Poly1-hexene: New impact modifier in HIPS technology

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ABSTRACT: Poly1-hexene was prepared using a conventional heterogeneous Ziegler–Natta catalyst and its stereoregularity was characterized using ^{13}C-NMR analysis. New kind of high impact polystyrene (HIPS) was prepared by radical polymerization of styrene in the presence of different amounts of synthesized poly1-hexene (PH) as impact modifier (HIPS/PH) and compared with conventional high impact polystyrene with polybutadiene (HIPS/PB) as rubber phase. Scanning electron microscopy (SEM) revealed that the dispersion of poly1-hexene in polystyrene matrix was more uniform compared with it in HIPS/PB. The impact strength of HIPS/PH was 29–79% and 80–289% higher than that in HIPS/PB and neat polystyrene, respectively. FTIR was used to confirm more durability of HIPS/PH samples toward ozonation. To study the effect of rubber type and amount on the T_gs of polystyrene, differential scanning calorimetry was employed. Results obtained from TGA demonstrated higher thermal stability of HIPS/PH sample in comparison with conventional HIPS/PB one. Our obtained results suggest new high impact polystyrene that in all studied aspects has better performance than the conventional HIPS. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43882.

INTRODUCTION

Radical polymerization is one of the most important commercial processes leading to high molecular weight polymers, because a wide variety of monomers can be polymerized and copolymerized under relatively simple experimental conditions.[1,2] Styrene is one of the monomers that can be polymerized under radical polymerization process. But neat polystyrene (PS) has rigid structure which limits its application.

Many attempts have been made to improve the toughness of polystyrene by incorporating rubber particles or inorganic particles.[3] It is well known that, polystyrene toughness may be greatly improved by incorporating a dispersed rubbery phase, usually polybutadiene (PB), via *in situ* polymerization, yielding the so-called high impact PS (HIPS). HIPS is the rubber reinforced polystyrene plastic,[4] which exhibits significantly enhanced impact strength compared to pure polystyrene. There are two phases in HIPS: polystyrene as continuous phase and rubber as dispersed phase.[5] This two-phases texture structure of HIPS is called salami or core-shell structure.[6] It is usually synthesized by bulk radical polymerization in which the rubber is added at the beginning of the polymerization.[5] Why is the salami morphology so important? When HIPS is subjected to force, the crazing will be initiated at the surface between rubber particle and PS

matrix. Because energy is absorbed with the formation and development of the crazing, the impact strength is improved. The further growth of crazing needs to be terminated by another rubber particle to avoid cracking and fracture of the materials. The number and strength of the rubber particles are crucial to the initiation and termination of crazing. With the salami structure, a large amount of PS is incorporated in the rubber particles. PS inside the rubber particle increases the strength and volume fraction of rubber phase, which means more rubber particles. Without the incorporation of PS in the rubber phase, the mechanical properties of HIPS will be seriously degraded.

How is the salami morphology formed? The salami morphology is closely related to phase inversion. The production process of HIPS starts in one homogeneous phase with PB dissolved in styrene monomer. The phase separation occurs at very low conversion of styrene. At this point, the PS/styrene (including a small amount of PB) forms the dispersed phase with the PB/styrene (including a small amount of PS) as the continuous phase. As more and more PS are generated, phase inversion may take place. The PB/styrene becomes the dispersed particles and the PS/styrene becomes the continuous matrix. The styrene incorporated in the PB particles will eventually be polymerized into

Table I. Temperature Programming Used in Postpolymerization Stage

Temperature (°C)	100	110	120	135	155	180
Time (h)	3	4	6	6	6	8

PS, which forms the micro-domain inside the rubber particles. The amount of PS enclosed in the rubber particles in the final products is decided by the amount of styrene in the rubber particles at the point of phase inversion.

Because of the commercial importance of HIPS, a lot of studies deal with synthesis, process modeling, and characterization of this polymer.[7] In 1986, Hobbs reported effects of rubber particle size on impact strength property of high impact polystyrene.[8] In 1990, Peng and coworkers studied the effects of grafting and cross-linking of polybutadiene during the bulk polymerization of high impact polystyrene.[9] They showed that when polybutadiene is grafted on polystyrenic chains, the impact strength on the obtained HIPSs was improved compared with the products based upon simple dispersion of PB in polystyrene. Kinetic studies revealed that, the density of grafting and degree of cross-linking increase with increasing of polymerization temperature and conversion. In the absence of cross-linking, the complex (salami-type) rubber particles may be broken down during mechanical shearing in typical melt fabrication processes. This disintegration of rubber particles causes loss of thoughtness. In 2003, Zhang and coworkers produced HIPS/nano-TiO_2 nanocomposites and studied their properties.[10] Obtained results showed that nano-TiO_2 particles had both toughing and reinforcing effects on HIPS, because in 2% concentration of nano-TiO_2, tensile strength, elastic modulus, and notched impact strength were increased. In 2010, Wang and coworkers synthesized blends of HIPS/styrene-butadiene rubber (SBR) and investigated its properties.[11] Results exhibited that tensile strength and hardness properties increase with increasing HIPS content in the dynamically vulcanized blends. In 2008, Nekoomanesh *et al.* investigated grafting of polystyrene on low molecular weight polybutadiene in thermal polymerization conditions.[12] In this respect, the effect of polymerization temperature and the type of polybutadiene on grafting degree were considered. They found that, grafting of polystyrene on polybutadiene increases

with increasing 1,2-vinyl content of polybutadiene and polymerization temperature. In 2011, Tang and coworkers studied the processing dependence of HIPS/styrene-butadiene-styrene triblock copolymers (SBS)/carbon black.[13] In this work, they produced two types of sheets by using two different processes: compression molding and extrusion calendaring. The SEM images showed that, with using extrusion calendaring, carbon black dispersion is improved and this lead to higher compression ratio and higher drawing speed. In 2014, Zhong-Kai and coworkers produced nanocomposites of HIPS/octavinyl polyhedral oligomeric silsesquioxane and characterized their properties.[5] Results showed that thermo-stability and mechanical properties of these nanocomposites have been improved. Also these nanocomposites had higher tensile and impact strength.

