positrons in the analysis of the products and neat HDPE were analyzed into components; τ_1 (the shortest-lived component with an intensity I_1) τ_2 (the intermediate-lived component with an intensity I_2) and τ_3 (the longestlived component with an intensity I_3). τ_1 and I_1 are associated with the annihilation of *parapositronium* (*p*-*Ps*), τ_2 and I_2 are allied with direct annihilation of positrons, and τ_3 and I_3 are associated with pick off annihilation of *ortho-positronium* (*o*-*Ps*). In calculation of the parameters, τ_1 was assumed as independent of free volume and used as fixed at 125 ps. Orthopositronium lifetime, τ_3 is sensitive to free volume hole size and I_3 has straight correlation with the number of free holes in the materials. Accordingly, τ_3 increases with increase in the size of the free volume, and a rise in the number of free volumes is accompanied with an intensification in I_3 [39].

The relation between the radius of free volume hole (R) and pick-off annihilation lifetime proposed by Tao[40] was modified by Eldrup et al.[41]. In the model, called Tao-Eldrup Model, the radius was related with the lifetime τ_3 by the equation;

$$\tau_3(ns) = \frac{1}{2} \left(1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \frac{2\pi R}{R_0} \right)^{-1}$$
(4)

where $R_0 = R + \delta R$ with $\delta R = 0.1656 nm$ as an adjustable parameter for a measure of electron layer inside the spherical potential well. By assuming spherical free volume, the size of free volume holes (V_f) is then calculated by using the equation;

$$V_f = \frac{4}{3} \pi R^3 \tag{5}$$

In polymers, the relation between the free volume fraction (f_v) and free volume hole size is given by following equation;

$$f_{\nu} = AI_{3}V_{f}(\tau_{3}) \tag{6}$$

where A refers to proportionality constant [42]. The obtained results from PALS measurements were tabulated in Table 2.

The lifetime τ_3 is proportional to size of free volumes in the materials [39]. The dependence of the free volume size calculated by using the free volume model on poly(ABCF13) content in the products was drawn in Fig. 8a. The size increased almost in consistence with the percentage of poly(ABCF13). It reached the maximum 178.2 ± 1.1 Å³ (42% raise comparing to virgin HDPE) with the sample involving 39.18% poly(ABCF13). It can be concluded that the poly(ABCF13) units with voluminous side groups bearing rigid, rod-like fluorinated segments presumably led to the formation of larger holes, cavities or openings in the material. The size of the free holes thus got larger as the content increased. In addition, since the free volume is higher in glassy and amorphous polymers with local kinks [43], the grafted poly(ABCF13) units might have played a role in the increasing of free volumes of the products with content. Furthermore, the weak secondary molecular interactions between polar groups of poly(ABCF13) units and nonpolar HDPE chains might have additionally contributed to the reduction in close packing of the chains in the matrix, and thus to form larger free volumes. Moreover, the free volume fractions (f_{ν}) of the products were determined by means of the equation 6. and the dependence of the free volume fractions (fv) on poly(ABCF13) content were drawn in Fig. 8b. Free volume fraction decreased considerably at the products including 4.17% poly(ABCF13). This reduction was probably due to the fact that the graft units occupied the free volume holes between the HDPE chains rather than creating new gaps and holes between them. The potential weak interactions between the polar groups of the graft units and the nonpolar HDPE chains may have played a role in filling these holes. After the minima, the free volume fraction exhibited an increase trend with the content. Especially, the sharp increase was observed at the product with 9.15% poly(ABCF13) and the maximum fraction among products was found to be 4.58% (2.47%) greater than that of virgin HDPE). This was probably caused by that the voluminous side groups of the graft units gave rise to increasing in both size and number of the free volumes. The voluminous side grafted groups, which presumably prevent the close packing of the chains in the material, might have played an effective role in the increase of the fraction at that percentage. Relatively slower decrease in the fraction after this content, at 13.71%

poly(ABCF13), probably resulted again from the occupation of the holes by the newly added graft units

