Investigation of the decomposition behavior of the fluoroalkyl acrylate homopolymer and its grafted copolymers onto high-density polyethylene

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Abstract — In this study, the thermal degradation behavior of both poly(3,3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-5-methyloctyl-4-(acryloyloxy) benzoate), poly(ABCF13) and its graft copolymers onto high-density polyethylene (HDPE) was investigated in detail. The homopolymers and grafted copolymers were synthesized using the bulk-melt polymerization method in the presence of benzoyl peroxide; 10% and 40% of ABCF13 were used in the graft copolymers. The combined analytical technique, Thermo Gravimetric Analysis coupled with Fourier Transform Infrared Spectroscopy (TGA/FTIR), was utilized to understand the obtained products' thermal behavior and formed decomposition chemicals. The thermal tests were carried out in both air and N_2 atmospheres. The experimental results showed that the first weight loss of poly(ABCF13) in air and N_2 atmospheres started at about 226°C (1.00%), and the primary and early decomposition product was determined as CO_2. The weight loss pattern in graft copolymers at lower concentrations closely resembled that of the homopolymer. However, at higher concentrations, the resulting products exhibited a distinct decomposition mechanism characterized by a gradual decrease in trend. This segmented behavior may indicate the coexistence of the homopolymer and grafted copolymers within the matrix. Moreover, the findings showed that the semi-fluorinated grafted unit had a substantial retardation effect on the polymer.

1. Introduction

Polymeric materials' thermal behavior is an important issue in polymer science since they have been used almost everywhere in our daily lives [1,2]. Polymeric materials are expected to have a high degree of thermal stability (which means late degradation) defined as the ability to endure heat action, making them more favorable to be used in many engineering fields [3]. The thermal behavior of the polymer substantially depended on various factors like chemical structure, molecular weight, degree of crystallinity, cross-linking, composition of the polymer, thermal history, amount of the additives and their compatibility with components, and degree of bonding (primary or secondary bonds) [4-6]. First, regarding the molecular structure, the arrangement of the monomer unit in the polymer chain and the functional groups belonging to the main chain greatly impact how the polymers respond to heat [7]. The polymers formed from relatively long and flexible monomer units generally have more amorphous polymer structures, which means that the thermal features of such polymers are worse when compared to the monomers with more rigid chemical

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groups. Accordingly, the presence of aromatic segments in the polymer backbone creates a positive effect on the thermal stability of the polymers, while the existence of double bonds or oxygen-including groups in the molecular chain of the polymer makes the material more vulnerable to the heat action [8].

Furthermore, due to the reduced crystallinity, a highly branched polymer shows a relatively lower melting point than a linear polymer at the same composition. Moreover, it must be said here that the polymer's chemical structure directly influences the degree of crystallinity of the polymers, another main parameter affecting the thermal behavior [9]. Polymers with a high degree of crystallinity typically exhibit elevated melting points and enhanced thermal stability compared to their amorphous counterparts. The arrangement of polymer chains in a crystalline structure constrains molecular mobility, influencing thermal transitions [10-12]. Accordingly, thermal stability of polymers directly links with the bond energies in the polymer structures, strength and type of covalent or non-covalent bonds, and degree of unsaturation. That is the chemical interactions, especially cross-linking, in the matrix also have a great effect on the thermal properties. For example, cross-linked polymers show better thermal stability due to the improved network structure and existence of the additional chemical bonding between the chains [13,14].

As we discussed, the thermal characteristics and behavior of polymeric materials depend on different factors, and these properties play a crucial role in determining the applications of polymers. Various methods are also used to modify the thermal properties of polymers. Grafting, which is a method to obtain hybrid material with properties derived from both the main chain polymer and the grafted side chains, is one of them. This structural complexity might impart distinctive thermal properties, significantly different from conventional homopolymers or copolymers. The interplay between the main polymer backbone and the grafted chains introduces intricate dynamics that influence the copolymer's response to temperature changes. This thermal responsiveness holds significant implications for designing and optimizing materials with tailored properties. For instance, using the grafted semi or fully-fluorinated polymer units brings about an increment in thermal stability and decrement in the flammability of the polymers [15-18]. As well as thermal behavior, it is important which gaseous substances are released when the polymers are exposed to the increasing temperature. At this point, thermo gravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA/FTIR) allows us to figure out the complex processes, weight loss, chemical changes, and various volatile products occurring during thermal degradation.

As mentioned above, the thermal behavior of polymers is a crucial factor that impacts their processing, performance, and reliability in various applications. It plays a key role in determining their usage in many fields. With this aspect, in this current study, we investigate the thermal behavior of both semi-fluorinated homopolymers and their grafted copolymers onto high-density polyethylene (HDPE) to figure out the effect of the chemical groups (especially phenyl and fluorinated tails) in grafted units on thermal stability. Moreover, the decomposition product also tried to determine during thermal degradation.

2. Materials and Methods

2.1. Synthesis of Monomer

To begin with, it must be stated here that the same raw materials, as announced in our previous work, were used for this study to synthesize the ABCF13 monomer [19]. Moreover, the syntheses of the starting material p-acryloyloxybenzoic acid (ABA) and the intermediate product p-acryloyloxybenzoyl chloride (ABC) were reported in our previous [20]. In more detail, to synthesize the monomer, the condensation reaction between p-acryloyloxybenzoyl chloride (ABC) and 3,3,4,4,5,6,6,7,7,8,8,8-dodecafluoro-1-octanol (F13) were conducted in triethylamine (TEA) alkaline medium, and the same preparation steps were also followed for this synthesis as presented in Figure 1[19]. The reaction yield was 81%, as announced previously [19].
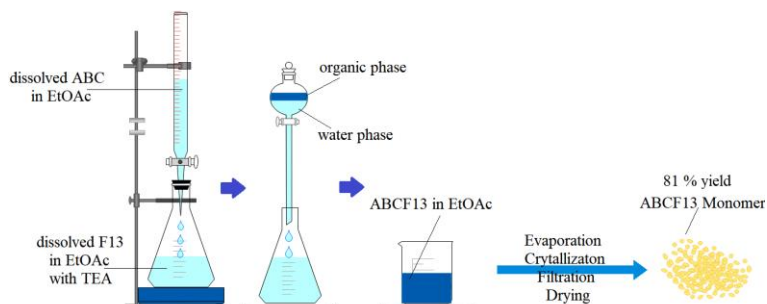
Figure 1. Preparation stages of ABCF13 monomer

