



Hyperbranched Polyester Polymer Preparation and Study Its Effect on Some Properties of Polypropylene

Nabeel Hasan Al-Mutairi¹*, Ali Al-Zubiedy¹, Ali J. Al-Zuhairi²

¹Polymer and Petrochemical Industries Department, University of Babylon, Hilla, Iraq.

²Department of Energy, College of Engineering, University of Babylon, Al-Musayyab, Iraq.



CrossMark

Abstract

In this work, a new hyperbranched polyester polymer (HBP) was prepared by using A2+B3 polycondensation polymerization methodology and blended with polypropylene PP. Both Nuclear magnetic resonance (NMR) and Fourier transform spectroscopy (FTIR) were used to characterize the HBP. The prepared HBP was blended with polypropylene (PP) in different weight compositions in order to study the effect of the addition of HBP on the polypropylene mechanical and thermal properties. A twin-screw extruder was used for the preparation of the polymeric blends (PP/HBP) and samples were manufactured using different blend compositions (5%, 10%, 20%) wt. Tensile test, impact test, density, hardness, and differential scanning calorimetry (DSC) were conducted to assess the blend properties. Results show that the blend properties and material characteristics were improved with the addition of the HBP. However, the tensile properties were decreased with the addition of HBP due to the immiscibility and different polarity of PP and HBP as indicated by SEM.

Keywords: Hyperbranched polyester (HBP); PP/HBP blend; DSC; Polymer blend; Crystallinity Xc.

1. Introduction

In the recent years many researchers show interest in dendritic and hyperbranched polymers. These materials exhibit unique properties, owing to their globular and non-entangled structures, low melt viscosity, large number of functional end groups and high reactivity when compared to their linear counterparts of comparable molecular weight[1]. Hyperbranched polymers (HBPs) have significant applications in various fields, such as drug delivery and coating [2]. HBPs show better characteristics compared with dendrimers generated by multistep synthesis [3]. HBPs can be easily manufactured using a one-pot polymerization technique [4], [5]. They have a three-dimensional dendritic architecture and are highly branched macromolecules [2]. HBPs exhibit low viscosity and strong reactivity and their three-dimensional structures allow them to improve their thermosets toughness and processability through a controlled reactive phase separation process [6]–[9]. Recently, many attempts have been made to study the properties of different types of hyperbranched polymers [10]–[13]. Huizhi Yan and

Yanmo Chen 2010 [14] prepared hyperbranched poly (phenylene sulphide) (HPPS) and studied the effect of its addition on the polypropylene for the production of dryable fibers. The results showed that the incorporation of HPPS has a minor effect on the mechanical characteristics and as well as the crystallinity (Xc) of HPPS/PP fibers was lower than that of neat PP fibers, as determined by Differential scanning calorimetry (DSC) thermograms. Qingchun Fan et- al. 2012 [15] investigated the PP/ hyperbranched polyester polymer (HBP) blends crystallization kinetics. Their findings show that HBP is a nucleating agent for polypropylene. Asım Davulcu 2015 [16] investigated the effect of the addition of HPEA on the dyeability of polypropylene with natural dyes. The study shows that both stress at break and elongation at break values were reduced with the HBP addition. The modified fiber samples have melting temperature (Tm) and Xc similar to those of unmodified PP fiber.

The aim of this study is to examine the effect of the addition of HBP polymer on the properties of PP. HBP polymer will be prepared by synthesizing

*Corresponding author e-mail: nabeeleng90@gmail.com.; (Nabeel Hasan Al-Mutairi).

Receive Date: 29 September 2021, Revise Date: 25 October 2021, Accept Date: 03 January 2022

DOI: [10.21608/ejchem.2022.98747.4594](https://doi.org/10.21608/ejchem.2022.98747.4594)

©2022 National Information and Documentation Center (NIDOC)

Pyrimidine-2,4,6-triol as an agent which will be used in the polymerization and synthesizing of HBP. HBP with different content ratios will be mixed and blend with PP. Samples will be cut out of PP/HBP sheets. The mechanical, physical and thermal properties will be evaluated using tensile test, impact test, hardness, density measurement and differential scanning calorimetry.