3.4. Mechanical Characteristics of the Products

In this part of the paper, we focus thoroughly on mechanical characteristics of the coproducts by examining the change in tensile strength, Young Modulus and impact strength with the extent of grafting. The coproduct samples with the shape of dogbones were prepared in the optimum processing condition by micro injection molding at 260 °C at which the samples were molded easily in spite of the formation of gummy state during processing. Also, since the molding temperature was above the crystalline melting temperature (at about 230 °C) of poly(ABCF13), the ideal dispersion for mechanical reinforcements was achieved. At the same time, the most striking point of this paper was the observation of the extreme and considerable mechanical improvements of the products, particularly, in tensile strength which possesses 133% larger tensile strength than virgin HDPE by using semi-fluorinated compound. The stress vs. strain curves of the coproducts designated with the 5cm.min⁻¹ elongation speed were illustrated in Fig. 9. According to the figure, all the sample except for virgin HDPE were mainly in brittle natures without any ductile failures with neck formation, which means breaking of the bonds in the structure, though virgin HDPE showed the great extension and orientation during cold drawing. The other important results deduce from the graph that the samples with 4.17, 9.15, 13.96 and 19.18 % poly(ABCF13) broken off after vield stress, whereas the others coproducts exhibited more brittle behaviours. It is clear that the brittleness of the obtained coproducts increased considerably with the enhancement of the poly(ABCF13) content in the coproducts, which provided by SEM images.

The experimental findings about the effect of percent grafting on mechanical properties of HDPE were numerically tabulated in Table 3. The ultimate strengths of the coproducts increased initially with the increments in grafting percentage. The higher tensile strengths were found to be 43.75 MPa and 34.40 MPa belonging to the products with 9.15 and 4.17% poly(ABCF13), respectively, whose values were impressively 133% and 83% larger compared with virgin HDPE. The first enlargements in the free volume probably gave rise to increase in the conformational freedom of the chains in the material, which resulted that the alignments and orientations of the chains became more effectively throughout draw direction during tests. Moreover, the presence of the semifluorinated side pendant units with rigid rod like characters may assisted to the ordering and orientation of HDPE chains in the matrix, which resulted in the increasing of tensile strengths like a fiber reinforcement effect [44].

Furthermore, it is well-known that the mechanical properties of polymer blends may be strongly influenced by the compatibility of components in the blend [45]. The in-situ poly(ABCF13)-g-HDPE polymers in matrix may be acted as compatibilizing agent between the components (poly(ABCF13) and HDPE). Thus, the perfect interfacial adhesion, lower interfacial tension and the higher stress transfer were obtained and this may give rise to showing the impressive mechanical performance in this product [46]. However, this increasing trend in ultimate strength was followed by dramatic decreasing with the further increment of poly(ABCF13) contents. This sharp decrease was presumably caused from the deterioration of the regularity of the molecular structure of HDPE main chains accounting for the viscoelastic deformation or yielding [47]. That is, at further extent of grafting, since poly(ABCF13) chains are composed of voluminous side groups bearing rigid, rod-like fluorine segments, the further presence of such groups in the polymer matrix might limit the ordering of HDPE chains by preventing the orientations and alignments in the draw direction. This effect, which becomes more dominant as the graft content increased in the products, probably caused the decreasing of tensile strengths. Fig. 10b. also enables us to illustrate change in Young's Modulus based on the content of the poly(ABCF13) in the coproducts. The same trend as being ultimate strength was seen in the figure but the slightly improvements were recorded in Young's Modulus of the coproducts. The maximum value was found to be 393 MPa (9% greater compared to virgin HDPE) at the product with 9.15% poly(ABCF13). The obtained findings showed that the grafting levels play an important role in the resistance to deformation of the coproducts. The improvements in the modulus may be attributed to enhancements of the alignments and orientation of the HDPE chains as in the tensile properties. Moreover, as well known, one of the main effect being responsible for mechanical properties is Van der Waals forces between molecule segments [48]. That is, the secondary hydrogen bonds between the -CF2 groups in poly(ABCF13) with three dimensional helix structure and -CH₂ groups in HDPE chains probably led to considerable advanced in the modulus by making better the deformation (fracture) mechanisms. The consistent decreasing of percent elongations of the products as seen clearly in stress-strain curves of the might be seen as experimental evidence for that these secondary bonds were formed. On the other hand, the decreases in the modulus of the products started to appear beyond the 9.15% poly(ABCF13) content., meaning that brittleness of the coproducts considerably increased by the copolymerization. This may be caused from the increasing of the brittle characters of the coproducts since the further presence of grafted units having rigid, rod-like and amorphous characters increased in the matrix, bringing about the lower withstanding performance to

applied load compared to the neat HDPE. That is, the further increment in the percent grafting led to damage seriously to the PE structures.