2.2. Homopolymerization and Graft Copolymerization of ABCF13 onto HDPE

Both homopolymerization and graft copolymerization were performed according to the methods described in our previous study [19]. Namely, ABCF13 and graft copolymers homopolymers were obtained using the bulk-melt polymerization method. The polymerization of ABCF13 was conducted by heating the mixture of ABCF13 and benzoyl peroxide (BPO, 2% weight of monomer) in a vacuum tube at 140 °C for 1 h [19]. For the graft copolymerization, first, the two mixtures were prepared with the composition of HDPE powder, granular form of ABCF13 (10% and 40% of the mix), and BPO initiator, which was 2% with regard to the weight of ABCF13 and these mixtures ground with hand in mortar. These wide addition levels were chosen to observe more obviously how grafting influences the thermal feature of the graft copolymers. Then, for the polymerization, the mixtures were annealed to 140 °C for 1 h in glass ampules cut previously with flame under vacuum, as shown in Figure 2. After that, the obtained products were washed comprehensively with ethyl methyl ketone to remove undesired residuals, products with low molecular weight, and other undesired products. As reported previously, the obtained experimental results showed a good correlation with the findings [19].
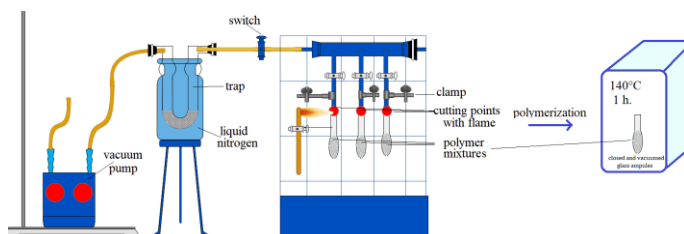

Figure 2. Schematic experimental steps for the preparation of the homo and graft copolymers

2.3. Instruments

The TGA/FTIR analyses of poly(ABCF13) and the coproducts containing 10% and 40% poly(ABCF13) were carried out by using a TGA/FTIR combined system consisting of an Exstar SII TG/DTA6300 Thermogravimetric Analyzer combined with a Perkin Elmer Spectrum 400 FTIR Spectrometer (USKIM, KSU). Approximately 10 mg of products were pyrolyzed with the TGA analyzer, and the released gases were directly reached by the Perkin Elmer Spectrum 400 FTIR Spectrometer through a connected gas line. FTIR spectra were obtained at specific frequency intervals. Thermogravimetric tests were performed in air and nitrogen atmospheres, with a 10 °C/min heating rate between 25 °C-600 °C temperature range.

3. Results and Discussion

3.1. TGA/FTIR Analysis of Homopolymer, poly(ABCF13)

Prior to the serious discussions, it must be stated here why poly(ABCF13) semifluorinated homopolymer and poly(ABCF13)-grafted-HDPE copolymers were preferred for this study. As well known, the replacement of

hydrogen with fluorine atoms in a number of fully or partially fluorinated polymer molecules brings about thermal stability, anti-adhesiveness, self-lubricating, lower friction coefficient, surface energy, etc. In addition to that, fluoroalkyl acrylates may create a positive effect on the thermal properties thanks to rigid perfluorinated pendant segments at the terminal position. Thus, we focused on both the semifluorinated homopolymer and its grafted copolymers with HDPE.

TGA/FTIR analysis of the obtained homopolymer was conducted in air and N_2 atmospheres to elucidate its response to the temperature increment and decomposition mechanism. The weight loss percentages with increasing temperature in both atmospheres are shown in Figure 3. The findings depicted that the initial weight loss of poly(ABCF13) in both air and N_2 atmospheres occurred at approximately 226 °C, equal to 1.00%. The weight loss showed a similar trend for both atmospheres, as seen in Figure 3. However, when the temperature increased, poly(ABCF13) in the air atmosphere decomposed at a slightly lower temperature. Specifically, a weight loss of nearly 6% was obtained at 305.8 °C and 307.4 °C in air and N_2, respectively. Thus, it was deduced that the thermal stability of poly(ABCF13) was slightly higher in the N_2 one. It might give rise to the fact that the functional groups in poly(ABCF13) molecules provide chemical reactions easily with atmospheric oxygen to offer decomposed products, which results in earlier decomposition. This difference may be attributed to the ease with which the functional groups in poly(ABCF13) molecules react with atmospheric oxygen, leading to earlier decomposition. Notably, gradual weight losses were observed in both atmospheres until around 300 °C. Subsequently, a significant weight loss occurred at temperatures above 300 °C, reaching its peak in the range of approximately 320-370 °C in not only air but also N_2 atmospheres, as seen in Figure 3. Within this temperature range, the weight loss percentages for both atmospheres were recorded as approximately 66%, decreasing from around 89% to 23%. At 350 °C, the homopolymers experienced roughly a 50% weight loss in both atmospheres during the analyses. Furthermore, the decomposition of the poly(ABCF13) persisted until 567 °C with a weight loss of 95.1% in the N_2 atmosphere and 572 °C with a weight loss of 94.9% in the air atmosphere.
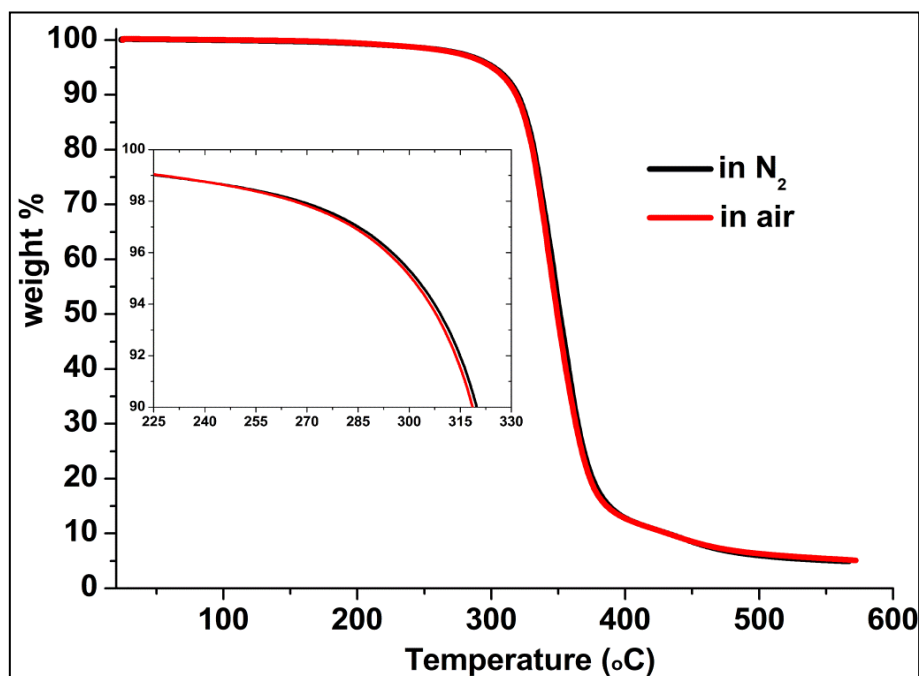