2. Materials and HBP/PP Blend preparation

2.1. Materials

The polypropylene (PP) used in this research was obtained from Saudi Arabia Basic Industries Corporation (Subic, Kingdom of Saudi Arabia). Table (1) shows the properties of PP used for blend preparation.

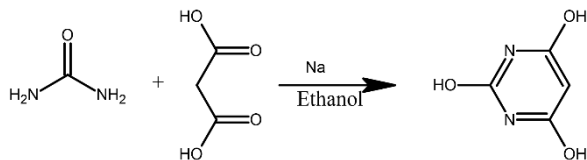
The materials used in synthesizing of Hyperbranched Polyester polymer were obtained from Sigma-Aldrich (UK) and Lancaster Synthesis (UK) and used without purification.

The synthesized materials were characterized. An open capillary method was used to determine melting points using an SMP30 melting point apparatus and the data were presented without any correction. An IR AFFINITY-1 CE Shimadzu spectrometer (Kyoto, Japan) was used to record the FT-IR spectra (KBr-discs) and an NMR spectrophotometer (Bruker, Japan) operating at 300 MHz was used to record H1-NMR spectra.

2.2. The Synthesis of Pyrimidine-2,4,6-triol (Scheme)

A 11.5 g of chopped sodium was dissolved in 250 ml of ethanol using an Erlenmeyer flask with a glass condenser protected by a calcium chloride tube. Then a 0.5 mol (52.03) g of malonic acid was added to the mixture followed by a 0.5 mol (30.03) g of dry urea dissolved in 250 ml of hot ethanol. A 20 g of molecular sieves were added then to the mixture. Subsequently, the ingredients were mixed for 10 hours at a temperature of 110 °C and after completion, a white precipitate was form. Then a 500 ml of hot water at 50 °C was added followed by a 45 ml of HCl. The mixture was then filtered and cooled in an ice bath for 24 hrs. and, after that, washed with

50 ml of cold water and dried at a temperature of between 105-110 °C for a period of 3-4 hrs. The final product (Pyrimidine-2,4,6-triol) was used as a raw material for the polymerization process.



Scheme 1: The synthesis of pyrimidine-2,4,6-triol.

Color: White; Yield: 69%; m.p: 255-259 dec; Mw: 148.11 g/mol; IR (v, cm⁻¹): 3477(OH), 1693 (C=N), 1240 (C-O) as shown in figure 1; H1-NMR (300 MHz, DMSO-d₆) δ (ppm): 4.35 (S, 1H, CH₂ pyrimidine), 8.49 (S, 1H, imidic OH), 10.11 (S, 1H, phenolic OH) as shown in figure 2.

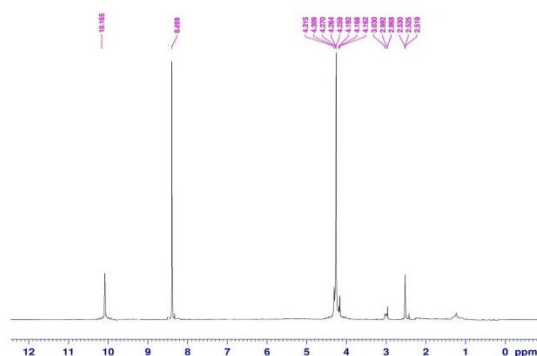


Figure 1: H¹-NMR of pyrimidine-2,4,6-triol.

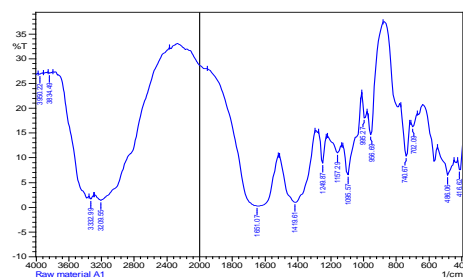


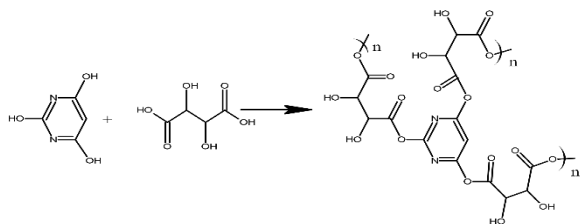
Figure 2: The FTIR spectrum of pyrimidine-2,4,6-triol.

Table (1): Properties of PP used.

