

Experimental and theoretical approaches for structural and mechanical properties of novel side chain LCP-PP graft coproducts

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Abstract: The monomers p-biphenyloxybenzoylphenyl acrylate (BPCPA) and p-biphenyloxybenzoylphenyl methacrylate (BPCPMA) were synthesized by the reaction of p-acryloyloxybenzoyl chloride and p-methacryloyloxybenzoyl chloride with 4-hydroxybiphenyl, respectively, and polymerized by bulk polymerization in vacuum by using dicumyl peroxide. The graft copolymerization of the monomers onto polypropylene were carried out by bulk melt polymerization at 170 °C with various concentration levels of the monomers and the initiator in reaction mixtures. The content of monomers in their graft coproducts increased with monomer-initiator percentage in the reaction medium. The graft coproducts were characterized by several available experimental techniques including differential scanning calorimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, and mechanical testing. Moreover, the crucial changes in the mechanical performances pertaining to the polypropylene product were investigated by theoretical computations performed based on the density functional theory (B3LYP) with the standard 6-311++G(d,p) level of theory. According to obtained results, the mechanical properties of the graft coproducts deteriorated significantly with the grafting of the homopolymers due to the damage of the rate-dependent viscoelastic deformation or yielding, leading to enhancement in the surface energy values. At the same time, experimental evidence confirmed that the poly(BPCPA) materials exhibited much weaker secondary Van der Waals bonds than those in the poly(BPCPMA) products.

Key words: Liquid-crystalline polymers, graft copolymerization, calculations, mechanical properties, glass transition

1. Introduction

A popular approach in the hope of obtaining advanced properties in polymers has been combining thermotropic liquid crystalline polymers (LCPs) and thermoplastics (TPs) in blends.^{1–10} Thermotropic LCPs exhibit very good mechanical properties owing to their stiff molecular backbones,¹¹ their relative ease of orientation, and their ability to retain this orientation for up to several minutes in the melt state.^{12,13} The interest in blending of LCPs with TPs arises from the findings that the LCP component often forms a fibrillar structure under appropriate processing conditions, and these fibrils reinforce the thermoplastic matrix in an analogous manner to that of fiber-reinforced composites.¹⁴ The reinforcement effect originates in the larger aspect ratio of the LCP fibrillar phase and load capacity of the LCP fibrils.¹⁵ In addition, because of their intrinsic low melt viscosities, the LCPs can serve as a processing aid by reducing the melt viscosity of the blends, thus improving

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the processability.¹⁶ However, the poor interfacial adhesion between the dispersed LCP phase and the TP matrix phase is the most important shortcoming, affecting the ability of LCPs to reinforce thermoplastics. Thus, in order to achieve effective reinforcement, the compatibility improvement of the components in the blends, characterized by reduced interfacial energy, finer dispersions, stability against segregation, and increased adhesion, has been attempted in a number of studies.^{17–23} In another approach, Lee et al. introduced silica fillers to a polypropylene (PP)/LCP blend to promote the deformability and fibrillation of the LCP phase.²⁴ With the presence of both the nanosilica particles and LCP reinforcements, the LCP/PP/SO₂ system possessed dual reinforcements and exhibited the highest strength and modulus among the composites.

The very strong nature of carbon-carbon bonds is not realized in the polymer because of the random entanglements of individual chains of PP. Any process that leads to orientation and alignment of the polymer chains may strongly result in preferable physical properties. Accordingly, the strength and modulus of this type of thermoplastics can be improved in the orientation direction by providing polymer chains organized into regular structures and reducing the degree of molecular randomization. In the reinforcement of PP with LCPs, besides the mentioned fiber-reinforcing effects of the LCP fibrils, as with the transfer of stress from the matrix to the fibrils, the fibrils may also additionally lead somewhat to a propensity in alignment and extension of entangled PP chains in the flow direction, which may presumably result in an increase in the mechanical properties. In one of our previous studies, as an alternative study on LCP-PP combinations,²⁵ side chain LCP chains were constituted as graft units on PP chains by graft copolymerization of p-acryloyloxybenzoic acid and p-methacryloyloxybenzoic acid, which were reported to exhibit mesomorphic behavior when polymerized, to improve the properties of PP by the aid of the presumed properties of LCPs.^{26,27} Very considerable improvements in tensile strength and modulus were achieved in the graft copolymers. With the same line of reasoning, high density polyethylene has been previously reinforced by graft copolymerization of p-benzophenoneoxycarbonylphenyl acrylate.²⁸ Besides the remarkable improvements in the tensile properties (38% in tensile strength and 67% in Young modulus), the grafting also led to significant increases in the crystalline melting temperature of the material (from 131 °C to 132–138 °C), in consistence with the graft content in the coproducts. The developments were explained by the advances in the orientation and alignment of PE chains, conducted by greater chain mobility in the larger basal area of the orthorhombic unit cell and intensifying cohesive forces arising from the glassy nematic structured graft units.

p-Biphenyloxy carbonylphenyl acrylate (BPCPA) and p-biphenyloxy carbonylphenyl methacrylate (BPCPMA) were polymerized by free radical initiation by Sainath et al.²⁹ In their study, the mesomorphic properties of the polymers, poly(BPCPA) and poly(BPCPMA), were investigated, and the polymers were reported to exhibit a smectic phase in the temperature ranges of 192–265 °C and 160–255 °C, respectively. There does not exist any work on the blends or copolymers of poly(BPCPA) and poly(BPCPMA) with a TP material to the knowledge of the researchers.

In this work, the announced side chain LCP molecules of the monomers BPCPA and BPCPMA were formed as graft units on isotactic PP backbones by graft copolymerization of these monomers. The synthesis, polymerization, and graft copolymerization of these monomers onto PP are presented. The tensile and impact behavior of the graft coproducts were investigated, and the thermal and decomposition behavior of the polymers poly(BPCPA) and poly(BPCPMA) and the graft coproducts were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Results and discussion

The graft copolymerization results are given in Table 1 in detail. Not soluble in any conventional solvent, the homopolymer poly(BPCPA) could not be extracted by solvent washings from its graft coproducts. In this respect, the amount of grafting could not be determined gravimetrically, and the experimental results were recorded as the total percentage of the polymer poly(BPCPA) in the products, being composed of the grafted units and homopolymer in the products. Nevertheless, though the extent of grafting could not be estimated, the completely homogeneous structure and absence of phase separation in the products, deduced from scanning electron microscopy (SEM) studies of the tensile and impact fractured surfaces of the samples, allow the conclusion that a considerable percentage of poly(BPCPA) is present as grafted units in the products. In a case other than grafting, the different nature of the graft unit from the PP with polar groups would virtually have resulted in a phase separation. As for poly(BPCPA), the poly(BPCPMA) contents in the coproducts were also totally recorded as the percentage of poly(BPCPMA) present either as homopolymer or as graft units, presented in Table 1. Although the homopolymer poly(BPCPMA) was soluble in N-methyl-2-pyrrolidone, in contrast to poly(BPCPA), it was not extracted from the products. On the other hand, the grafted poly(BPCPA) and poly(BPCPMA) units in their graft coproducts acted as the effective compatibilizers between the PP and ungrafted poly(BPCPA) and poly(BPCPMA) units that were present as homopolymers in the products, as revealed in SEM studies.