Figure 3. TGA graph for poly(ABCF13) in N_2 and air atmospheres

The homopolymer's decomposition products were identified using an FTIR spectrometer in conjunction with TGA under nitrogen (N_2) and air atmospheres. In the N_2 atmosphere, the results revealed that the observed absorption bands remained largely consistent throughout the heating process. However, there were notable changes in the intensities of these absorption bands, as illustrated in Figure 4. Throughout the heating process in N_2 atmosphere, carbon dioxide (CO_2) was consistently generated, and characteristic absorption

bands indicated its presence at approximately ~2300 cm^{-1} [21,22]. These bands were due to the C=O stretching vibrations of CO_2. The intensity of these absorption bands varied during the heating, providing insights into the dynamic nature of CO_2 formation within the homopolymer.

At the onset of decomposition (around ~330 °C with a 17.6% weight loss), IR bands, which were weak and tentative, were detected in the spectrum, as depicted in Figure 4. a. However, specific IR bands related to C-F bond stretching vibrations emerged in the 1100-1300 cm^{-1} range during the early stages of decomposition. As the decomposition accelerated, prominent absorption bands became apparent, and all distinctive vibration bands associated with the decomposition products belonging to poly(ABCF13) in N_2 atmosphere were observed in the spectrum recorded at 390 °C, as shown in Figure 4. b. The intensity of the IR bands attributed to C-F stretching vibrations reached a maximum and became more pronounced. Additionally, the I.R. band at approximately 3642 cm-1 was likely attributable to the O-H stretching vibration of the phenolic groups in poly(ABCF13) [23]. The faint I.R. bands at ~3100 and ~2900 cm^{-1} were due to the stretching vibration of aromatic and aliphatic C-H bonds, respectively [21]. The absorption bands at about 1740 cm^{-1} were related to stretching vibrations of the C=O bond in the ester groups [24].

Moreover, the vibration peaks at 1500 and 1600 cm^{-1} were presumably due to the stretching vibration of carbon-carbon double bonds in both the vinylic and aromatic groups, respectively [25]. The stretching vibrations belonging to the C-O bond were found at approximately 1240 cm^{-1}. The I.R. vibrations at ~700 and 840 cm^{-1} were due to out-of-plane bending vibrations of C-H bonds in vinylic groups [26]. As the temperature increased, the I.R. bands exhibited a reduction in intensity, and certain characteristic bands either disappeared or weakened notably after reaching approximately 420 °C, as illustrated in Figure 4. c.

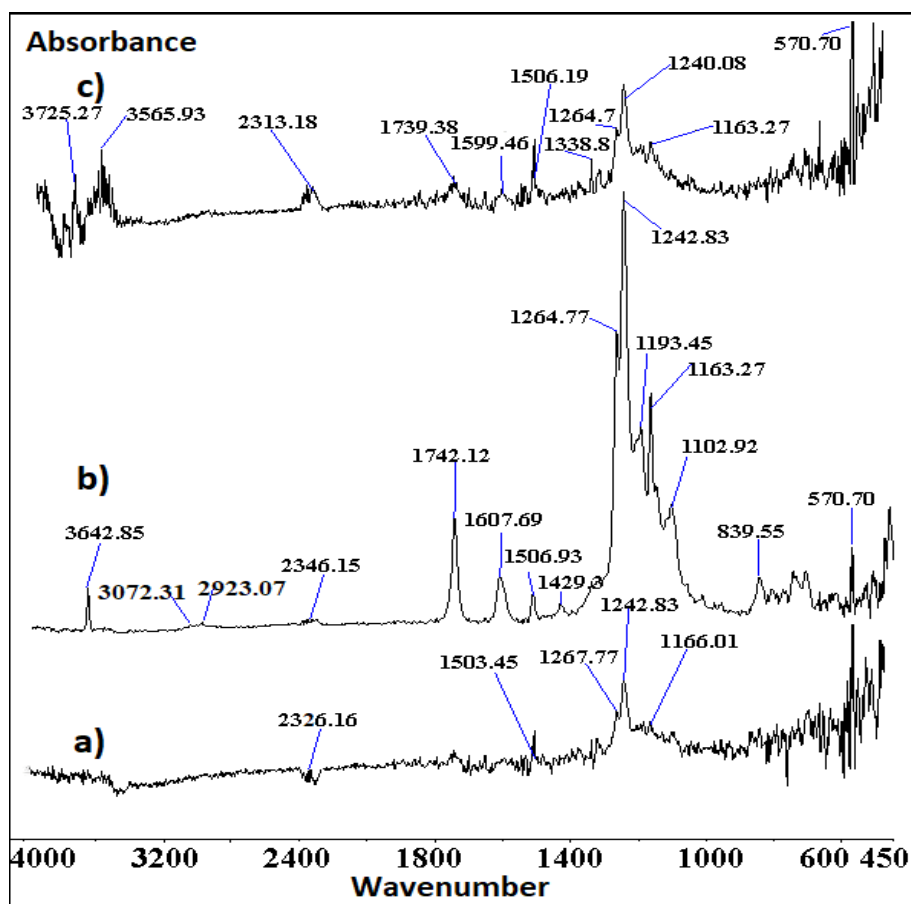**Figure 4.** FTIR spectrum of poly(ABCF13) during decomposition formed at a) 330°C, b) 390°C, and c) 440°C in N_2