It is well known that traditional HIPS that has been prepared with PB suffers from poor resistance to the weathering factors, UV and oxidation. The poor weathering resistance of HIPS, resulting from photooxidative attack on the unsaturated PB, greatly limits the outdoor use of it. In several grades of HIPS, in order to improve notched impact strength and weatherability, PB is replaced by saturated rubbers consisting of copolymers or terpolymers of ethylene and propylene (EPR or EPDM).[14–16] Although EPDM and EPR are widely used in outdoor applications, investigation on new rubbers toughened HIPS is still going on.

Poly α-olefins have flexible alkyl branches with different lengths. These alkyl groups, which can shape themselves in numerous conformations, make it very difficult for the polymer molecules to align themselves up side-by-side in an orderly way. This results in lower contact surface area between the molecules and decreases the intermolecular interactions between molecules.[17] Therefore, many poly α-olefins do not form crystallized structure. Specially, poly1-hexene, because of its side branches (C_4), exhibits good elastic properties. In other words, existence of branches that joined to the backbone of polymer causes to slip of polymer chains on each other, and this leads to elastic behavior despite the lack of unsaturated bonds in the backbone.[18] The dynamic mechanical properties of this polymer were studied by Kurath and coworkers.[19] It was shown that poly1-hexene is amorphous at room temperature and has the lowest softening

Table II. Different Monomer Compositions for the Synthesizing of HIPS Samples with the Same Reaction Condition[a]

Label	Styrene (gr)	PB (gr)	PH (gr)	Conversion[b] (%)	Real concentration of rubber[c] (%)
PS	100	—	—	91.45	3.12
HIPS/PB2	98	2	—	93.70	5.80
HIPS/PB5	95	5	—	91.23	8.32
HIPS/PB8	92	8	—	94.11	2.86
HIPS/PH2	98	—	2	90.03	5.69
HIPS/PH5	95	—	5	96.25	8.12
HIPS/PH8	92	—	8	91.14	—

[a] Polymerization condition: [BPO] = 0.1 wt % of styrene; polymerization temperature = 90 °C.
[b] Conversion = gr HIPS/(gr styrene + gr rubber) ×100.
[c] Determined by using of methanol for extraction of remained styrene monomers.

Table III. Characteristics of Polybutadiene and Poly1-Hexene

	Polybutadiene	Poly1-hexene
M_n (g/mol)	2.2×10^5	2.1×10^5
Tacticity	98% cis	87% (77% mmmm and 10% rrrr)

point ($-45\,^{\circ}$C) among the series.[20] A well-known poly1-hexene elastomer was commercialized under the trade name of hexsyn. Hexsyn-rubber which was offered by goodyear tyre and rubber company, is a copolymer of 1-hexene (97%) with 4,5-dimethyl 1,5-hexadiene (3%). The curing of Hexsyn is similar to EPDM. The volcanized rubber has a low modulus and shows the high oxidation and ozone resistance that is expected of a largely saturated hydrocarbon. A property which makes this rubber a unique one among the series, is its superior fatique resistance in high dynamic loads.[21] These mentioned factors would make this rubber prone in HIPS technology.

In this work we prepared high impact polystyrene/polybutadiene (HIPS/PB) and high impact polystyrene/poly1-hexene (HIPS/PH) samples by radical polymerization process of styrene in the presence of different amounts of PH and PB as rubber phase. After synthesis and full characterization by SEM, DSC, and FTIR analysis, their impact behavior was concerned and compared.

EXPERIMENTAL

Materials
Styrene (Tabriz Petrochemical, Iran) was purified by distillation under reduced pressure over CaH_2. Polybutadiene was purchased from Arak petrochemical (Iran) (PBR1210S grid). Benzoyl peroxide (Aldrich, Germany) was recrystallized twice from chloroform solution by methanol. Ethyl benzene and 1-hexene were provided by Aldrich, Germany.

Synthesis of Poly1-Hexene Sample
Poly1-hexene was synthesized in our lab by using of $Mg(OEt)_2$/$FeCl_3$/$TiCl_4$/DNBP catalyst according to a procedure in Ref. 22.