Table 1. The content of polymer (poly(BPCPA)/poly(BPCPMA)) in the graft coproducts with concentration of monomer (BPCPA/BPCPMA) in the reaction mixture.

% monomer in rxn mixture	5	10	15	20	30	40
% poly(BPCPA) in products	3.7	8.8	13.8	19.4	29.9	39.4
% poly(BPCPMA) in products	3.6	7.3	11.2	15.2	24.7	34.5

Regarding the formation of the polymers, poly(BPCPA) and poly(BPCPMA) grafted onto the PP and ungrafted present as homopolymer in the products. The percentage of conversion increased apparently with the concentration of monomer in the reaction mixture owing to the increase of monomer-DCP percent in the reaction mixture as given in Table 1 and Figure 1. According to the results obtained, it is suitable to say that the percent conversion was found to be lower at the low concentrations of monomer due to both the direct reactions between PP chains and radicals formed by the decomposition of the DCP and the sterical hindrance between the radicals on the PP chains and the monomer molecules.

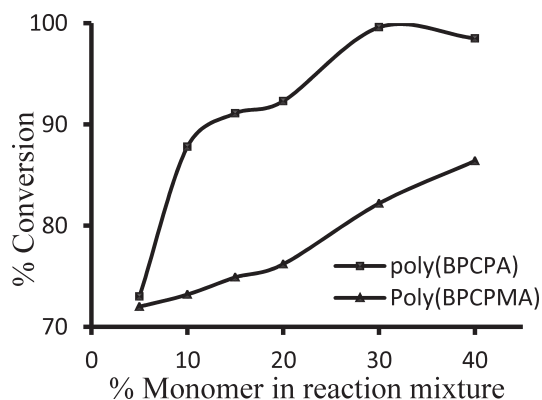


Figure 1. The dependence of percent conversion on the concentration of monomer in the reaction mixture.

Accordingly, at high concentrations, the effect was presumably weakening as a consequence of the high probability of direct reactions between initiator radicals and monomers, and thus the conversion increased. On the other hand, the conversion in the poly(BPCPA) remained above that in poly(BPCPMA) due to the sterical hindrance, arising from the presence of the methyl group in the BPCPMA product

2.1. Characterization of the products by DSC and TG-IR system

Differential scanning calorimetry analyses were carried out to find out the effect of graft copolymerization of BPCPA and BPCPMA onto PP on the thermal behavior of the graft coproducts. While decrements were observed in the melting temperature of PP (164 °C) in the poly(BPCPA)-PP coproducts, no appreciable change was recorded in the coproducts of poly(BPCPMA)-PP (Figure 2, lines c and d). Melting at 157.7 °C was recorded in the product containing 3.65% poly(BPCPA). On the other hand, no endotherm that could be attributed to the melting of poly(BPCPA) or poly(BPCPMA) graft units was detected in any thermogram of graft coproducts as neither was in those of the homopolymers, while melting was reported to be at 195 °C and 162 °C, respectively, by Sainath et al.²⁹ The endotherms observed at the value of about 348 °C and 359 °C in the thermogram of poly(BPCPA) and at about 284 °C in poly(BPCPMA) indicated the decompositions of the polymers (Figure 2, lines a and b).

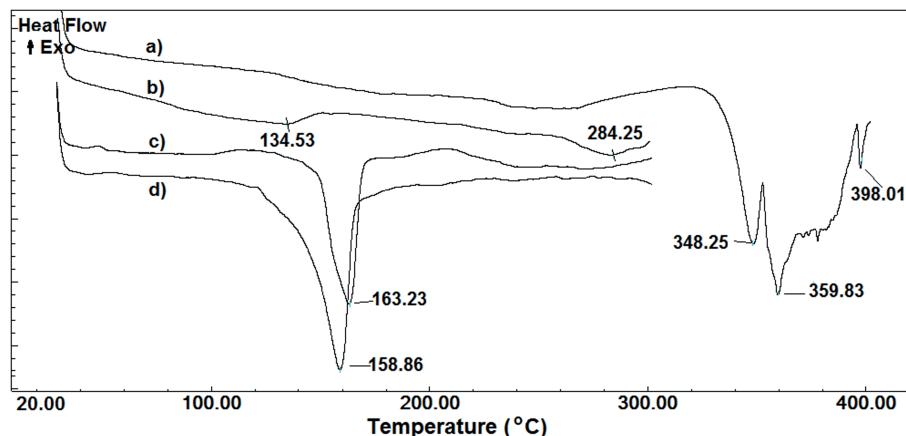


Figure 2. DSC thermograms of the homopolymers, a) poly(BPCPA) and b) poly(BPCPMA), and of the graft coproducts with c) 11.2% poly(BPCPMA) and d) 29.88% poly(BPCPA).

In order to comprehend the optimum conditions at which the products are stable for processing, TGA of the homopolymers poly(BPCPA) and poly(BPCPMA) and of the coproducts containing 39.4% poly(BPCPA) and 34.5% poly(BPCPMA) was carried out in both air and N₂ atmosphere. The analyses carried out in N₂ atmosphere showed that very slight weight loss in poly(BPCPA) started to be seen around 250 °C. In the poly(BPCPMA) sample the initial losses were recorded at about 240 °C. The expressive weight losses due to decomposition, but with a slow rate, commenced at about 275–280 °C. Fast and significant losses prevailed especially after 300 °C and continued to 575–600 °C in both polymers. The decomposition products were also analyzed by Fourier transform infrared spectroscopy (FT-IR) combined with the thermogravimetric analyzer. In the FT-IR spectra similar absorption bands, which were weak and imperceptible at early stages of the decompositions, were commonly observed throughout the heating. Indicative and significant bands were markedly detected when the decompositions were fast, especially at temperatures higher than 300 °C. They