Furthermore, poly(ABCF13) was analyzed in an air atmosphere. The FTIR spectra revealed a decomposition mechanism in the air atmosphere similar to that observed in a nitrogen (N_2) atmosphere, as illustrated in Figure 5. Characteristic bands of poly(ABCF13) were largely consistent in spectra obtained in air. Notably, stronger absorption IR bands attributed to decomposition products, particularly CO_2, were evident at early and subsequent temperatures during the analysis. However, several new peaks around the characteristic absorption bands of poly(ABCF13) remained unassigned. Moreover, these undefined absorption bands persisted throughout the heating process, as depicted in Figure 5. a, b, and c.
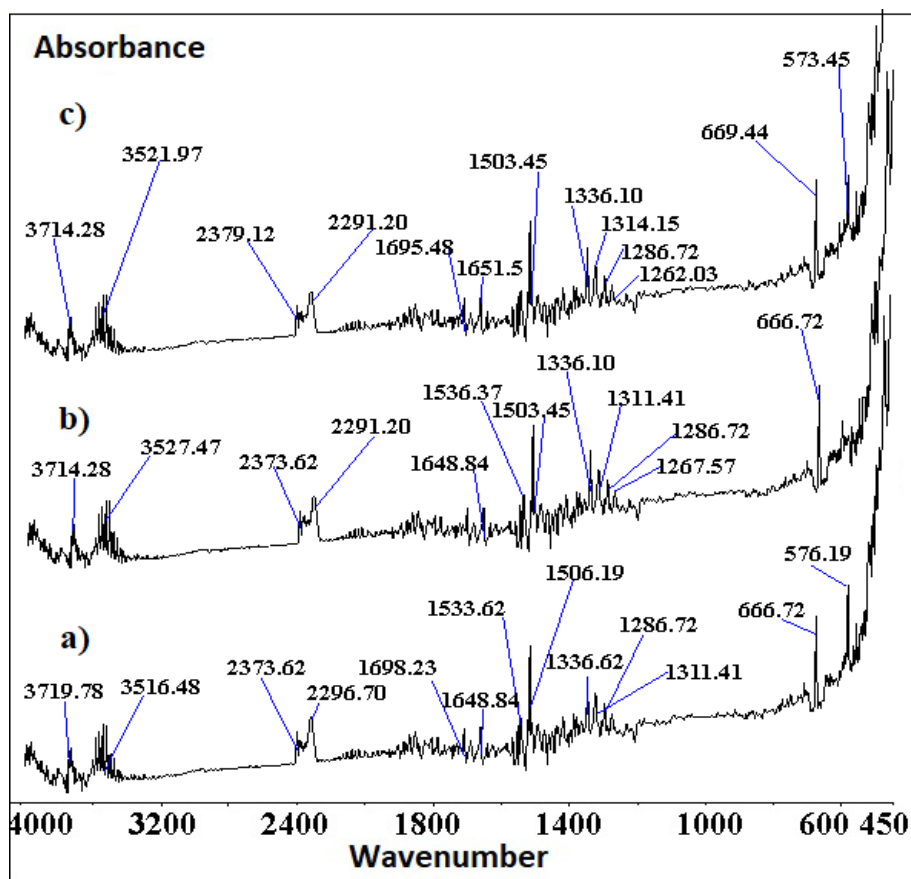

Figure 5. FTIR spectrum of poly(ABCF13) during decomposition formed at a) 320°C, b) 370°C, and c) 450°C in air

3.2. TGA/FTIR analysis of graft products

To begin with, TGA analyses for the graft copolymers with 10% and 40% poly(ABCF13)were conducted in a nitrogen atmosphere. The variations in weight loss percentages with temperature are illustrated in Figure 6. a and b. At low content, the weight loss pattern closely resembled the homopolymer. However, at higher content, the products exhibited a distinct decomposition mechanism with a gradual decrease in trend. This segmented manner indicated the presence of both homopolymer and grafted units in the polymer matrix. The obtained data also indicated that the first weight loss for the graft products, including 10% and 40% poly(ABCF13), began at approximately 299.5 °C and 236.2 °C with 0.99% and 1.2% values, respectively. This implied a significant effect of poly(ABCF13) and HDPE contents on the weight loss and decomposition mechanism, as depicted in Figure 6. In more detail, an increase in the percentage of poly(ABCF13) (corresponding to a decrease in P.E. percentage) resulted in the product decomposition being relatively easy and early. This could be attributed to the diminished retardation effect of HDPE during heating. In accordance with that, comparing the products to homopolymers regarding thermal stability, Figure 6. highlighted the retardation effect of HDPE in the product with 10% poly(ABCF13).