Property	Test method	Data	Unit
Elastic Modulus	ASTM D-638	0.12-0.13	GPa
Tensile Strength	ASTM D-638	35	MPa
MFR	ASTM D-1238	10	g/10min
Mw		195.69	g/mol

2.3. The Synthesis of Hyperbranched Polyester Polymer (Scheme 2)

A 0.2 mol (25.6g) of the white precipitate (pyrimidine-2,4,6-triol compound) was mixed with 0.3 mol (45 g) tartaric acid in a round bottom flask set over an oil bath. The bath temperature was steadily increased to 170°C and then held at 160 °C for 4 hours. A continuous mixing was used until the reactants were fully melted producing a pale brown material (Hyperbranched Polyester Polymer).



Scheme 2: The synthesis of Hyperbranched polyester polymer.

Color: Pale brown; Yield: 85%; m.p: 148-175; Mw:360.49 g/mol; IR (v, cm⁻¹): 3471.87 (OH), 2962.66 (C-H aliph), 1620.21 (C=O aliphatic) as shown in figure 3; H¹-NMR (300 MHz, DMSO-d₆) δ (ppm): 3.05 (d, 6H, OH tartaric group), 4.05 (s, 1H, CH₂ pyrimidine), 5.15 (d, 6H, CH tartaric group) as shown in figure 4.

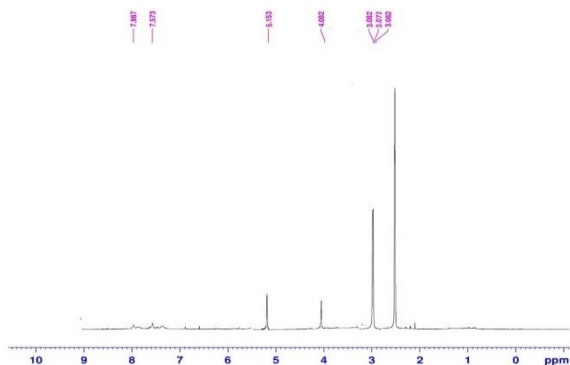


Figure 3: H¹-NMR of Hyperbranched polyester polymer.

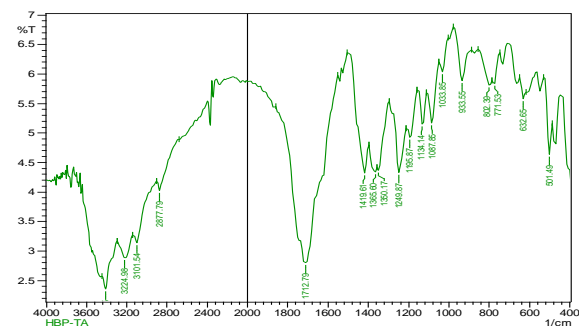


Figure 4: The FTIR spectrum of Hyperbranched polyester polymer.

2.4. Blend Preparation

PP and HBP were mixed and then blended in an SLJ30A type co-rotating twin-screw extruder (manufacturer, China) equipped with two heating sections working at a screw speed of 35 rev./min and a temperature of 155-165 °C using the materials composition listed in table 2. The molten material was passed between two rollers to make a thin sheet. The thickness of the sheet can be controlled by adjusting the distance between the rollers, and then the sheets were cut according to ASTM-D specifications.

3. Characterization

3.1. Mechanical Properties

A universal testing machine (WDW_5E, manufacturer, China) was used to determine the tensile characteristics under ASTM D638-IV. The test was performed at a speed rate of 10 mm/min. Charpy impact strength was determined using a WP 400 impact tester (Gunt, Germany) following ASTM D-256. Three samples were tested, and the average of these values was taken. The hardness of the blend samples was determined using a Shor D hardness tester TH 210 FJ (China) following ASTM D 2240 and performed at room temperature.

3.2. Density

The GP-120 S density tester (China) was used to determine the density of the blends under ASTM D-792, using Archimedes principle at room temperature.

Table (2): Percentages of the polymer blends.