Synthesis of HIPS/PB and HIPS/PH Samples
At the first stage, appropriate amount of polybutadiene or poly1-hexene was dissolved in styrene monomer and 10 mL of ethylbenzene solvent using a mechanical stirrer. The process of dissolving was carried out at room temperature in a glass reactor. It took 16 and 12 h for poly1-hexene and polybutadiene,

Scheme 1. Poly1-hexene structural unit.

respectively, to reach a uniform solution. Then under nitrogen atmosphere, benzoyl peroxide (in an amount equal to 0.1 wt % of styrene) was added and temperature was raised to $90\,^{\circ}$C. After 110 and 160 min for poly1-hexene and polybutadiene, respectively, by occurring phase inversion, the viscosity of solutions increased (phase separation observed). Then, this highly viscous solution moved to a glass mold which had cylindrical shape with diameter of 12 cm and height of 2.7 cm. Inorder to obtaining high conversation of polymerization, the mold was placed in an oven and temperature of oven was raised according to temperature programming that is shown in Table I. To remove the remaining styrene, obtained sheets were put under reduced pressure of 0.1 bar at $130\,^{\circ}$C for 4 h.

A series of HIPSs with different weight percentages of poly1-hexene and polybutadiene were synthesized, characterized, and to name them, abbreviations according to the weight rubber content were used (see Table II).

Measurements
The tacticity of poly1-hexene was obtained from the ^{13}C-NMR spectrum recorded on a Bruker Avance-400 spectrometer (Germany) in $CDCl_3$ at a frequency of 500 MHz. The molecular mass and their distributions were determined through gel permeation chromatography (Waters GPCV 150+, USA), using THF as the eluent at room temperature. Polystyrene standards were used for calibration. Notched specimens were tested with a Zwick 4 impact Tester (Germany), according to the ASTM D-256 standard. A 70 tone press machine was used to prepare impact bars for the impact tests. V-shaped notches were produced using a CSI automatic notcher (CS-93M). The tests were carried out at $23\,^{\circ}$C and humidity of 45%. The glass transition temperature (T_g) of the neat PS and synthesized HIPSs was determined from first heating scans with a Perkin Elmer (Diamond 7, USA) differential scanning calorimeter (DSC) under N_2 atmosphere with a heating rate of $10\,^{\circ}$C/min. Glass transition (T_g) and melting (T_m) temperatures were reported from the first heating scans. T_g was measured as the midpoint of the temperature range bounded by the tangents to the two flat regions of the heat flow curve. Scanning electron microscopic (SEM) observations were carried out on fracture surfaces. The fracture surfaces were coated with gold under reduced pressure and then examined using a VEGA\\TESCAN apparatus (Czech Republic). Samples were placed under ozone for 4 h at $40\,^{\circ}$C and with ozone concentration of 100 ppm. The presence of C-O and carbonyl bonds was confirmed by FT-IR technique infrared spectroscopy (FT-IR EQUINOX55 Bruker made in Germany) with a resolution of 4 cm^{-1} using a KBr method. Thermogravimetric measurements were performed by a Hi-Res TGA 2950 thermogravimetric Analyzer (TA instruments) attached to a thermal analyst 2100 (DuPont Instruments) thermal analyzer, under nitrogen from room temperature to $700\,^{\circ}$C, with a heating rate of $10\,^{\circ}$C/min.

Determination of Real Concentration of Rubbers in Final Samples
Real concentration or percentage of rubbers is percentage of rubbers in final product, without considering weight of unreacted monomers. For determination of real concentration of rubbers in final samples, produced HIPSs were placed in
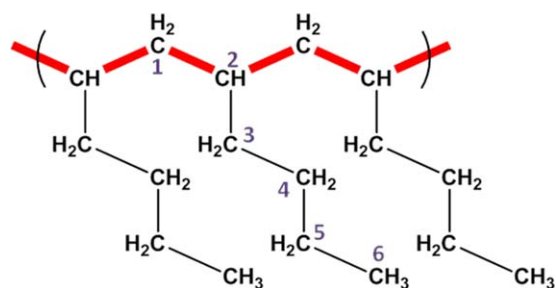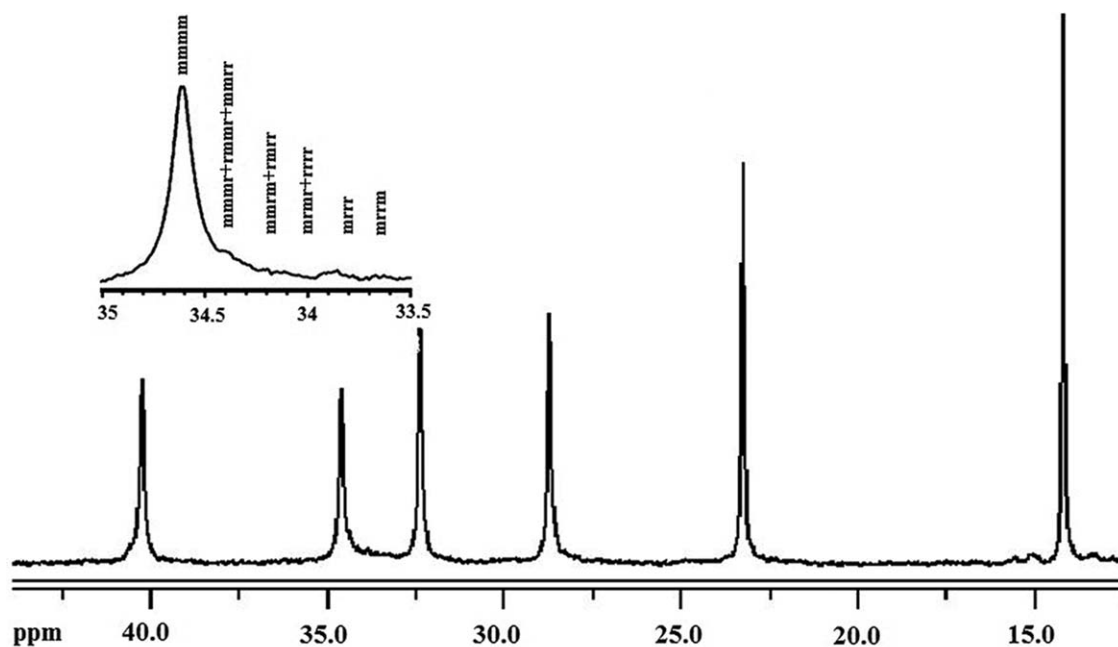
**Figure 1.** Expanded side chain methylene (C3) resonance patterns of synthesized poly1-hexene obtained from ^{13}C-NMR analysis in chloroform solvent.