Moreover, at a given temperature, the percentage weight losses of products with high poly(ABCF13) content were greater than those with low poly(ABCF13) content, as shown in Figure 6. a and b. When the heating temperature reached 350°C during the test, the weight losses for 10% and 40% poly(ABCF13) graft products were recorded to be 5.6% and 16.10%, respectively. Between the 420-490 °C temperature range, remarkable weight losses for the graft products were recorded, which reached approximately 99% weight loss at around 484 °C, as indicated in Figure 6. a and b.
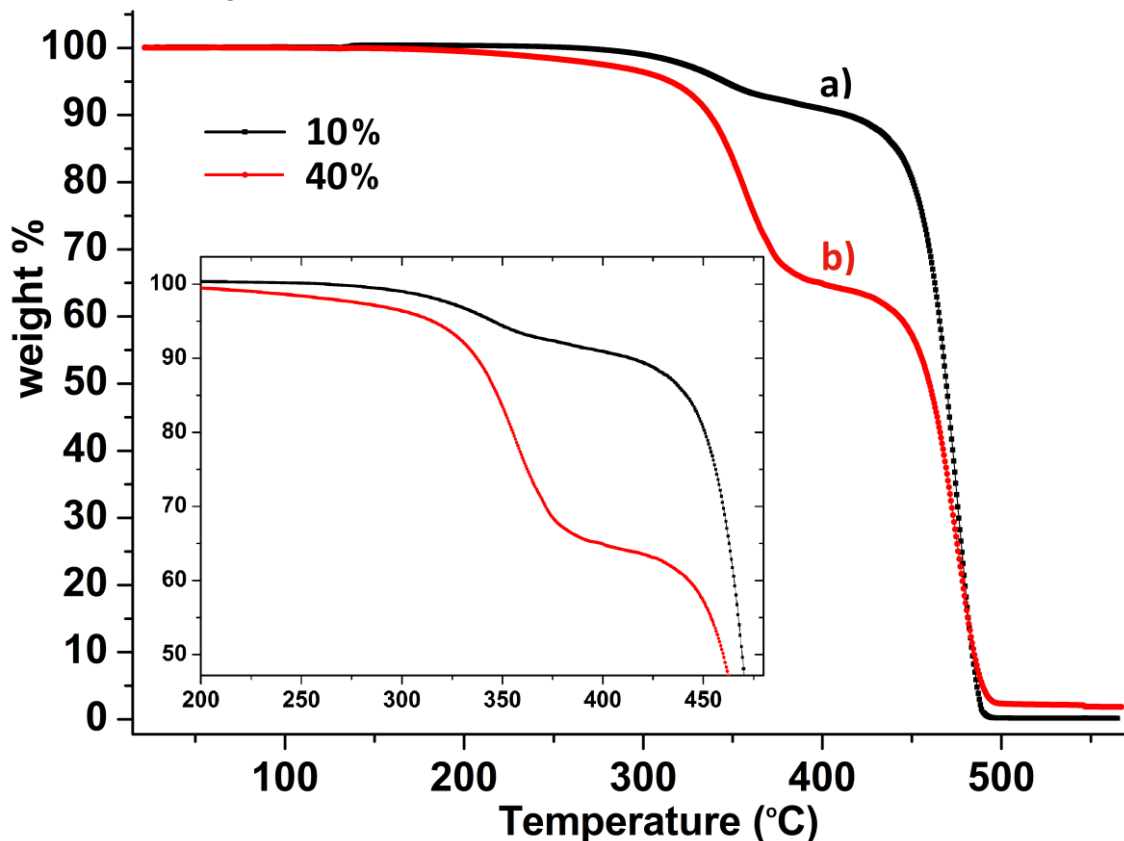

Figure 6. TGA graph for the graft copolymer containing a) 10%, and b) 40% of poly(ABCF13) in N_2

FTIR spectra taken under the N_2 atmosphere showed that 10% and 40% poly(ABCF13) products exhibited similar I.R. bands to the homopolymer, as shown in Figures 7 and 8, respectively. However, individual absorption I.R. bands at approximately 2920, 2860, and 760 cm^{-1}, characteristic of P.E., were absent in the homopolymer spectra. These bands, attributed to stretching vibrations of -CH$_2$ groups in P.E., became more pronounced at higher temperatures, particularly above 440 °C (Figure 7. c). Notably, the 760 cm^{-1} bands associated with C-C bending vibrations of P.E. were absent in the early stages of decomposition for both 10% and 40% poly(ABCF13) products (Figures 7. a, 8. a, and b). The distinct absorption I.R. bands of decomposition products regarding poly(ABCF13) became considerably prominent in the spectra of the 40% poly(ABCF13) product due to its higher poly(ABCF13) content. This suggests that homopolymers initially decomposed with significant weight loss around 350 °C, followed by the extensive decomposition of grafted units at approximately 450 °C. Accordingly, the segmental behaviors observed in Figure 6 can be attributed to the differential decomposition mechanisms of poly(ABCF13) and grafted copolymers in the matrix.