The changes in Izod impact strengths of the products with the grafting percentage were illustrated in Fig.10.c in detail. The virgin HDPE and the coproducts with 4.17, 9.15, 13.96 and 19.18% poly(ABCF13) contents were not broken while the samples containing 28.89 and 39.18 % poly(ABCF13) failed during tests. Moreover, it is visible from the figure that the variation of impact strengths of the coproducts depicted the good correlation with tensile strength, Young's Modulus and grain size results. Namely, the impact strengths increased initially and reached to maximum value (38.72 kj/m^2) with the sample containing 9.15% poly(ABCF13) and this value was 100% larger compared to that of the virgin HDPE. This appreciable advance in impact strength could be corresponding to three main effects (I) higher chain mobility in the relatively larger basal area and (II) the largest grain size due to more ordered packing and organized regularly of HDPE chains in crystalline [23] and (III) increase in the free volume. In another words, the impact energy, defined as the absorbed energy in the certain area by the samples during test in a short time, could be delocalized effectively by means of the dimensional order of HDPE chains with largest grain size in relatively higher lattice structures. As for free volume, the increased conformational freedom and mobility of the chains accompanied with the enlargements in the free volume probably resulted in the more absorbed energy in the test. However, the maxima were followed by a decreasing trend towards the value of about 3,09 kJ/m₂, which was substantially smaller than virgin HDPE. It may be concluded that the increment in the content of poly(ABCF13) seriously damaged to the HDPE domains. At high content, the samples showed lower endurance to break as a result of the considerable decrements in both HDPE crystal sizes and basal areas, as previously shown in Fig. 6 and 7. That is, the shrinked basal area reduced the chain mobility in the matrix, and also the formation of large number of grain boundaries due to decrement in crystal size, weak cohesive interactions and irregular orientation distribution may create an easy fracture path along those boundaries, which ending up lower impact strength [49].

3.4. Morphological Properties of the Products

In this part of this paper, the morphological characteristics of the fractured surfaces obtained from tensile and impact tests were investigated by SEM and the taken SEM photographs were depicted Fig. 11. It is apparent from SEM images that there existed no phase separation and the samples illustrated completely homogeneous structures although the nature of HDPE differed from the graft units of poly(ABCF13). These results confirmed not

only the formation of the chemical bonds by graft polymerization of poly(ABCF13) onto the HDPE chain but also the presence of the good interfacial adhesion between components. The fractographs additionally showed that the morphological properties of fractured surfaces changed significantly with percent grafting. At low contents, the products exhibited ductile behaviour with the formation of large, thick and long fibrillar structures formed probably as a consequence of the orientations and alignments of the HDPE chains in the matrix, Fig. 11a and b. Hence, these images might be evaluated as the empirical evidence for how the products withstood against the applied force during mechanical tests. However, the images also displayed that the percent elongations decreased with the increase of poly(ABCF13) percentage. At relatively high content, the thick and long extensions were replaced by shorter and thin fibrillar structures, Fig.11c,d,e and f. In addition, as the content increased further, layered structures with holes, openings and microcracks began to appear. Especially, the microstructural defects were found to be high in the products especially containing 28.89% and 39.18% poly(ABCF13) and these products had substantially brittle character, Fig.11.e and f. these findings presented the significant visible evidence for why the tensile strengths of the products decreased with the further increasing of poly(ABCF13) content in the products. On the other hand, the surface fractographs obtained from the impact tests revealed that the brittleness enhances monotonously with the increment of poly(ABCF13) contents. Besides, no fibrillation was observed in SEM images of the impact fractured surfaces of broken samples, Fig. 11g and h. This may be related to the increase of the restriction of polymer chain orientations. Namely, absorption of impact energy with the effectively delocalization during the tests could be inhibited due to lower mobility of polymer chains. Thus, the layered and tortuous fracture surfaces with considerable numbers of voids, cracks and holes were formed and this was sign of that the products had the brittle nature