methanol solvent for 16 h in order to extraction of unreacted monomers. After that, samples were dried until a constant weight was achieved and weighted exactly. The ratio of initial weight of rubbers to final weight of HIPS, gives the real concentration of rubbers in the final samples.[23]

RESULTS AND DISCUSSION

Poly1-hexene was prepared by polymerizing the 1-hexene monomer in hexane in the presence of $Mg(OEt)_2/FeCl_3/TiCl_4/DNBP$ (dibutylphthalate) catalyst.[20,22] The specifications of synthesized
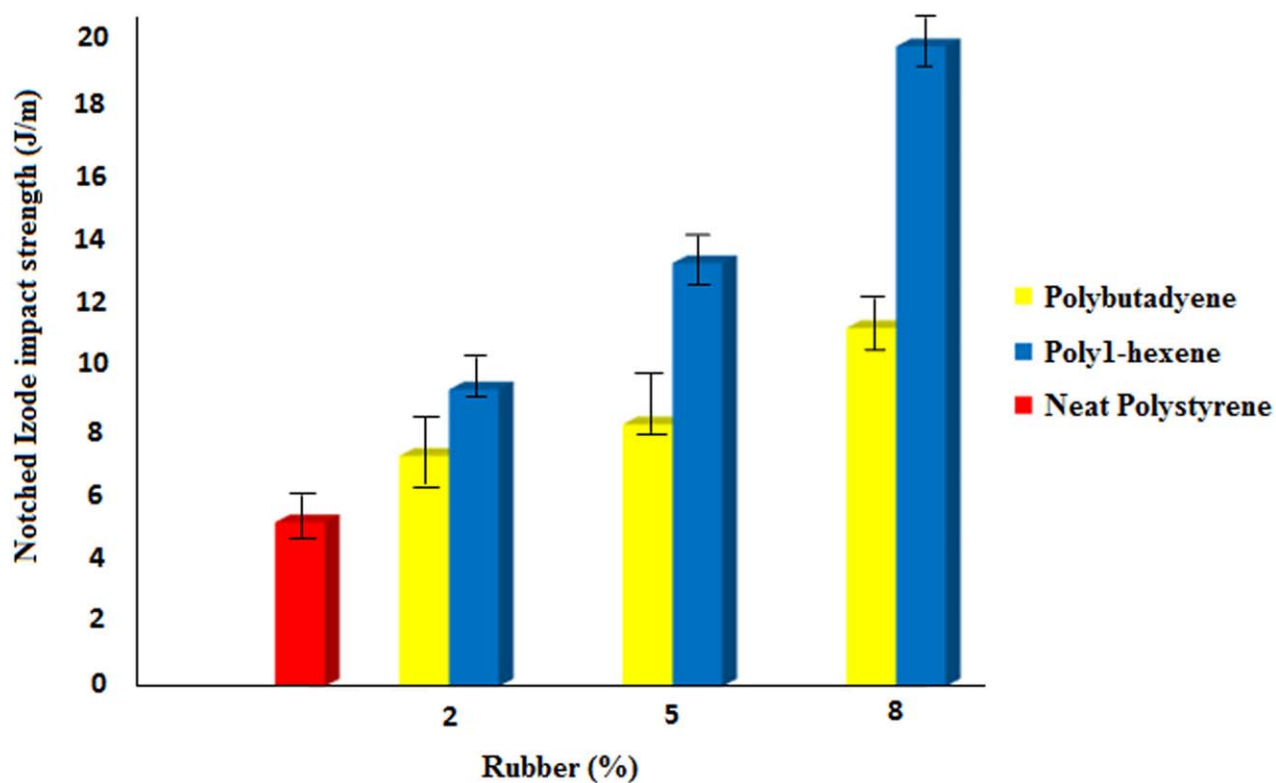
Figure 2. Notched Izod impact strength of the neat PS and high impact polystyrenes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
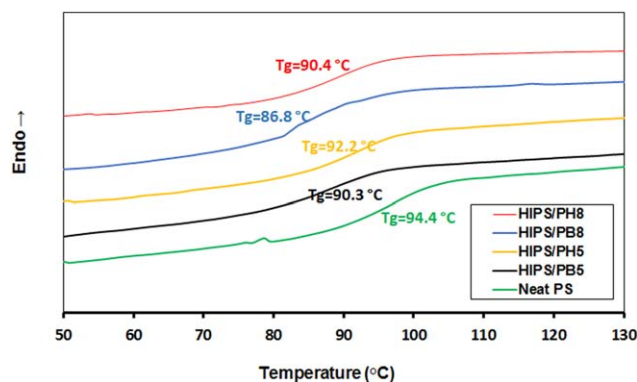
Figure 3. DSC curves of neat PS and synthesized HIPS samples with 5% and 8% rubber concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

poly1-hexene and polybutadiene that was purchased from Arak petrochemical (Iran) were summarized in Table III.