Furthermore, I.R. bands at around 2300 cm^{-1}, indicative of CO_2, were consistently present throughout heating for both products. These bands became more observable in the case of the product with 10% poly(ABCF13) (Figure 7. b). Additionally, the peculiar I.R. band due to C-F bonds at around 1260 cm^{-1} was recorded throughout heating for 10% and 40% poly(ABCF13) products, as seen in Figures 7 and 8). The spectra of these products also displayed newly forming and undefined absorption bands. All the observed absorption bands correlated well with the literature [25-27].
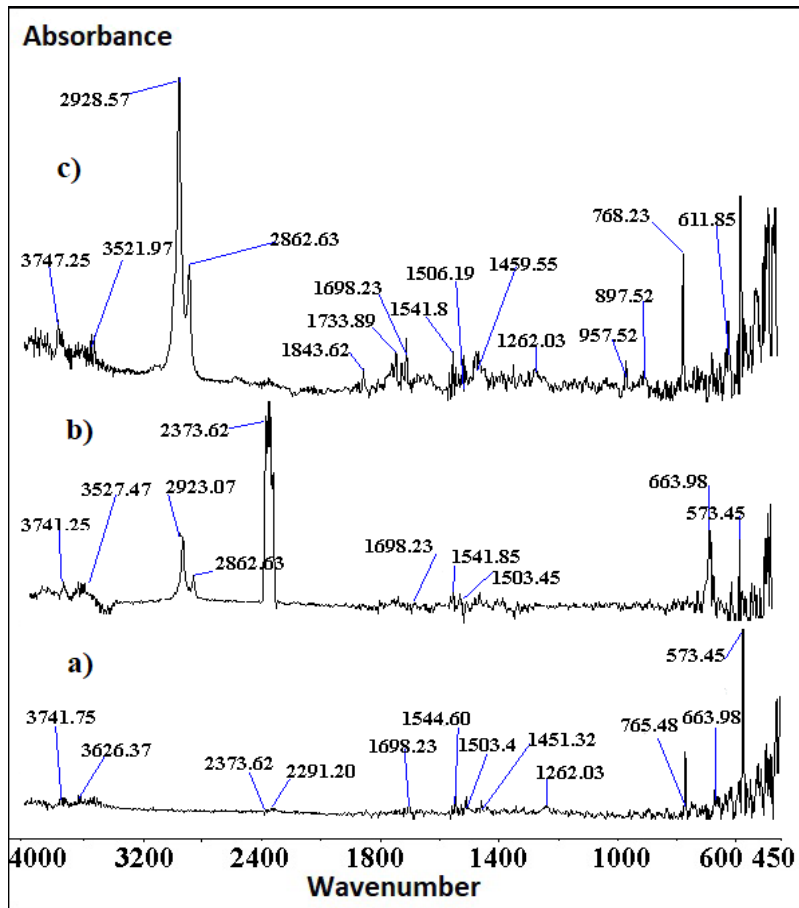
Figure 7. FTIR spectrum of the product with 10% poly(ABCF13)during decomposition recorded at a) 360 °C, b) 480 °C, and c) 510 °C in N_2
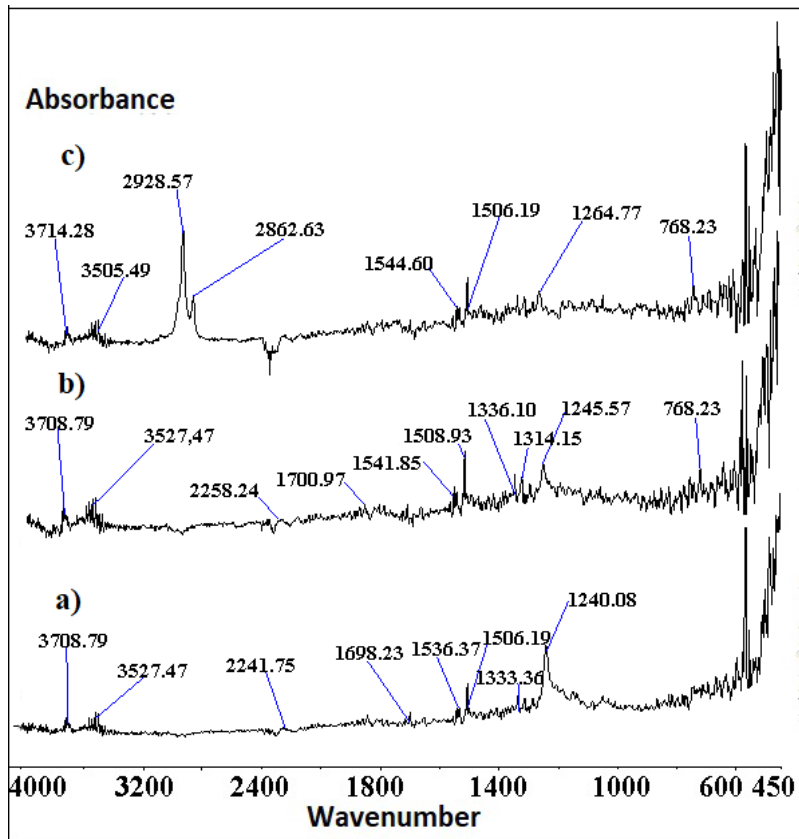

Figure 8. FTIR spectrum of the product with 10% poly(ABCF13)during decomposition was recorded at a) 380 °C, b) 430 °C, and c) 500 °C in N_2

The investigation extended beyond TGA/FTIR analysis conducted in an N_2 atmosphere, encompassing analyses in air for identical products. Figures 9a and b present the thermograms of products featuring 10% and 40% poly(ABCF13). The findings indicated a decomposition mechanism similar to that observed in an N_2 atmosphere. The initial temperatures for weight loss were approximately 274.2 °C (0.99%) and 235.2 °C (0.99%) for the 10% and 40% poly(ABCF13) products, respectively. The first weight losses in air occurred at slightly lower temperatures compared to N_2, considering their relative contents. As the heating temperature reached around 350 °C, the weight losses for the 10% and 40% poly(ABCF13) products in the air were 13.10% (5.6% in N_2) and 19.7% (16.10% in N_2), respectively. This suggested that the products in the air exhibited higher weight loss at certain heating temperatures than those in N2, indicating lower thermal stability. Significant weight losses with a sharp decrease were noted between approximately 380 to 470 °C, as depicted in Figures 9a and b. Furthermore, FTIR spectra obtained in an air atmosphere for all mentioned products revealed nearly identical characteristic absorption bands. This consistency in absorption bands supported the notion of a similar decomposition mechanism, as seen in Figure 10.
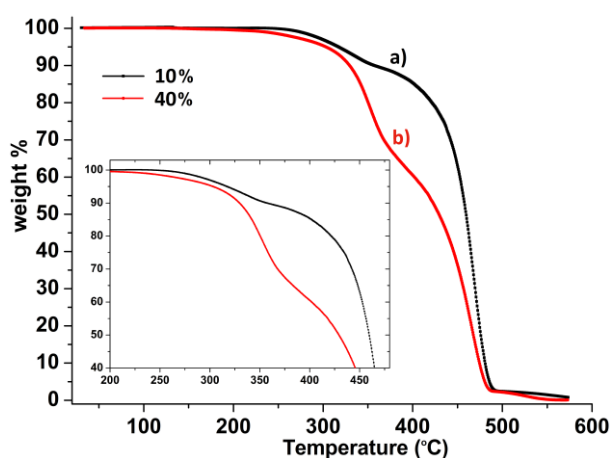