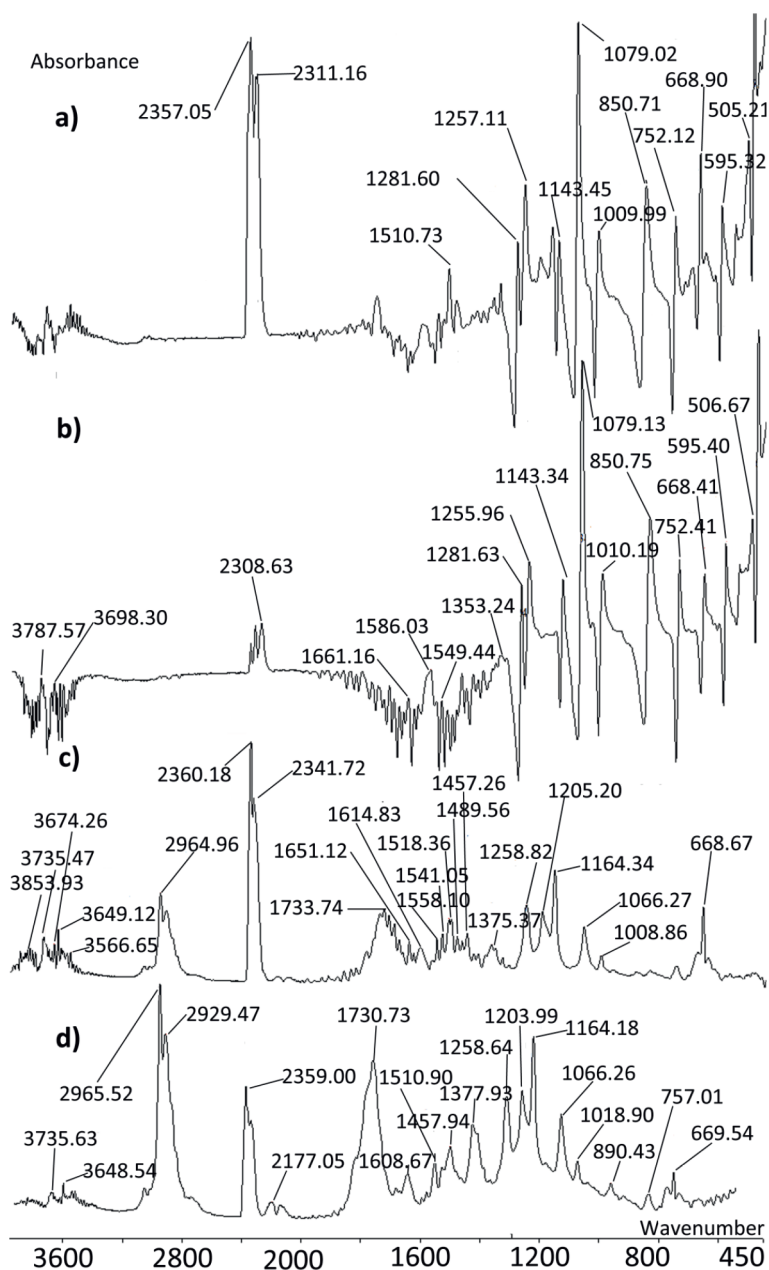


Figure 3. The FT-IR spectra of the decomposition products formed during heating: a) poly(BPCPA) at 364 °C in N₂ atmosphere, b) poly(BPCPMA) at 364 °C in N₂ atmosphere, c) the coproduct with 39.4% poly(BPCPA) at 375 °C in air, d) the coproduct with 34.5% poly(BPCPMA) at 350 °C in air, with 10 °C/min.

weakened again after about 500 °C. The formation of carbon dioxide as a decomposition product started to appear at early stages of decompositions, detected with the C=O stretching bands at about 2357 and 2311 cm⁻¹, and was observed almost in all stages of the decompositions. The spectra, most of the bands of which were commonly observed in both polymers, indicated a band at around 3649 cm⁻¹ assigned to phenolic O-H stretching vibrations, the formation and assignment of which were reported in a similar analysis,³⁰ and bands at about 1606 and 1510 cm⁻¹ seemingly due to aromatic C=C stretching vibrations. The bands at about

1281, 1257, 1143, 1079, and 1010 cm^{-1} were attributed to C-O stretching vibrations. The bands at about 850, 752, and 668 cm^{-1} probably correspond to C-H out-of-plane bending vibrations (Figure 3, lines a and b). In air atmosphere, on the other hand, initial weight loss started to be seen at relatively lower temperatures in the former homopolymer, at about 235 °C, and at higher temperatures, around 270 °C, in the latter. In the FT-IR spectra of the decomposition products, although some absorption peaks were commonly observed as those observed in nitrogen atmosphere, numerous peaks concentrated around 1700 and 1540 cm^{-1} , which were difficult to interpret, were observed. The formation of carbon dioxide was identically detected with peaks at about 2360 cm^{-1} in almost every stage of decomposition in both polymers.

TGA of the graft coproducts involving 39.4% poly(BPCPA) and 34.5% poly(BPCPMA) carried out in N_2 atmosphere demonstrated that the first weight loss started at earlier temperatures compared to the homopolymers, around 220 °C in the former and at about 240 °C in the latter coproduct. The FT-IR spectra additionally displayed the absorption bands, besides those similarly observed in the spectra of the homopolymers, at about 2966 and 2929 cm^{-1} , attributed to the stretching vibrations of CH_3 and CH_2 groups, and at about 1750 and 1730 cm^{-1} , assigned to stretching vibrations of the C=O group. In air atmosphere, while a similar decomposition trend was observed in the former, the initial losses in the latter were recorded at earlier temperatures, around 225 °C. The FT-IR analysis of the decomposition products displayed relatively broad bands in the spectra compared to those recorded in nitrogen atmosphere. A number of bands that were very hard to interpret were observed in the spectra of the poly(BPCPA)-PP coproduct (Figure 3, lines c and d).

The results revealed that the degradations in the products proceeded predominantly by the breaking up and decomposition of side groups of poly(BPCPA) and poly(BPCPMA) chains, giving mainly carbon dioxide, aromatic, and vinylic groups. Methyl and methylene groups were also detected in the decompositions of the coproducts, apparently due to the breaking up of PP chains. Relatively complex mechanisms prevailed in the decompositions in air atmosphere.

2.2. Mechanical properties of the graft coproducts

The mechanical properties of the graft coproducts were studied to find out the effect of the graft copolymerization of BPCPA and BPCPMA onto PP. Although considerable improvements were achieved in elastic modulus, tensile and impact strength of the coproducts decreased with loss of yield stress and loss in percent elongation, and the breaking of the products showed their brittle nature.