Polypropylene (PP) wt.%	Hyperbranched polyester polymer (HBP) wt.%
100	0
95	5
90	10
80	20

3.3. Differential Scanning Calorimetry DSC

The thermal characteristics of PP and PP/HBP blends were evaluated using a differential scanning calorimetry DSC type TA-60 WS instrument (Shimadzu, Japan). The samples with an average weight of (8-10±0.5) mg were heated at a heating rate of 10 °C/min from 30 to 250 °C, then cooled down at the same rate from 250 to 30 °C under an inert gas. The following equation (1) was used to estimate the degree of crystallinity (X_c) of the blends [17]:

$$X_c = (\Delta H_m / \Delta H_o * W_f) * 100\% \dots \dots \dots (1)$$

Where: ΔH_m : melting enthalpy as determined by DSC, ΔH_o : melting enthalpy, which is (209 J/g) of fully crystalline PP [17] and W_f : weight fraction percentage of PP in the blend.

3.4. Scanning electron microscope SEM

The morphology of PP and PP/HBP blends have been studied using SEM Inspect S50. The samples were cut into small pieces and then coated with thin layer of gold to obtain good conductivity.

4. Result and Discussion

4.1. Mechanical Properties

Figure 5 shows the influence of HBP level on tensile strength of PP/HBP. The results show that the tensile strength was slightly reduced by 0.865 MPa, 1.55 MPa and 0.97 MPa for the 5%, 10% and 20% of HBP samples, respectively. The weak interfacial adhesion between HBP and PP, as well as the lack of entanglements between PP and HBP with various polarities, results in inadequate stress transfer between dispersed phase HBP and matrix PP [18], [19]. The HBP molecules increase the distance between PP chains and allow the chains to move more freely past each other. These results indicate that the blends of PP and HBP are immiscible [20].

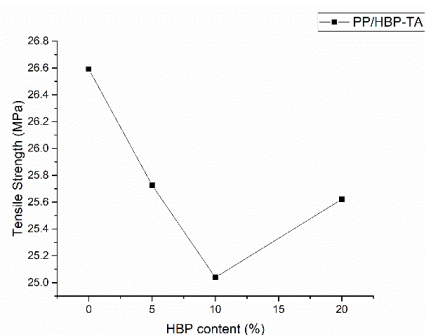


Figure 5: Tensile strength of PP/HBP vs. HBP content.

The influence of HBP content on the elastic modulus of PP Blends is shown in Figure 6. It was found that the elastic modulus increased by 0.18 GPa, 0.185 GPa and 0.06 GPa for the 5%, 10% and 20% of HBP, respectively. This behaviour could be attributed to the stiffening effect and absence of entanglements of HBP, resulting in a brittle material with poor mechanical properties.

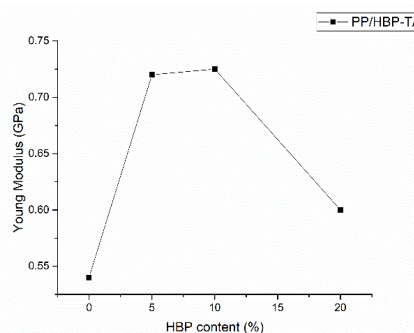


Figure 6: Modulus of Elasticity of PP/HBP vs. HBP content.

Figure 7 represents the influence of HBP on the elongation at the break of PP/HBP blends. The result shows that the elongation of the blends decreased by 17.56 %, 20.1 % and 7.25 % for 5 %, 10 % and 20 % of the HBP, respectively. This happens because the HBP did not interact with the PP and remained a free particle, reducing the PP ability to elongate [21],[22].

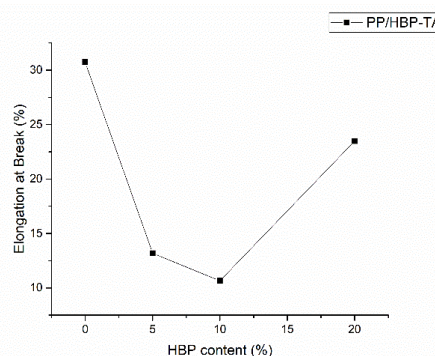


Figure 7: Elongation at break of PP/HBP vs. HBP content.

The toughness or resistance of a stiff material to rapid deformation is referred to as impact strength. Figure 8 shows the influence of HBP content on the impact strength of PP/HBP blends. The result shows that the addition of HBP enhanced the impact strength of the blends by 7.4 KJ/m², 13.3 KJ/m² and 11.6 KJ/m² for the 5%, 10 % and 20% of HBP, respectively compared to the neat PP. The addition of

HBP, up to a certain level, increases the impact strength of PP due to the good compability at low levels and good dispersion of HBP particles. This result agrees with the findings in [23][24].