4. Conclusion

Along the present paper, it was investigated in details that how the extent of grafting in the products affects the crucial properties (thermal, microstructural, mechanical, free volume and morphological characteristic) of HDPE. The synthesis of ABCF13 monomer and its graft polymerization on HDPE were performed successfully. The homopolymer and copolymers were prepared by annealing the reaction mixtures involving both HDPE powder and varying contents of ABCF13 at 140°C via bulk melt polymerization technique. As for copolymerization process, the percent grafting increased consistently with the increasing of the monomer content in the reaction mixtures. At higher content of HDPE in the matrix, the

HDPE chains act as inhibitor due to steric hindrance for the formation of grafted poly(ABCF13). In addition, the result showed that the crucial characteristic features of HDPE depended strongly on the grafting percentage in the matrix. The graft copolymerization brought about the significant increments in the melting temperature of HDPE crystalline domains. The initial increases were believed to arose from the improvements in the packing order of the chains due to the attractive interactions between the polar groups belonging to graft units. After maximum, the a sharp decreases in crystalline melting temperature of HDPE were observed in the products. These decreases presumably resulted from that the assisting function of the graft units with polar groups in more ordered packing of HDPE chains might be lost with the increase of poly(ABCF13) percentage in the products. According to the XRD patterns, considerable lateral expansions were recorded in a and b unit cell parameters of the HDPE orthorhombic structure with the increasing of grafting percentage. These increments in a and b unit cell parameters were probably caused from that the grafted polar units probably forced the HDPE chains apart laterally to expand lateral dimensions. After the maxima, the contraction trends in the dimensions were observed, which probably arose from the molecular attractions of polar groups presenting in the graft units. The c parameter remained almost unchanged since the chain axis of HDPE molecular segments was parallel with the unit cell axis. The grafting onto HDPE gave rise to linearly increasing of the free volumes in consistence with the extent of grafting. The poly(ABCF13) units with voluminous side groups bearing rigid, rod-like fluorinated segments presumably led to the formation of larger holes, cavities or openings in the materials. Moreover, the fluctuation in the free volume fraction values of the products was recorded with the increasing of poly(ABCF13) content in the matrix. The reduction in the fraction probably due to the fact that the graft units occupied the free volume holes between the HDPE chains rather than creating new gaps or holes. The mechanical measurement results revealed that the grafting levels at initial stages led to the extreme enhancement of mechanical performance of the coproducts. Remarkable improvements were achieved in the tensile properties of the material; with the maxima of 133 % increase in tensile strength and 9% rise in Young's modulus with the coproduct comprising 9.15% poly(ABCF13). Moreover, 100% increase was recorded in impact strength at the same content. The improvement of mechanical performance of HDPE with the grafting probably results from the increment in the orientations and alignments of HDPE chains moving in larger ab basal area with the formation of higher cohesive forces occurring between components. Additionally, it was deduced from the SEM images that all the samples illustrated completely homogeneous structures without any phase separation. Although the excessive fibrillations and relatively higher extensions were seen at the low grafting levels in

the coproducts, the holes, microcracks and openings among the layers started to appear with the insufficient fibril extensions encountered in the higher grafting percentage.

Declaration of interests

There are not known competing financial interests or personal relationships regarding to the this article.

Acknowledgments

This research was supported by BAIBU research fund grant no. BAP-2016.03.03.1075. The authors sincerely thank to Prof. Dr. T. Tinçer for providing his laboratory for the mechanical tests and Prof. Dr. A. Varilci for SEM analyses. Moreover, authors are especially grateful to Innovative Food Technologies Development Application and Research Center (YENIGIDAM) for the valuable supportings.

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Fig. 1. Simplified demonstration of reaction steps for the synthesis of ABCF13.



Fig. 2. The possible graft copolymerization of ABCF13 onto HDPE.