Poly1-hexene and polybutadiene had similar molecular weights of around 2.1×10^5 g/mol. In order to understand the configurational arrangement of 1-hexene monomer unit in the synthesized PH, the side chain methylene carbon (C3 in Scheme 1) was analyzed as the most sensitive carbon nuclei of pendant group toward stereo-regularity. The tacticity pentad content was calculated and shown as tacticity (%) in Table III. As can be seen, poly1-hexene had 77% isotactic, 10% syndiotactic, and 13% atactic configuration (see Figure 1).

Furthermore, typical composition of used polybutadiene was 98% cis, 1% trans, and 1% 1,2-vinyl.

In the next step, HIPS samples were synthesized by *in situ* polymerization of styrene in the presence of different amounts of PH and PB as impact modifier using BPO as initiator. To understand the effect of rubber content on HIPS properties, we synthesized HIPS samples with different amounts of rubbers containing 2, 5, and 8 w/w % of the initial monomer composition and named as HIPS/PB2, HIPS/PB5, and HIPS/PB8 in PB case and HIPS/PH2, HIPS/PH5 and HIPS/PH8 in PH case, respectively. Table II shows monomer compositions, labels and polymerization yields for different HIPS samples.

To ascertain the role of the rubber nature in determining the impact response of HIPS samples, it was of interest to compare the observed increase in Izod impact because of the presence of PH and PB rubbers. The notched Izod impact strength of the neat polystyrene, HIPS/PB and HIPS/PH samples was shown in Figure 2.

These results clearly indicate that the degree of impact strength increases with increasing rubber content from about 5.1 J/m in neat PS to 7.1, 8.1, and 11.0 J/m for HIPS/PB2, HIPS/PB5 and HIPS/PB8 samples, respectively. Furthermore, the impact strength of HIPS/PH samples in all weight ratios was greater than HIPS/PB ones. Indeed, changes in rubber nature from PB to PH lead to a significant increase in impact strength of about 29%, 61%, and 79% in 2, 5, and 8 wt % rubber contents, respectively. In the higher rubber content of 8%, the impact strength of PS was improved by 118% and 289% in HIPS/PB8 and HIPS/PH8 samples, respectively. This increase in impact strength was much higher than it in similar HIPS/EPDM samples (58% and 208% in the samples containing 8% and 17% of EPDM rubber, respectively) which was obtained by Lourenco *et al.*[24] We suggested that this may be because of highly elastic properties of poly1-hexene.[25,26] This elastic property arises from the presence of pendant groups that allows polymer chains to slipping on to each other. Existence of the rubber with high elastic property in the structure of HIPS causes to increasing impact strength, when this polymer placed under load.

Thermal behavior of polymers was studied by DSC analysis. Figure 3 shows the DSC thermographs of neat PS, HIPS/PH,
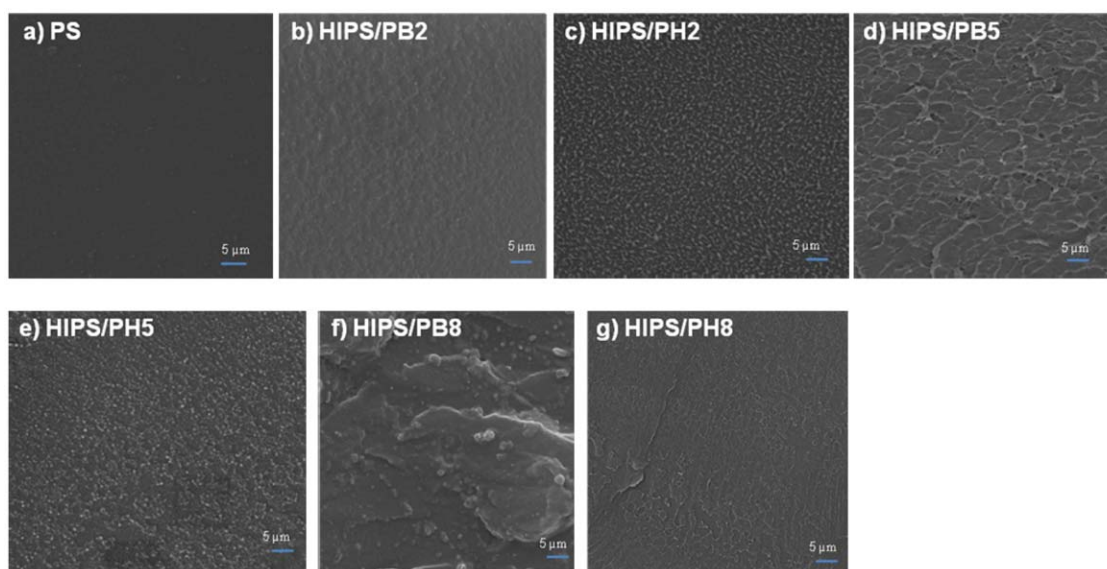
Figure 4. SEM micrographs of (a) neat polystyrene, (b) HIPS/PB2, (c) HIPS/PH2, (d) HIPS/PB5, (e) HIPS/PH5, (f) HIPS/PB8, and (g) HIPS/PH8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
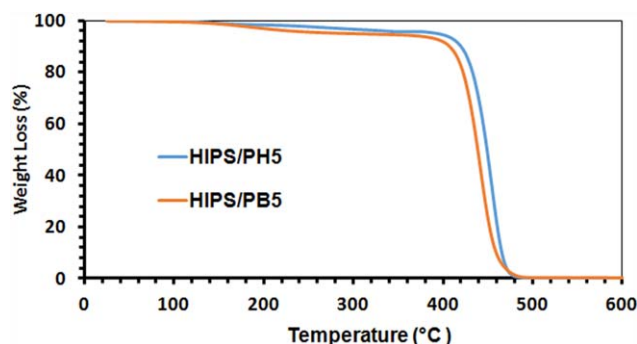
Figure 5. TGA curves of the HIPS/PH5 and HIPS/PB5 samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal Analysis of the HIPS Samples