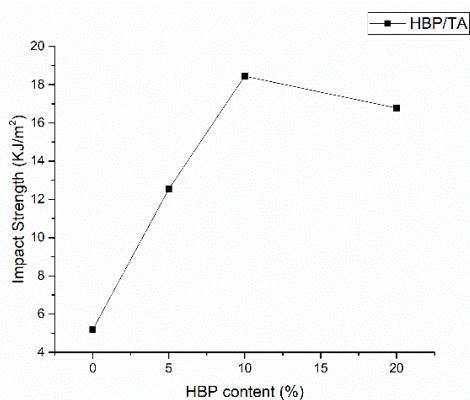


Figure 8: Impact strength of PP/HBP vs. HBP content.

Hardness is defined as the resistance of a material to scratches or penetration. The presence of plasticizers in materials reduces their hardness, while crosslinks increase it. Figure 9 shows the influence of HBP content on the Shore D hardness of the blends. The PP/HBP blend hardness increases by 0.8, 1.5 and 3.4 as the amount of HBP increases from 5% to 20% respectively, which may be attributed to the HBP molecule's stiffness and the increased compatibility of HBP with PP. These results are in agreement with S. Mahapatra and N. Karak [21],[25].

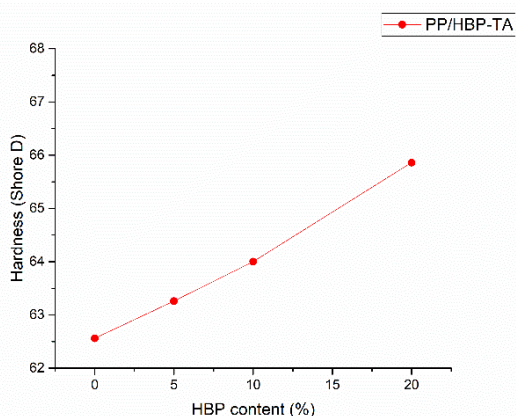


Figure 9: Shore D hardness of PP/HBP vs. HBP content.

4.2. Density

The influence of HBP on the density of PP/HBP is shown in Figure 10. The density of PP/HBP blends is increased by 0.026 g/cm³, 0.029 g/cm³ and 0.051 g/cm³ for 5%, 10% and 20% of HBP, respectively.

This increase in PP/HBP blend density is directly proportional to the greater density of HBP [26], which occupies the spaces between the chains of PP and increase the total density of the blends.

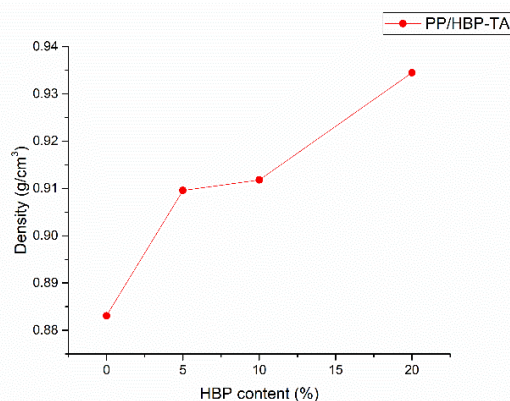


Figure 10: Density of PP/HBP vs. HBP content.

4.3. Differential Scanning Calorimetry (DSC)

The effect of HBP content on the melting (T_m) and crystallization (T_c) temperature of PP and the blends were studied using DSC. The polymer's crystallization can be affected by the addition of a heterogeneous or inorganic material. Generally, these fillers can act as a nucleating site. Figure 11 and 12 shows the effect of HBP addition on the melting and crystallization temperature of PP blends. The result shown in figure 11 indicates that the melting temperature did not change with the addition of HBP. Figure 12 also shows slight differences in the crystallization temperature and the HBP addition has shifted the crystallization temperature of neat PP to a higher value. Additionally, Table 3 shows that the crystallinity of blends increased with the addition of HBP. These results are in agreement with Diao, Jian Z [27] and Wu, Lingyan [28],[29].