Stress-strain curves of the graft coproducts are given in Figures 4 and 5 in detail. It is visible from the figures that although the virgin PP material showed a great extent of cold drawing or orientation, we did not observe any yield stress behavior in the grafted polymers, and percent elongation consistently diminished with the graft content. Thus, the surface energy values belonging to the coproducts increase consistently and each coproduct prepared exhibits perfectly the brittle nature (considerable break of the bonds in the structure). In other words, the grafting of the homopolymers onto the polypropylene deteriorates the molecular structure of polymer chains, leading to the damage of the rate-dependent (large-scale) viscoelastic deformation or yielding. It is another probable result obtained from the present work that more crack growth by chain scission (known as the fracture on the atomic level) may appear in new systems as a result of either the contraction of the lattice structure or the decrement of the lattice absorption energy along the crack propagation. In more detail, only the coproduct prepared with 3.7% poly(BPCPA) broke just at the beginning of plastic deformation due to the considerable shrink of the lattice structure. As is well known, there are two main bonds involved

in the mechanical response: covalent bond between the carbon atoms and secondary Van der Waals forces between molecule segments. The secondary bonds often play an important role in the deformation (fracture) mechanisms.³¹ Based on the experimental results, it is unambiguous that the secondary Van der Waals bonds in the poly(BPCPA) material are much weaker than those in the poly(BPCPMA) product as well as the primary bonds in the system.³¹ On the other hand, the tensile strength parameter is found to decrease with the enhancement of the homopolymer content level. In fact, the grafting of the poly(BPCPA) causes more damage to the PP structures. The decreasing trend of the coproducts started at 32.2 MPa belonging to the ultimate tensile strength of virgin PP and continued until the plateau of 13–14 MPa, where the strengths of the coproducts produced with about 14% poly(BPCPA) and higher percentages of poly(BPCPA) were observed. Conversely, in the coproducts of poly(BPCPMA), the decrement trend towards about 21 MPa was attributed to the coproduct comprising about 25% poly(BPCPMA) as given in Figures 6a and 6b. This is related presumably to the differences in the degree of polymerization.³² Useful findings from the ultimate tensile strength measurements show that the differentiation between the molecular weight or polydispersity in the systems considerably influences the mechanical performance of the polypropylene.³³ In contrast to the decreasing trend of tensile strength, the modulus values for both the coproduct classes were found to increase with the contents, reaching a local maximum value of 1125 MPa for the coproduct prepared with 14% poly(BPCPA) and 1071 MPa for the coproduct containing 15% poly(BPCPMA) (Figures 7a and 7b). It is reasonable to conclude that the coproducts produced by poly(BPCPA) obtain relatively higher modulus parameters as a consequence of the restriction of the molecular motions (contraction of the lattice structure). Moreover, it is another important point deduced from the work that the maxima were followed by a decreasing trend towards the value of about 1000 MPa. Regardless, the moduli each were observed to be higher as compared to the modulus value of virgin PP (635 MPa). This is in accordance with the fact that the stiffness pertaining to the materials was effectively increased by the graft copolymerizations.

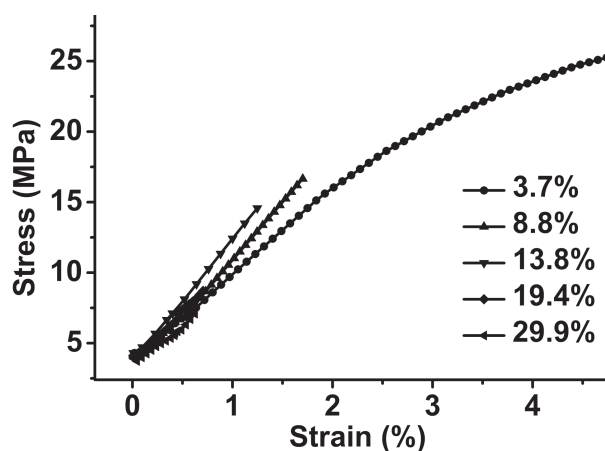


Figure 4. Stress–strain curves of PP and the poly(BPCPA)-PP graft coproducts with varying percentages of poly(BPCPA).

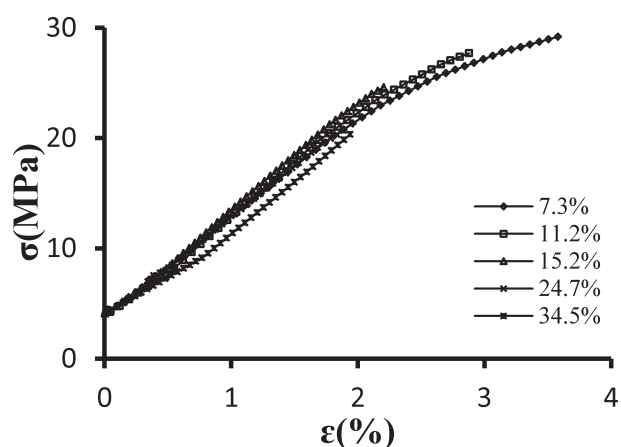


Figure 5. Stress–strain curves of the poly(BPCPMA)-PP graft coproducts with varying percentages of poly(BPCPMA).

The graft copolymerizations of the monomers onto the PP material were expected to result in the improvements of the mechanical characteristics (especially tensile strength) due to the regular and organized structure of side chain LCPs.²⁸ In other words, the grafted monomers led to development of the orientation

and alignment in the polymers (chain disentanglement) besides the probable fiber reinforcement effect noted.¹⁴ Hence, the mechanical performances belonging to the coproducts enhanced considerably, similar to the significant improvements in our previous work.²⁵ In the current work the graft copolymerizations, however, gave rise to lower tensile properties in the coproducts. This is in correspondence to amorphous characteristics of the homopolymers and graft units prepared.

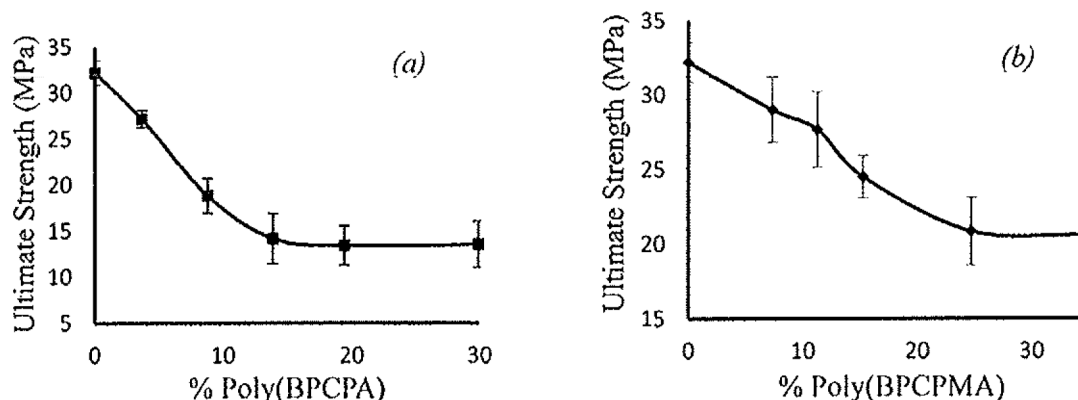


Figure 6. The dependence of ultimate tensile strengths of a) poly(BPCPA)-PP graft coproducts on the content of poly(BPCPA) and b) poly(BPCPMA)-PP graft coproducts on the content of poly(BPCPMA).