Polymer	T_i (°C)	T_5 (°C)	T_{max} (°C)
HIPS/PH5	268	395	449
HIPS/PB5	210	309	439

T_i: initial decomposition temperature or temperature for 2.5% weight loss; T_5: temperature for 5% weight loss; T_{max}: maximum decomposition temperature.

and HIPS/PB in 5 and 8 wt % of rubber as obtained from the first heating scan.

Neat PS showed glass transition temperature at 94.4 °C. By adding 5% of PB and PH, T_g of the samples decreased to 90.3 °C and 92.2 °C, respectively. Furthermore, by additional increase in the rubber content to 8%, T_g decreased in respect to neat PS and HIPS/rubber4 samples and reached to 86.8 °C and 90.4 °C in both PB and PH containing samples, respectively. The lowering of T_g is the proof of dispersion of rubbers (poly1-hexene or polybutadiene) in the PS matrix.

SEM was used to determine the morphology of dispersion of rubbers in polystyrene matrix. Figure 4 shows the morphology of neat PS, HIPS/PB, and HIPS/PH samples in different rubber

percentages of 2%, 5%, and 8%. The morphology of HIPS/PB2, HIPS/PH2, HIPS/PH5, and HIPS/PH8 samples had the appearance of small particles (around 1 μm) in the PS matrix with homogeneous dispersion. This particle size that we obtained in our research is in accordance with the findings of many other groups in which the rubber particle was reported to be less than 5 μm,[27–30] or even rubber particles were hardly seen.[31] It shows that rubber particles had an advance adhesion and was harmonious with its PS matrix structure.[31] This type of morphology arose from good dispersion of rubbers in our samples, and subsequently these samples should show high impacct strength that this issue was proven in impact strength test (see Figure 2). While that in the case of HIPS/PB5 and HIPS/PB8 the fracture surface showed randomly oriented fish scale morphology.

Indeed, poly1-hexene was well dispersed since in HIPS/PH cases no agglomeration of rubber particles was seen, while that in higher polybutadiene contents, rubber particles were not well dispersed and lead to a kind of heterogeneity in SEM micrographs which results in poorer impact strength of HIPS/PB samples.

Thermogravimetric analysis (TGA) in air at a heating rate of 10 °C/min is usually applied for the evaluation of thermal stability.[32–34] It provides information about polymer stability upon heating.[35,36] Thermal stability of the HIPS/PH5 and HIPS/PB5 samples was investigated by TGA. TGA curves of these samples were shown in Figure 5 and the obtained data from this analysis were collected in Table IV. The temperatures for 2.5% weight loss (T_i) of HIPS/PH5 and HIPS/PB5 were at 268 °C and 210 °C, and the temperatures for 5% weight loss (T_5) that is important criteria for evaluation of thermal stability[37] were at 395 °C and 309 °C, respectively. Higher thermal stability of HIPS/PH sample is because of the lack of unsaturated bonds in PH structure. It seems that existence of unsaturated bonds in PB, leads to less stability of HIPS/PB sample when compared with HIPS/PH one.