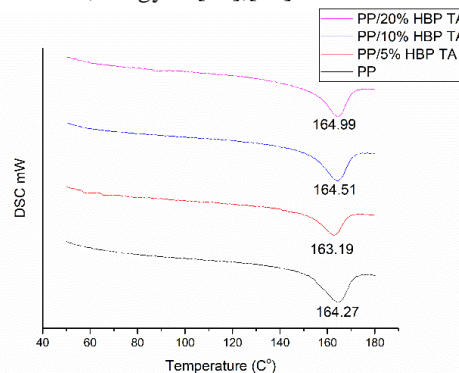


Figure 11: DSC heating thermograms for PP and PP/HBP.

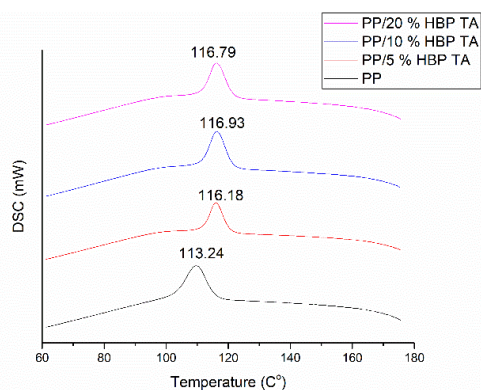


Figure 12: DSC cooling thermograms for PP and PP/HBP.

Table (3): The PP and PP/HBP DSC data.

Samples	T _m (°C)	T _c (°C)	X _c %
PP	164.27	113,24	42.1
PP/5% HBP-TA	163.19	116.18	45.99
PP/10% HBP-TA	164.51	116.93	57.4
PP/20% HBP-TA	164.99	116.79	51.21

4.4. Scanning electron microscope (SEM)

Figure 13 shows the SEM micrographs of PP and PP/HBP samples at two magnifications 50 μm and 10 μm . It's shown from the Figure 13 (A, B) that PP sample has smooth, continuous, and uniform surface. While the sample of PP blended with HBP shows rough and non-uniform surface, due to the difference in polarity of PP and HBP that results in poor adhesion between the two polymers as in Figure 13 (C, D) and thus reflected on the mechanical properties as shown above.

5. Conclusion

The HBP polymer has been prepared using A₂+B₃ monomers with polycondensation polymerization and then blended with PP at different ratios of HBP. The tensile strength of the blends PP/HBP was reduced as the amount of HBP increased for samples containing 5%, 10% and 20% of HBP due to the lack of interaction and immiscibility of the two polymers. The Young modulus has been increased due to the increased stiffness of PP/HBP blends. Also, the impact strength, hardness, and density increased at all levels of HBP. The thermal properties such as melting point did not change with HBP level while the crystallization temperature and the degree of

crystallinity have increased with increasing HBP level in blends this increment is due to that HBP acting as a nucleating agent. SEM images shows that there is no interaction between blend components and the blends were immiscible.

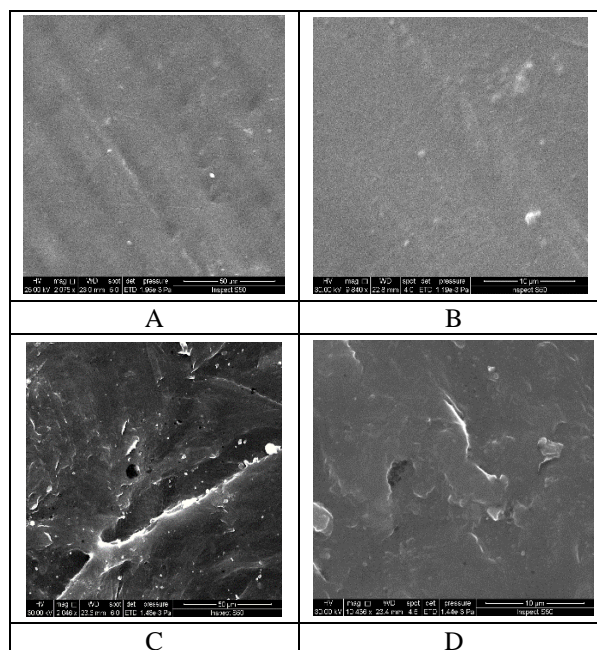


Figure 13: SEM images of PP (A, B) and PP/HBP (C, D) at two magnifications 50 μm and 10 μm .