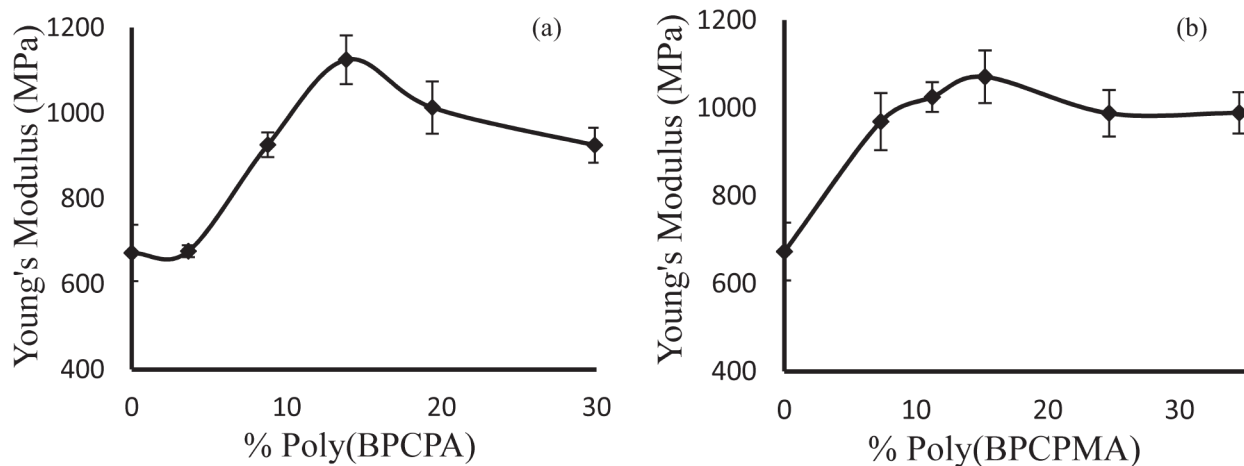


Figure 7. The dependence of Young's moduli of a) poly(BPCPA)-PP graft coproducts on the content of poly(BPCPA) and b) poly(BPCPMA)-PP graft coproducts on the content of poly(BPCPMA).

The variation of impact strength with respect to poly(BPCPA) and poly(BPCPMA) content in the graft coproducts is given in Figures 8a and 8b in detail. The impact strength values of the graft coproducts were found to be lower as compared to that of the virgin PP. The parameter remained at about 15–17 kJ/m² in the coproducts of poly(BPCPA) while the strengths in the latter coproducts dramatically decreased with the increment of the poly(BPCPMA) concentration and in fact reduced towards the value of 6–7 kJ/m² for the coproducts prepared with 24.7%–35.4%. All the parameters obtained are noted to be much lower than that of the pure PP (48.8 kJ/m²). This is another conformation that the graftings severely increased the brittle nature of the PP material. What stands out clearly here is that the enhancement of the brittleness in the coproducts

with poly(BPCPA) and poly(BPCPMA) contents presumably resulted from the systematic decrement in the molecular weight of grafting units. Namely, the impact energy loaded rapidly onto a certain area of the test samples along with the impact test might not be delocalized effectively in a short time due to lower molecular weight of the grafting units. As a result, the coproducts exhibit more and more brittle nature with the increment of the graft concentration level in the system. The increased brittleness was perfectly displayed with the aid of the loss in percent elongation and missing yield stress inferred from the tensile tests. It is another probable result evaluated from this work that the brittleness of the products was sensitively dependent upon the glass transition temperature values. For example, the glass transition value was recorded to be 77 °C for the coproduct of poly(BPCPMA), being comparatively higher for the delocalization of impact energy, since the tests were carried out at room temperature. Thus, it is fair to conclude that the relatively high glass transition temperature of the graft units may have cooperated with the molecular weight factor as revealing the facile failure of the products throughout the mechanical tests. This is one of the most striking discussions extracted from this paper.

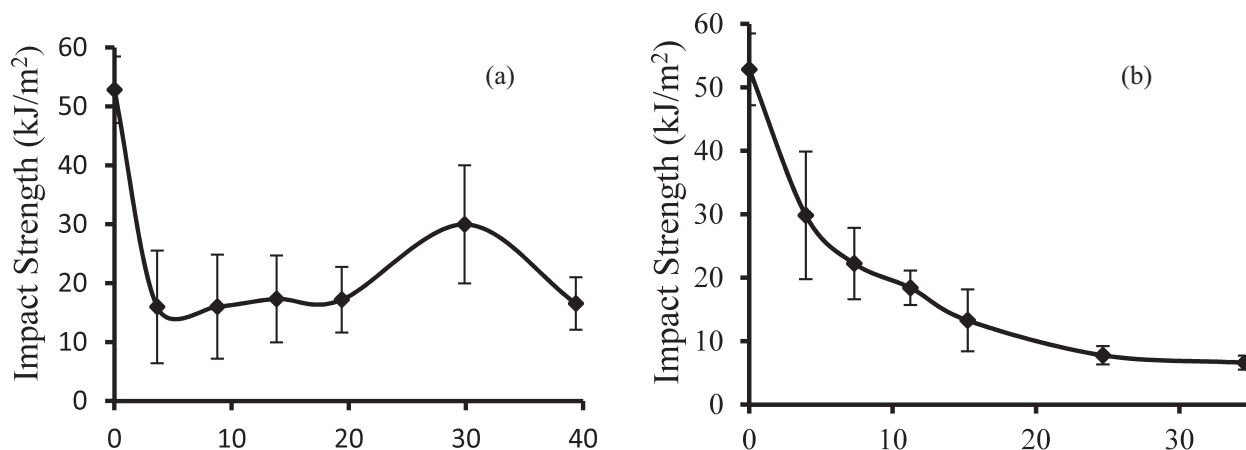


Figure 8. The dependence of impact strengths of a) poly(BPCPA)-PP graft coproducts on the content of poly(BPCPA) and b) poly(BPCPMA)-PP graft coproducts on the content of poly(BPCPMA).

Additionally, the theoretical calculations performed based on the density functional theory (B3LYP) with the standard 6-311++G(d,p) calculation level enable us to explain why the mechanical performances belonging to the PP product degrade with the grafting mechanism of homopolymers. For this aim, only statistical thermodynamic energies and functions as regards total, thermal, and zero-point vibrational energy, heat capacity, entropy, and rotational constants pertaining to the monomers of BPCPA and BPCPMA are determined and the theoretical evidence achieved is numerically tabulated in Table 2. Prior to the significant discussions, it is to be mentioned here that the less self-consistent field (SCF) energy and dipole moment a material exhibits, the more stable a structure it has. In this respect, it can directly be said that the monomer of BPCPMA obtains much more stable structures. Moreover, it is apparent from the table that the other crucial computations belonging to the BPCPMA monomer are found to be slightly greater as compared to those of the BPCPA monomer. Naturally, the former product is a bit more stable (lower energy) than the latter one. Consequently, the grafting conducted by the BPCPMA monomer onto a polymer exhibits more balanced behaviors as compared to the features of the grafting exerted by the monomer of BPCPA. As for the last parameter, dipole moment is received as a generalized measure of the charge densities (nonuniform distribution of charges on various atoms or polar nature) and bond properties in a product. Namely, the dipole