FTIR spectroscopy was used to study durability of HIPS/PH and HIPD/PB samples toward atmospheric ozone. To accelerate polymer degradation, HIPS/PH5 and HIPS/PB5 samples were
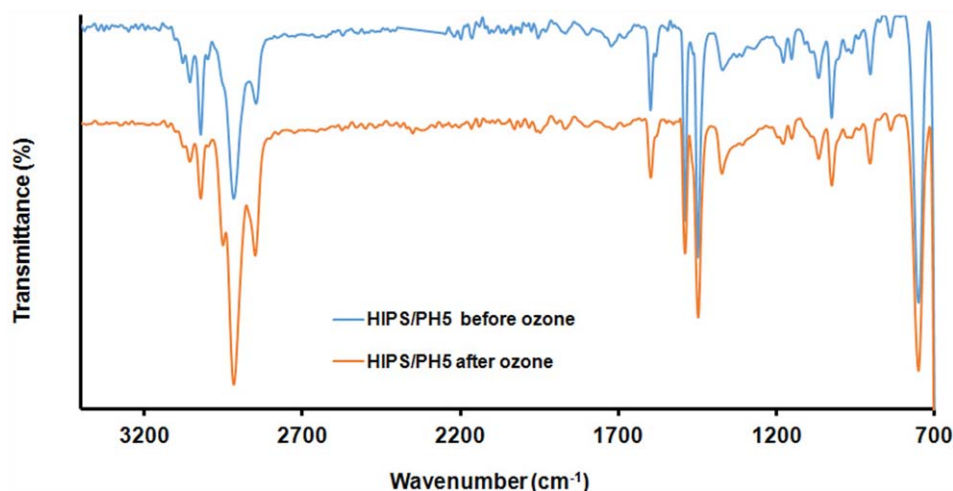
Figure 6. FTIR spectra of HIPS/PH5 after and before of ozone test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
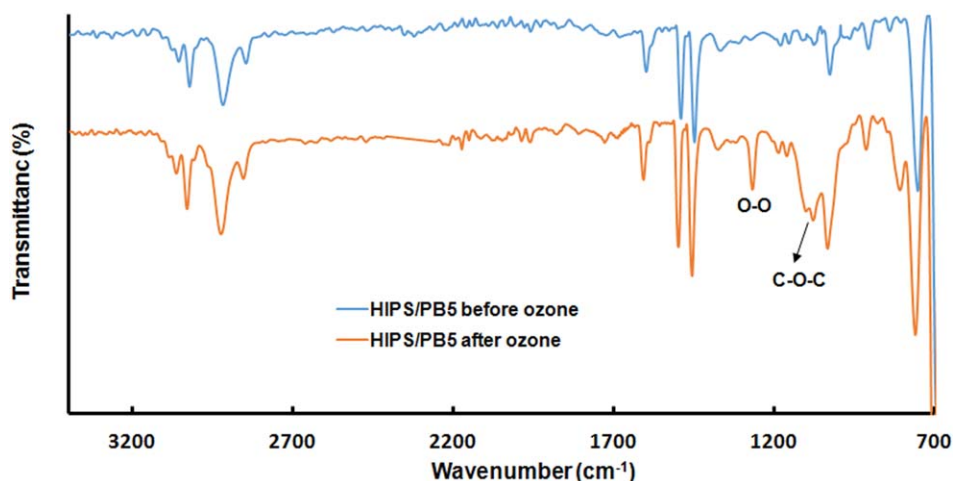
Figure 7. FTIR spectra of HIPS/PB5 after and before of ozone test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exposed to ozone for 4 hours with concentration of 100 pphm at 40 °C. Then, samples were brought out from ozone atmosphere and got ready for FTIR testing. Figure 6 shows the FTIR spectrum of HIPS/PH5 after and before of the ozone test. It is clear from IR spectrum that, HIPS/PH5 sample did not undergo degradation since PH does not have any unsaturated bonds that can be oxidated with ozone. On the other hand, the FTIR spectroscopy of the ozone treated HIPS/PB5 sample demonstrated the introduction of two peaks at 1026–1100 and 1260 cm^{-1} (see Figure 7) which correspond to stretching vibration of C—O—C and O—O bonds, respectively. In fact, PB has unsaturated C=C bonds in its structure. Although, a part of these unsaturated bonds undergo thermal cross-linking during HIPS synthesis, some unsaturation will remain in the PB rubber, even after severe thermal treatment during HIPS synthesis. These unsaturated C=C bonds are oxidated to C—O according to a

mechanism in Figure 8 after exposure to ozone,[38–40] which appears as two peaks in 1026–1100 and 1260 cm^{-1} regions in IR spectrum.

In the last part of this study, ozone treated HIPS/PB5 and HIPS/PH5 samples were placed in the oven, at a temperature of 200 °C for 10 h to test color stability of the polymers after exposure to both ozone and heat. Surprisingly, in the accelerated conditions, a drastic change in the color of HIPS/PB5 sample from white to brown was observed, while that HIPS/PH5 sample was not changed considerably (see Figure 9). This experiment is another proof for the good stability of HIPS/PH samples in outdoor applications.
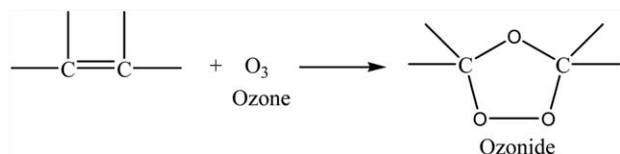
Our obtained characteristic results confirm higher impact strength and more durability of HIPS/PH samples which make this polymer prone for outdoor and high temperature applications.

CONCLUSIONS

In this study, new kind of high impact polystyrene, with poly1-hexene as rubber phase, was synthesized by radical polymerization of styrene and compared with conventional HIPS/PB one. Results showed that, by using poly1-hexene as rubber phase, Izod impact strength was improved up to 79% compared to HIPS with polybutadiene modifier. Durability of synthesized HIPS/PH samples toward ozonation and high temperatures was superior in compare with HIPS/PB ones. The morphology of HIPS/PB and HIPS/PH samples was observed using SEM pictures, which showed better dispersion of poly1-hexene phase, especially in higher rubber contents. Our obtained results presented new HIPS sample that in all studied aspects has superior properties compared with conventional HIPS with polybutadiene as dispersed rubbery phase.

Figure 8. Ozonization mechanism of unsaturated bond.

Figure 9. Color change of HIPS/PH5 and HIPS/PB5 samples after exposure to ozone and heat. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

2. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.;

Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.