6. References

- [1] P. D. Tatiya, R. K. Hedao, P. P. Mahulikar, and V. V. Gite, "Novel polyurea microcapsules using dendritic functional monomer: synthesis, characterization, and its use in self-healing and anticorrosive polyurethane coatings," *Ind. Eng. Chem. Res.*, vol. 52, no. 4, pp. 1562–1570, 2013.
- [2] C. Gao and D. Yan, "Hyperbranched polymers: from synthesis to applications," *Prog. Polym. Sci.*, vol. 29, no. 3, pp. 183–275, 2004.
- [3] C. J. Hawker, E. E. Malmström, C. W. Frank, and J. P. Kampf, "Exact linear analogs of dendritic polyether macromolecules: design, synthesis, and unique properties," *J. Am. Chem. Soc.*, vol. 119, no. 41, pp. 9903–9904, 1997.
- [4] K. E. Uhrich, C. J. Hawker, J. M. J. Frechet, and S. R. Turner, "One-pot synthesis of hyperbranched polyethers," *Macromolecules*, vol. 25, no. 18, pp. 4583–4587, 1992.
- [5] E. Malmström, M. Johansson, and A. Hult, "Hyperbranched aliphatic polyesters," *Macromolecules*, vol. 28, no. 5, pp. 1698–1703, 1995.