moment enables the researchers to easily describe the electronic property. At the same time, the intermolecular interactions regarding Van der Waals type and dipole–dipole forces can be examined completely.³⁴ Solubility of the product in the polar solvents and the capacity of polarizing other atoms or molecules can also be discussed by means of the dipole moment value. In the present study, the dipole moment values related to the BPCPA and BPCPMA monomers are calculated to be about 4.9979 and 3.5356 D, respectively (Table 2). According to the result obtained, BPCPA exhibits a more polar nature with nonuniform charge distributions on the atoms as compared to BPCPMA. Thus, the theoretical computations of dipole moment rely on the fact that the grafting with the BPCPA homopolymer gives more and more damage than that with the BPCPMA homopolymer. The lattice structure of the graft coproducts prepared with the BPCPA homopolymer shrinks much more and so the lattice absorption energy diminishes through the crack propagation. This result is also supported by the experimental evidence of other parts of the study.

Table 2. Theoretically calculated energies (a.u.), zero-point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K⁻¹), heat capacities (cal mol⁻¹ K⁻¹), thermal energies (kcal mol⁻¹), and dipole moment (D).

Parameters	BPCPA	BPCPMA
SCF energy	-1148.81497429	-1188.22626735
Zero-point vibrational energy	201.48267	220.71404
Rotational constant	0.99994	1.11804
	0.05263	0.04498
	0.05117	0.04393
Entropy		
Total	138.241	172.100
Translational	43.402	43.521
Rotational	36.033	36.230
Vibrational	58.807	92.350
Heat capacity		
Total	78.698	89.361
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	72.737	83.400
Total (thermal) energy		
Total	213.007	253.364
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	211.230	233.586
Dipole moment		
μ_x	-4.3037	1.7251
μ_y	1.7930	-2.7655
μ_z	-1.8006	-1.3715
μ	4.9979	3.5356

2.3. SEM analysis of the products

The tensile and impact fractured surfaces of the graft coproducts were investigated by SEM to resolve the morphology of the fracture surfaces. The SEM photographs demonstrated in Figures 9–12 show that the coproducts displayed no phase separation although the graft units of poly(BPCPA) and poly(BPCPMA) with

polar groups in their structures were essentially different from PP in nature. Their structures were found to be completely homogeneous. Meanwhile, it should be noted here that the coproducts used in all the characterizations and tests involved the ungrafted poly(BPCPA) and poly(BPCPMA) as well as the grafted units in their coproducts. The absence of phase separation and the completely homogeneous structure of the products confirmed the graft copolymerization of BPCPA and BPCPMA onto PP. The fractographs additionally indicated that the grafted units (poly(BPCPA)-g-PP and poly(BPCPMA)-g-PP) acted as compatibilizers between the PP and ungrafted units, poly(BPCPA) and poly(BPCPMA), respectively. In the absence of the compatibilization activity of the grafted units, the phase separation would have been inevitably observed owing to the presence of the essentially different structures in the components.

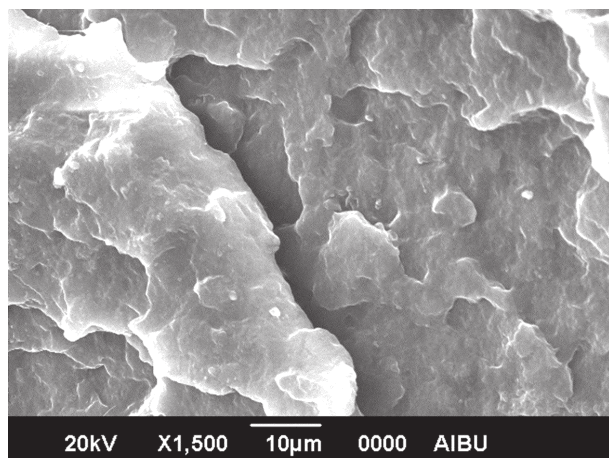


Figure 9. SEM photograph of the graft coproduct with 3.65% poly(BPCPA), tensile test.

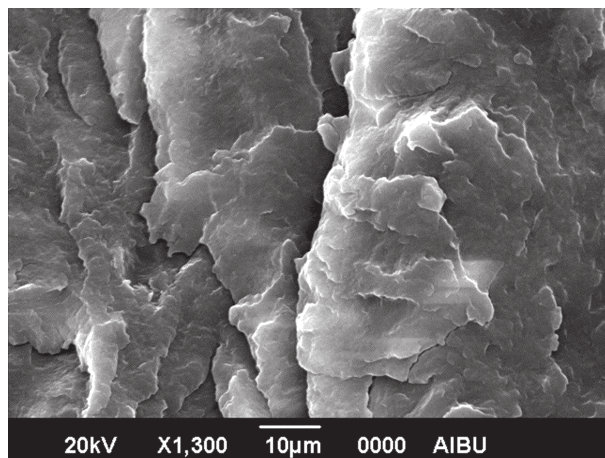


Figure 10. SEM photograph of the graft coproduct with 13.84% poly(BPCPA), impact test.

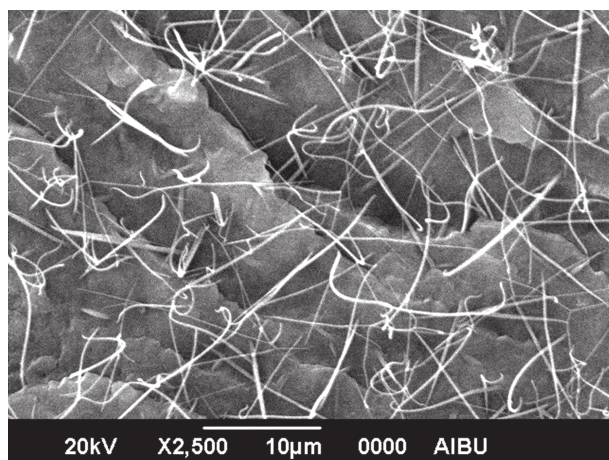


Figure 11. SEM photograph of the graft coproduct with 15.23% poly(BPCPMA), impact test.

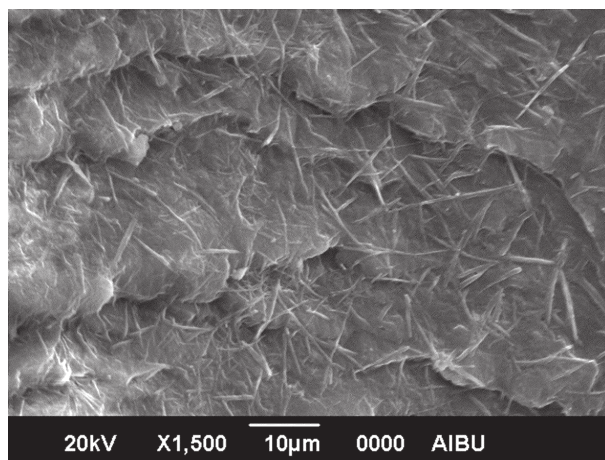


Figure 12. SEM photograph of the graft coproduct with 15.23% poly(BPCPMA), tensile test.