Figure 9. TGA graph for the graft copolymer containing a) 10% and b) 40% of poly(ABCF13) in air
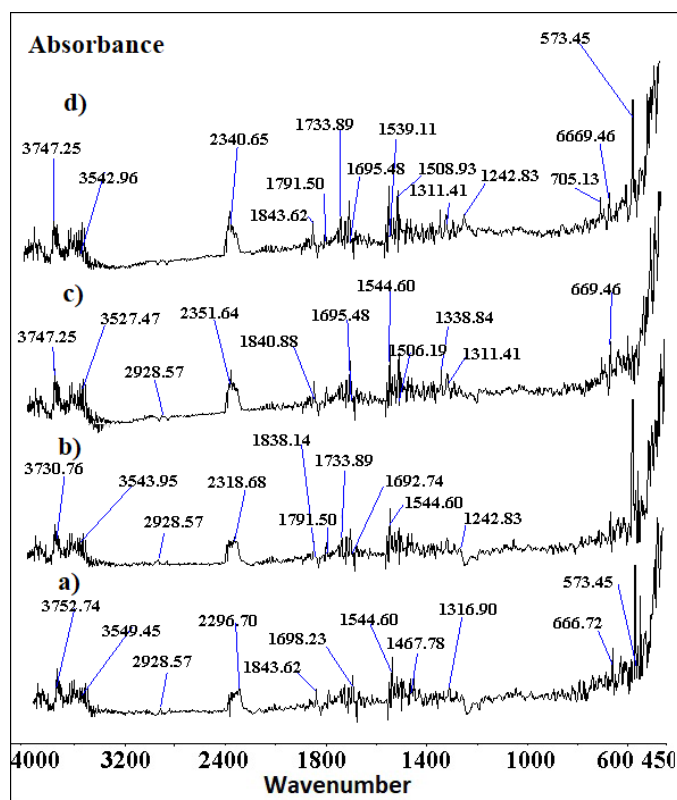

Figure 10. FTIR spectrum of the products with 10% poly(ABCF13) recorded at a)340°C, b)530°C and with 40% poly(ABCF13) taken at c) 330°C, and d) 400°C during decomposition

4. Conclusion

In this current study, we tried to figure out the thermal decomposition behavior of poly(ABCF13) semifluarinated homopolymer and poly(ABCF13)-grafted-HDPE copolymers and their formed products during decomposition in air and nitrogen atmospheres. Moreover, the grafting effect on the decomposition mechanism of the graft coproducts was also examined. The initial weight loss for poly(ABCF13) was found at about 226 °C in air and N2 atmosphere. The degradation mainly occurred by decomposing the groups (especially side chains) belonging to poly(ABCF13). These groups were mostly vinylic, fluorinated, aliphatic, phenolic parts, and carbon dioxide in poly's molecular structure (ABCF13). In the graft copolymers, the increment in the poly(ABCF13) percent in the matrix, which means the decrement in the percentage of HDPE) gave rise to the decomposition of the products in the air, and N2 atmospheres commenced easier and earlier.

Furthermore, a two-stage degradation mechanism began in the nitrogen atmosphere as the poly(ABCF13) percentage increased in the coproducts. Depending on that, at further poly(ABCF13) contents, it was found that the retardation effect of HDPE diminished. Moreover, one could assert that the temperatures at which initial weight losses in the graft coproducts were recorded in the air atmosphere were slightly lower than those observed in the nitrogen atmosphere when considering the relative contents.

The thermal degradation of graft copolymers could be seen as a critical point of scientific research due to its implications in various advanced materials. As we continue to push the limits of polymer science, it becomes imperative to investigate the challenges associated with the thermal stability of such graft copolymers. For this reason, this study outlines potential avenues for future work in better understanding the thermal degradation and decomposition mechanism of these specific polymers.

Author Contributions

All the authors equally contributed to this work. This paper is derived from the first author's doctoral dissertation thesis supervised by the second author. They all read and approved the final version of the paper.

Conflicts of Interest

The authors declare no conflict of interest.

Acknowledgment

References

[1] D. Rajesh, N. Lenin, R. Cep, P. Anand, M. Elangovan, *Enhancement of thermal behaviour of flax with a ramie fibre-reinforced polymer composite*, Polymers-Basel 15 (2) (2023) Article Number 350 16 pages.

[2] X. Zhang, R. Z. Huang, *Thermal decomposition kinetics of basalt fiber-reinforced wood polymer composites*, Polymers-Basel 12 (10) (2020) Article Number 2283 15 pages.

[3] D. Lázaro, A. Alonso, M. Lázaro, D. Alvear, *A simple direct method to obtain kinetic parameters for polymer thermal decomposition*, Applied Science 11 (23) (2021) Article Number 11300 18 pages.

[4] J. Charles, G. R. Ramkumaar, S. Azhagiri, S. Gunasekaran, *FTIR and thermal studies on nylon-66 and 30% glass fibre reinforced nylon-66*, E-Journal of Chemistry 6 (1) (2009) 23-33.

[5] A. G. Jineesh, S. Mohapatra, Thermal properties of polymer-carbon nanocomposites, Carbon-Containing Polymer Composites, Springer, Singapore, 2019, Ch. 7, pp. 235--270.