- [6] L. Boogh, B. Pettersson, and J.-A. E. Månson, "Dendritic hyperbranched polymers as tougheners for epoxy resins," *Polymer (Guildf.)*, vol. 40, no. 9, pp. 2249–2261, 1999.
- [7] R. Mezzenga, L. Boogh, and J.-A. E. Månson, "A review of dendritic hyperbranched polymer as modifiers in epoxy composites," *Compos. Sci. Technol.*, vol. 61, no. 5, pp. 787–795, 2001.
- [8] A. Gopala, H. Wu, J. Xu, and P. Heiden, "Investigation of readily processable thermoplastic-toughened thermosets: IV. BMIs toughened with hyperbranched polyester," *J. Appl. Polym. Sci.*, vol. 71, no. 11, pp. 1809–1817, 1999.
- [9] O. Gryshchuk, N. Jost, and J. Karger-Kocsis, "Toughening of vinyl ester-urethane hybrid resins through functionalized polymers," *J. Appl. Polym. Sci.*, vol. 84, no. 3, pp. 672–680, 2002.
- [10] A. J. Al-Zuhairi, A. S. Allw, K. A. Obaid, S. R. Rasool, and A. O. Mousa, "Synthesis of hyperbranched polymers and study of its optical properties," *J. Eng. Appl. Sci.*, vol. 12, no. Specialissue6, pp. 7800–7804, 2017, doi: 10.3923/jeasci.2017.7800.7804.
- [11] A. Al-zuhairi, "Synthesis of Hyper Branched Polyester Polymers Containing Thiobarbituric Acid and Study of its Optical Properties," vol. 12, no. 1, pp. 1–11, Apr. 2020.
- [12] M. M. H. AL-Abayechi, A. J. AL-Zuhairi, and M. N. AL-Baiati, "Physical properties of hyperbranched polymers containing melamine derivative," in *AIP Conference Proceedings*, 2020, vol. 2290, no. 1, p. 30027.
- [13] M. M. H. AL-Abayechi, A. J. AL-Zuhairi, and M. N. AL-Baiati, "Synthesis and identification of a novel hyper branched polymers containing melamine derivative," in *IOP Conference Series: Materials Science and Engineering*, 2019, vol. 571, no. 1, p. 12092.
- [14] H. Yan and Y. Chen, "Blends of polypropylene and hyperbranched poly(Phenylene sulphide) for production of dyeable PP fibres," *Iran. Polym. J. (English Ed.)*, vol. 19, no. 10, pp. 791–799, 2010.
- [15] Q. Fan, F. Duan, H. Guo, and T. Wu, "Isothermal crystallization kinetics of polypropylene and hyperbranched polyester blends," *Adv. Mater. Res.*, vol. 396–398, pp. 1688–1691, 2012, doi: 10.4028/www.scientific.net/AMR.396-398.1688.
- [16] A. Davulcu, "Investigation the dyeability of hyperbranched polymer modified polypropylene fibers with natural dyes," *Tekst. ve Konfeksiyon*, vol. 25, no. 1, pp. 73–79, 2015.
- [17] C. Yu, C. Jiang, and Y. Chen, "Yttria-polystyrene-polypropylene composite for fine dyeable fibers," *J. Appl. Polym. Sci.*, vol. 107, no. 3, pp. 1563–1567, 2008.
- [18] Z. J. A. Ameer and N. H. Hameed, "Miscibility improvement of LDPE/PVA blends by using silane-coupling agent," *J. Univ. Babylon Eng. Sci.*, vol. 26, no. 3, pp. 98–109, 2018, doi: 10.29196/jub.v26i3.621.
- [19] Z. J. A. Ameer and N. H. Al-Mutairi, "Miscibility Improvement of LDPE/PVA Blends with Maleic Acid Additions," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 433, no. 1, 2018, doi: 10.1088/1757-899X/433/1/012074.
- [20] J. Z. Diao, H. F. Yang, J. M. Zhang, and X. H. Song, "Preparation and characterization of PP and PP-g-(MAH-co-St)/hyperbranched poly(amide-ester) blends," *Iran. Polym. J. (English Ed.)*, vol. 16, no. 2, pp. 97–104, 2007.
- [21] S. S. Mahapatra and N. Karak, "Hyperbranched Polyamine as Multipurpose Polymeric Additives for LDPE and Plasticized PVC," *Eurasian Chem. J.*, vol. 9, no. 1, pp. 29–38, 2007.
- [22] M. M. A. Zeid, S. T. Rabie, A. A. Nada, A. M. Khalil, and R. H. Hilal, "Effect of gamma and UV radiation on properties of EPDM/GTR/HDPE blends," *Polym. Plast. Technol. Eng.*, vol. 47, no. 6, pp. 567–575, 2008.
- [23] N. Xu, W. Shi, M. Gong, and J. Feng, "Effects of modified hyperbranched polyester as a curing agent on the morphology and properties of dynamically cured polypropylene/polyurethane blends," *J. Mater. Sci.*, vol. 41, no. 12, pp. 3707–3713, 2006, doi: 10.1007/s10853-006-6252-1.
- [24] J. Z. Diao, J. Zhang, H. F. YANG, and Q. ZHAO, "Mechanical properties and morphology of blends of hyperbranched polymer with polypropylene and poly (vinyl chloride)," *Iran. Polym. J. (English Ed.)*, vol. 15, no. 67, pp. 91–98, 2006.
- [25] K. F. El-Nemr, A. M. Khalil, and E. S. Fathy, "Thermoplastic elastomers based on waste rubber and expanded polystyrene: role of devulcanization and ionizing radiation," *Int. J. Polym. Anal. Charact.*, vol. 23, no. 1, pp. 58–69, 2018.
- [26] D. Konkolewicz, A. Gray-Weale, and S. Perrier, "Describing the structure of a randomly hyperbranched polymer,"

-
- Macromol. Theory Simulations*, vol. 19, no. 5, pp. 219–227, 2010, doi: 10.1002/mats.201000006.
- [27] P. D. Tatiya, M. R. Nevare, P. P. Mahulikar, and V. V. Gite, “Melt Processing and Characterization of Nanocomposites of PP/Na+ MMT Blending with Hyperbranched Polyester,” *Polym. - Plast. Technol. Eng.*, vol. 53, no. 9, pp. 941–951, 2014, doi: 10.1080/03602559.2014.886064.
- [28] L. Wu, S. Lu, L. Pan, Q. Luo, J. Yang, and L. Hou, “Enhanced thermal and mechanical properties of polypropylene composites with hyperbranched polyester grafted sisal microcrystalline,” *Fibers Polym.*, vol. 17, no. September 2017, pp. 2153–2161, 2016, doi: 10.1007/s12221-016-6257-6.
- [29] M. M. Abou Zeid, N. A. Shaltout, A. M. Khalil, and A. A. El Miligy, “Effect of different coagents on physico-chemical properties of electron beam cured NBR/HDPE composites reinforced with HAF carbon black,” *Polym. Compos.*, vol. 29, no. 12, pp. 1321–1327, 2008.