In general, brittle fracture was observed in poly(BPCPA) coproducts. Fibrillation or extension was almost not seen in the impact and tensile fractographs in any of the poly(BPCPA) graft coproducts, even at lower percentages (Figures 9 and 10). The microcracks, holes, and openings among the layers encountered in

the photographs indicated that the fractures proceed with brittle fracture and the products exhibit the brittle nature, being also revealed in the mechanical tests. However, it is noteworthy that the material did not present any phase separation during the SEM analyses.

Brittle nature was also observed in poly(BPCPMA) coproducts as depicted in Figures 11 and 12. It is visible from the figures that, in contrast to the poly(BPCPA) coproducts, some extent of ductility was detected in the samples throughout both the tests. In impact tests, the fibrillations were found to be thinner fibrils, emerging from the specimen surfaces of the layers besides microcracks and openings (Figure 11). In addition to the thin fibrils, the short, bulky, and thick fibrillations and extensions were detected in the tensile tests. Nevertheless, the major fracture is consistent with the brittle fracture as revealed from the microcracks, voids, and holes in the fractographs (Figure 12).

In an exhaustive study, we investigate the thermal and morphological characteristics and the variation of the mechanical performance pertaining to the PP grafted with poly(BPCPA) and poly(BPCPMA) by means of thermogravimetry/differential scanning calorimetry (TG/DSC), FT-IR spectroscopy, SEM, and mechanical testing. The main aim of the study is to improve the mechanical characteristics as regards the modulus, impact, and tensile strength parameters of the PP with the grafting mechanism. Furthermore, the remarkable conclusions from the current work are as follows:

- The DSC analyses showed that the polymers, poly(BPCPA) and poly(BPCPMA), exhibit an amorphous character. The thermograms of the polymers did not present any heat flow, implying the melting of crystalline domains or isotropic transitions.
- The TG-IR studies revealed that the degradations in the products proceeded predominantly by the breaking up and decomposition of side groups of poly(BPCPA) and poly(BPCPMA) chains giving mainly carbon dioxide, aromatic, and vinylic groups.
- The mechanical tests of the graft coproducts revealed that the graft copolymerization of the monomers onto the PP significantly deteriorates the molecular structure of polymer chains, resulting in the damage of the rate-dependent viscoelastic deformation or yielding. This is attributed to the increment in the surface energy values pertaining to all the coproducts where the brittle nature plays a dominant role. Besides, the mechanical performance tests show that the poly(BPCPA) materials obtain much weaker secondary Van der Waals bonds than those in the poly(BPCPMA) product.
- Additionally, the tensile properties are noted to degrade with the graft content level as a consequence of the amorphous characteristics of the homopolymers and graft units prepared. Namely, the probably lower molecular weight of the graft units with their amorphous nature makes tensile strength parameters reduce rapidly. On the other hand, the graftings resulted in effectively increased stiffness in the material, as revealed from the increased modulus parameters with the graft contents.
- The changes of the impact strength versus poly(BPCPA) and poly(BPCPMA) contents in the graft coproducts verify that the grafting mechanism leads to harshly increase the brittle nature in the PP material. This is in association with the effective delocalization problems that appeared in the samples due to lower molecular weight of the grafting units. The glass transition temperature values enable us to explain the increment in the brittleness with the content.
- At the same time, the theoretical approaches based on the density functional theory (B3LYP) with the standard 6-311++G(d,p) level of theory reveal that the mechanical performances pertaining to the PP

product diminish with the grafting mechanism of homopolymers. In fact, the computations including the statistical thermodynamic energies and functions confirm that the monomer of BPCPMA obtains much more stable structures as compared to that of BPCPA. The grafting performed by the BPCPMA monomer, in this respect, exhibits more balanced features than the behavior of the grafting performed by the monomer of BPCPA.

- As for the dipole moment calculations, it was found that the monomer of BPCPA shows a more polar nature with nonuniform charge distributions on the atoms. Hence, the grafting with the BPCPA homopolymer leads to considerable contraction (restriction of the molecular motion) of the lattice structure of the polypropylene. Namely, the lattice absorption energy (more crack growth) severely retrogrades along with crack propagation due to the presence of lattice damages, as supported by the experimental evidence of other parts.
- The brittle nature belonging to the coproducts was also revealed in SEM studies. The coproducts of poly(BPCPMA) additionally displayed some ductility. In contrast, almost no fibrillation or extension was seen in any of the poly(BPCPA) graft coproducts.
- In conclusion, the poly(BPCPMA) and especially poly(BPCPA) presented as homopolymer and grafting units in the products are able to improve the mechanical performances belonging to the polypropylene.

3. Experimental

3.1. Materials

Granular isotactic PP (coded as MH 418), a product of Petkim (Aliğa, Turkey), was used in the preparation of powder PP. The PP granules were dissolved in boiling xylene and precipitated by ethanol. The precipitate was then ground by cooling in liquid nitrogen.

The monomers, BPCPA and BPCPMA, were prepared in three steps. In the first step, p-acryloyloxybenzoic acid (ABA) and p-methacryloyloxybenzoic acid (MBA) were synthesized by condensation reaction of p-hydroxybenzoic acid with corresponding acid chlorides in alkaline medium as described previously.²⁹ The products, ABA and MBA, were purified by repeated recrystallizations from acetone. In the second step, p-acryloyloxybenzoyl chloride (ABC) and p-methacryloyloxybenzoyl chloride (MBC) were prepared by refluxing the ABA or MBA with thionyl chloride in the presence of a trace amount of dimethyl formamide for 5–6 h. The products, ABC and MBC, were recrystallized from CH₂Cl₂ in which the solubilities were decreased by adding hexane until cloudiness. In the last step, BPCPA was synthesized by refluxing an equimolar solution of ABC and p-hydroxybiphenyl in xylene for about 3–4 days. The product, BPCPA, was purified by repeated recrystallizations from xylene and acetone. The yield was above 55%. The refluxing of MBC and p-hydroxybiphenyl, however, was not successful for BPCPMA, and it was prepared by condensation reaction of p-hydroxybiphenyl with MBC in ethyl methyl ketone in the presence of triethylamine as described.²⁹ In all steps, the structures of the products, ABA, MBA, ABC, MBC, BPCPA, and BPCPMA, were confirmed by FT-IR and ¹H-NMR techniques. The FT-IR spectrum of BPCPA indicated the bands at 1747 and 1735 cm⁻¹ (C=O of ester groups), at 1636 cm⁻¹ (C=C), at 1601 and 1502 cm⁻¹ (C=C of aromatic groups), at 980 and 906 cm⁻¹ (vinylic C-H), at 762 and 808 cm⁻¹ (aromatic C-H), and at 696 cm⁻¹ (aromatic C=C). The FT-IR spectrum of BPCPMA demonstrated the bands at about 2980 cm⁻¹ (CH₃), and the bands at 1739, 1730, 1636, 1603, 1500, 950, 941, 760, and 810 cm⁻¹ and at 690 cm⁻¹, similarly assigned as those for BPCPA. DSC melting temperatures of

BPCPA and BPCPMA were determined as 135 °C and 165 °C, respectively, in N₂ atmosphere with a heating rate of 10 °C/min. Their ¹H-NMR spectra are presented in Figures 13a and 13b.