3. Lin, Y.; Ng, K. M.; Chan, C. M.; Sun, G.; Wu, J. *J. Colloid Interface Sci.* **2011**, *358*, 423.

4. Meira, G. R.; Luciani, C. V.; Estenoz, D. A. *Macromol. Reac. Eng.* **2007**, *1*, 25.

5. Hu, K.; Cui, Z. K.; Yuan, Y.; Zhuang, Q.; Wang, T.; Liu, X.; Han, Z. *Polym. Compos.* **2016**, *37*, 1049.

6. Fischer, M.; Hellmann, G. P. *Macromolecules* **1996**, *29*, 2498.

7. Kavousian, A.; Nekoomanesh, M.; Leamen, J.; Penlidis, A. *J. Appl. Polym. Sci.* **2004**, *92*, 3368.

8. Hobbs, S. Y. *Polym. Eng. Sci.* **1986**, *26*, 74.

9. Peng, F. M. *J. Appl. Polym. Sci.* **1990**, *40*, 1289.

10. Zhang, J.; Wang, X.; Lu, L.; Li, D.; Yang, X. *J. Appl. Polym. Sci.* **2003**, *87*, 381.

11. Wang, Z.; Zhao, H.; Zhao, J.; Wang, X. *J. Appl. Polym. Sci.* **2010**, *117*, 2523.

12. Ziaee, F.; Nekoomanesh, M.; Arabi, H. *Iran. Polym. J.* **2008**, *17*, 379.

13. Tang, W.; Liu, B.; Liu, Z.; Tang, J.; Yuan, H. *J. Appl. Polym. Sci.* **2012**, *123*, 1032.

14. Utracki, L. A. *Commercial Polymer Blends* **1998**,

15. Shaw, S.; Singh, R. P. *J. Appl. Polym. Sci.* **1990**, *40*, 685.

16. Loureno, E.; Felisberti, M. I. *Eur. Polym. J.* **2006**, *42*, 2632.

17. Ivanciuc, O. *Curr. Comput. Aided Drug Des.* **2013**, *9*, 153.

18. Lin, F. C.; Stivala, S. S.; Biesenberger, J. A. *J. Appl. Polym. Sci.* **1973**, *17*, 1073.

19. Kurath, S. F.; Passaglia, E.; Pariser, R. *J. Appl. Polym. Sci.* **1959**, *1*, 150.

20. Nouri-Ahangarani, F.; Bahri-Laleh, N.; Nekomanesh Haghighi, M.; Karbalaei, M. *Des. Monomers Polym.* **2016**, *19*, 394.

21. Pearce, E. M. *J. Polym. Sci. Part C Polym. Lett.* **1987**, *25*, 233.

22. Bazvand, R.; Bahri-Laleh, N.; Nekoomanesh, M.; Abedini, H. *Des. Monomers Polym.* **2015**, *18*, 599.

23. Yee, E.; Lien, F. S.; Keats, A.; D'Amours, R. *J. Wind Eng. Ind. Aerod.* **2008**, *96*, 1805.

24. Lourenço, E.; Felisberti, M. I. *J. Appl. Polym. Sci.* **2008**, *110*, 1804.

25. Lin, F. C. *J. Appl. Polym. Sci.* **1973**, *17*, 1073.

26. Kurath, S. F.; Passaglia, E.; Pariser, R. *J. Appl. Phys.* **1957**, *28*, 499.

27. Zhang, S.; Zhu, S.; Feng, X.; Han, K.; Huan, Q.; Song, J.; Ma, Y.; Yu, M. *RSC Adv.* **2013**, *3*, 6879.

28. Alfarraj, A.; Bruce Nauman, E. *Polymer* **2004**, *45*, 8435.

29. Correa, C. A.; de Sousa, J. A. *J. Mater. Sci.* **1997**, *32*, 6539.

30. Bucknall, C. B.; Cote, F. F. P.; Partridge, I. K. *J. Mater. Sci.* **1986**, *21*, 301.

31. Sahin, T. l.; Sinmazcelik, T.; Sahin, S. *Mater. Des.* **2007**, *28*, 2303.

32. Mehdipour-Ataei, S.; Amirshaghaghi, A.; Bahri, N. *Eur. Polym. J.* **2006**, *42*, 2646.

33. Mehdipour-Ataei, S.; Bahri-Laleh, N.; Amirshaghaghi, A. *Polym. Degrad. Stabil.* **2006**, *91*, 2622.

34. Bahri-Laleh, N.; Seifali Abbas-Abadi, M.; Nekoomanesh - Haghighi, M.; Akbari, Z.; Tavasoli, M. R.; Mirjahanmardi, S. H. *J. Appl. Polym. Sci.* **2010**, *117*, 1780.

35. Mirmohammadi, S. A.; Imani, M.; Uyama, H.; Atai, M.; Teimouri, M. B.; Bahri-Lale, N. *Polym. Int.* **2014**, *63*, 479.

36. Mehdipour-Ataei, S.; Bahri-Laleh, N.; Rabei, A.; Saidi, S. *High. Perform. Polym.* **2007**, *19*, 283.

37. Mehdipour-Ataei, S.; Bahri-Laleh, N. *Polym. Adv. Technol* **2008**, *19*, 291.

38. Molander, G. A.; Cooper, D. J. *J. Org. Chem.* **2007**, *72*, 3558.

39. Ackman, R. G.; Retson, M. E.; Gallay, L. R.; Vandenheuvel, F. A. *Can. J. Chem.* **1961**, *39*, 1956.

40. Marston, D. J a G. *Chem. Soc. Rev* **2008**, *37*, 699.