[6] O. Vambol, M. Shevtsova, A. Tsaritsynskyi, T. Nabokina, A. Kondratiev, *Temperature effect on elastic*, Thermomechanical and Thermal Properties of Polymer Composite Materials, Lecture Notes in Networks and Systems 536 (2023) 466-476.

[7] A.A. Askadskii, *The influence of chemical-structure on the thermal-characteristics of polymers,* International Journal of Polymeric Materials and Polymeric Biomaterials 24 (1-4) (1994) 95-105.

[8] Y. I. Matveev, A. A. Askadskii, I. V. Zhuravleva, G. L. Slonimskii, V. V. Korshak, *Influence of the chemical-structure of polymers on their thermal-stabilit*y, Vysokomol Soedin A+ 23(9) (1981) 2013-2026.

[9] M. C. Tanzi, *Characterization of thermal properties and crystallinity of polymer biomaterials*, Woodhead Publishing (2017) 123-146.

[10] J. A. Simao, C. F. Bellani, M. C. Branciforti, *Thermal properties and crystallinity of PCL/PBSA/cellulose nanocrystals grafted with PCL chains*, Journal of Applied Polymer Science 134 (8) (2017) Article Number 44493 9 pages.

[11] H. S. Hafid, F. N. Omar, J. Y. Zhu, M. Wakisaka, *Enhanced crystallinity and thermal properties of cellulose from rice husk using acid hydrolysis treatment*, Carbohydrate Polymers 260 (2021) Article Number 117789 12 pages.

[12] N. F. Mazuki, Y. Nagao, M. Z. Kufian, A. S. Samsudin, *The influences of PLA into PMMA on crystallinity and thermal properties enhancement-based hybrid polymer in gel properties*, Materials Todays-Proceeding 49 (2022) 3105-3111.

[13] K. Formela, J. T. Haponiuk, P. Stankiewicz, M. Cysewska, M. Chojnacka, *Cross-link density, thermal properties and morphology of SER-devulcanizate rubber vulcanizate with varying total content of carbon black*, Przemysl Chemiczny 91 (12) (2012) 2403-2406.

[14] A. W. M. Kahar, H. Ismail, A. A. Hamid, *The correlation between cross-link density and thermal properties of high-density polyethylene/natural rubber/thermoplastic tapioca starch blends prepared via dynamic vulcanization approach*, Journal of Thermal Analysis and Calorimetry 123 (1) (2016) 301-308.

[15] B. Ameduri, H. Sawada, Fluorinated Polymers Volume 2: Applications Preface, Fluorinated Polymers, Vol 2: Applications, Royal Society Of Chemistry Polymer Chemistry Series, Cambridge, 2017.

[16] B. Ameduri, H. Sawada, Fluorinated Polymers Volume 1: Synthesis, Properties, Processing and Simulation, Royal Society Of Chemistry Polymer Chemistry Series, Cambridge, 2017.

[17] U. Soykan, Y. Sert, G. Yıldırım, DFT, *Molecular Docking and Drug-likeness Analysis: Acrylate molecule bearing perfluorinated pendant unit*, Journal of Molecular Structure 1244 (2021) Article Number 130940 15 pages.

[18] U. Soykan, *Role of percent grafting and chain length of fully fluorinated pendant units in the grafted acrylic compound on crucial characteristic properties of high-density polyethylene*, Journal of Fluorine Chemistry 236 (2020) Article Number 109591 15 pages.

[19] U. Soykan, B. O. Sen, S. Çetin, U. Yahşi, C. Tav, *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 233 (2020) Article Number 109511 13 pages.

[20] U. Soykan, S. Cetin, B. Ozturk, F. Karaboğa, Y. Zalaoğlu, M. Dogruer, G. Yıldırım, C. Terzioğlu, *Synthesis and characterization of p-benzophenoneoxycarbonylphenyl acrylate by means of experimental measurements and theoretical approaches, and bulk melt polymerization*, Journal of Molecular Structure 1049 (2013) 479-487.

[21] S. Zhou, M. Ning, X. F. Wang, Z. J. Yan, D. F. Guo, Q. He, Y. P. Zhang, S. K. She, Y. Hu, *The influence of γ-irradiation on the mechanical, thermal degradation, and flame-retardant properties of EVA/LDPE/ATH blends*, Journal of Thermal Analysis and Calorimetry 119 (1) (2015) 167-173.

[22] K. Wu, L. Song, Y. Hu, H. D. Lu, B. K. Kandola, E. Kandare, *Synthesis and characterization of a functional polyhedral oligomeric silsesquioxane and its flame retardancy in epoxy resin*, Progress in Organic Coating 65 (4) (2009) 490-497.

[23] K. Wu, Y. Hu, L. Song, H. D. Lu, Z. Z. Wang, *flame retardancy and thermal degradation of intumescent flame-retardant starch-based biodegradable composites*, Industrial and Engineering Chemistry Research 48 (6) (2009) 3150-3157.

[24] Z. X. Li, Z. Wang, X. N. Qiu, L. Bai, J. P. Zheng, *Effect of acid-treated multi-walled carbon nanotubes on thermo-oxidative stability and degradation behavior of silicone rubber*, Journal of Thermal Analysis and Calorimetry 133 (3) (2018) 1353-1364.

[25] B. J. Mcgrattan, Examining *the decomposition of ethylene-vinyl acetate copolymers using TG/GC/IR,* Applied Spectroscopy 48 (12) (1994) 1472-1476.

[26] S. Çetin, B. Ö. Sen, U. Soykan, E. E. Fırat, G. Yıldırım, *Experimental and theoretical approaches for structural and mechanical properties of novel side chain LCP-PP graft coproducts*, Turkish Journal of Chemistry 40 (3) (2016) 467-483.

[27] X. P. Hu, Y. Y. Guo, L. Chen, X. L. Wang, L. J. Li, Y. Z. Wang, *A novel polymeric intumescent flame retardant: Synthesis, thermal degradation mechanism and application in ABS copolymer*, Polymer Degradation and Stability 97 (9) (2012) 1772-1778.