Fig. 2. FTIR spectrum of a) neat HDPE, b) poly(ABCF13) and c) the copolymer containing 8.29% grafted poly(ABCF13).



Fig. 3. DSC thermograms of neat HDPE and the coproducts formed with different ABCF13 contents.



Fig. 4. Dependence of (a) melting temperature and (b) degree of crystallinity on poly(ABCF13) content in products.



Fig. 5. The XRD patterns of HDPE and the products with varying compositions of poly(ABCF13).



Fig. 6. The dependence of cell parameters a) a, b) b, c) c and d) unit cell basal area ab on the poly(ABCF13) percentage in the products.



Fig. 7. The dependence of grain size (crystal size) on poly(ABCF13) in coproducts.



Fig. 8. The dependence of a) free volume hole sizes (A³) and ortho-positronium lifetime (τ_3) and b) free volume fraction on poly(ABCF13) content in the products.







Fig. 10. The variation of the a) ultimate strength, b) Young's Modulus, c)impact strength of the samples with % poly(ABCF13) content.



Fig. 11. SEM micrographs of the products with a) 4.17, b) 9.15, c) 13.96, d) 19.18 e) 28.89 and f) 39.18% poly(ABCF13), Tensile Tests and also g) 28.89 and 39.18% poly(ABCF13), Impact Tests.

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Sample	1.	2.	3.	4.	5.	6.
% HDPE in the rxn. mixture	95	90	85	80	70	60
% ABCF13 in the rxn. mixture	5	10	15	20	30	40
% Total poly(ABCF13)	4.17	9.15	13.96	19.18	28.89	39.18
in the products	±0.44	±0.39	±0.10	±0.03	±0.14	±0.53
% Grafted poly(ABCF13)	3,69	8.29	12.89	17.95	27.38	37.57
in the products	±0.18	±0.32	±0.23	±0.35	±0.11	±0.19
% Grafting	88.5	90.7	92.4	93.6	94.8	95.9
	±1.8	±0.9	±0.7	±0.1	±0.5	±1.3

Table 1. The percentage of HDPE and ABCF13 in the reaction mixtures, content of poly(ABCF13) in the products and percent conversion.

Table 2. The dependence of the lifetimes of the positrons, the intensities, the radii of the free volume holes, the free volume hole sizes and the free volume fractions on poly(ABCF13) content in the coproducts.

wt. (%)	$ au_2(ns) \ (\pm 0.001)$	τ ₃ (ns) (±0.01)	$I_2(\%)$ (±0.2)	<i>I</i> ₃ (%) (±0.1)	R(Å) (±0.01)	fv(%) (± 0.06)	υ _{f3} (Å ³)
0	0.37	2.30	48.5	19.8	3.11	4.47	125.7±0.8
4.17	0.34	2.36	62.1	15.1	3.16	3.58	132.0±1.0
9.15	0.35	2.43	56.8	18.3	3.21	4.58	138.6±0.9
13.96	0.37	2.46	59.6	16.1	3.24	4.12	142.0±1.1
19.18	0.36	2.53	62.3	15.8	3.29	4.24	149.1±0.9
28.89	0.37	2.69	61.2	15.7	3.41	4.69	166.1±1.0
39.18	0.36	2.80	64.5	14.4	3.49	4.62	178.2±1.1

wt. (%)	Ultimate Strenght(MPa)	Young's Modulus(MPa)	Impact Strenght (kJ/m ²)
0	18.78±3.15	362.16±15.12	19.30±2.64
4.17	34.40 ± 2.08	381.82±13.22	32.23±2.55
9.15	43.75±0.75	393.15±16.72	38.72 ± 2.90
13.39	19.17±1.19	280.32 ± 14.86	33.19±3.00
19.18	17.69±0.3	272.18±9.28	20.99 ± 4.17
28.89	$9.84{\pm}0.69$	253.63±3.71	10.23 ± 0.42
39.18	8.86±0.38	237.58 ± 3.43	3.09±0.69

Table 3. The mechanical properties of HDPE and graft coproducts with the content of 5, 10, 15, 20, 30 and 40% of ABCF13.