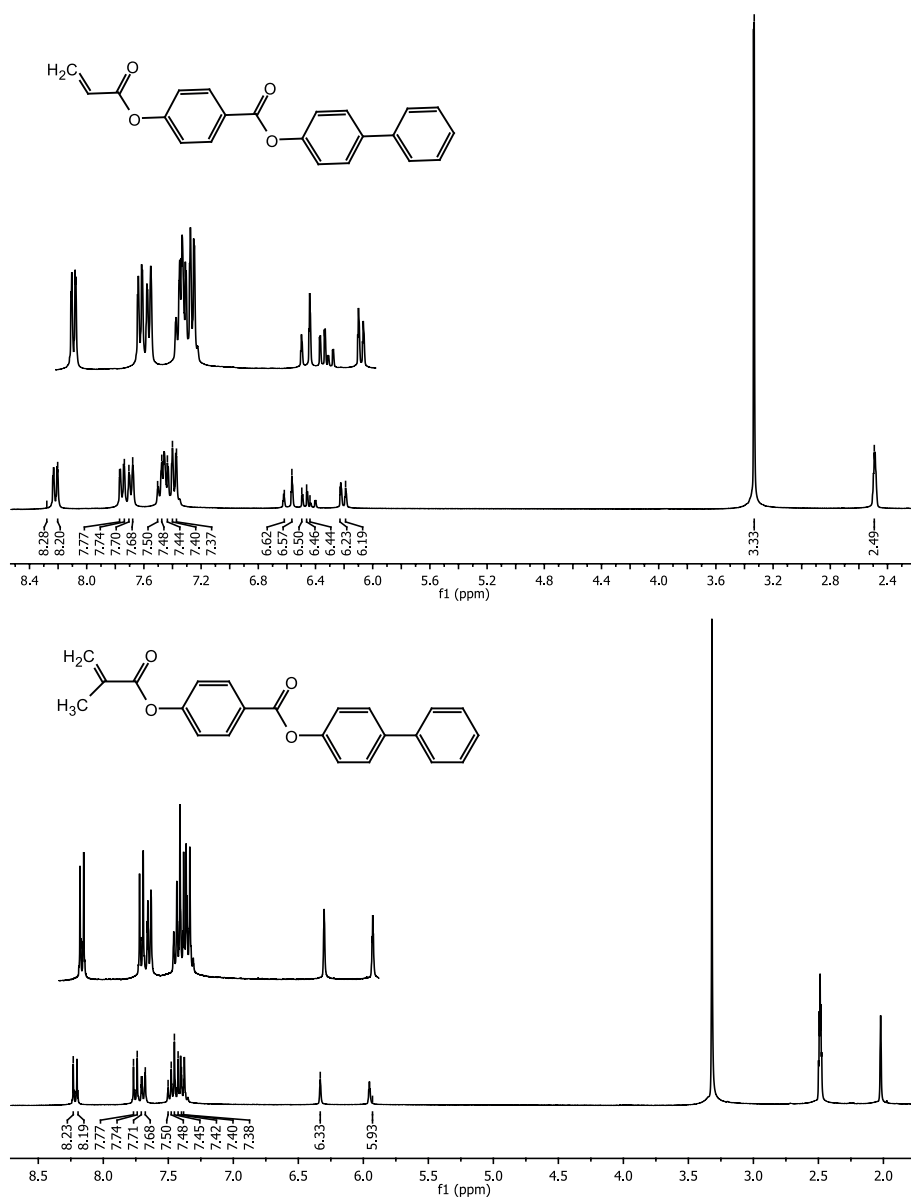


Figure 13. ¹H-NMR spectra of a) BPCPA and b) BPCPMA.

3.2. Polymerization and thermally induced graft copolymerization of BPCPA and BPCPMA onto PP

The monomers, BPCPA and BPCPMA, were polymerized by bulk polymerization by using dicumyl peroxide (DCP; 2% for BPCPA and 3% for BPCPMA, with respect to weight of the monomer) in vacuum at constant temperature, the former at 150 °C and the latter at 170 °C, for 40 min of reaction time. The polymer yield was above 95% for the former and at about 90% for the latter. The poly(BPCPA) could not be dissolved in any conventional solvent, but poly(BPCPMA) was soluble in N-methyl-2-pyrrolidone.

The graft copolymerization experiments were then carried out as follows: the reaction mixtures prepared by mechanical mixing of the powder PP, the monomer (BPCPA or BPCPMA) at different compositions (5%, 10%, 15%, 20%, 30%, and 40% of the mixture), and DCP (2% with respect to weight of monomer) were heated to 170 °C, being kept constant for 40 min in vacuum. The products were extensively washed with dimethyl sulfoxide and then with methanol to remove ungrafted and unpolymerized monomer and other soluble parts formed in the reactions. The proposed structures of the copolymer units in the products are presented in Figure 14.

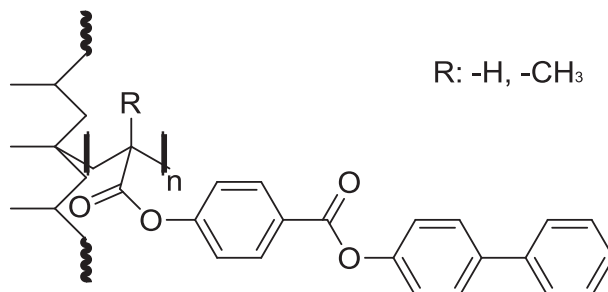


Figure 14. The proposed structure of the copolymer units in the products.

The FT-IR spectra of the coproducts of poly(BPCPA) and poly(BPCPMA) displayed the C=O stretching vibration bands, characteristic of the ester groups, at about 1740 cm^{-1} (in the former) and 1736 cm^{-1} (in the latter) and the bands of C=C stretching vibrations of aromatic groups at about 1602 and 1502 cm^{-1} , besides the characteristic absorption bands of CH₃ and CH₂ groups of PP chains. The bands at 980 and 906 cm^{-1} observed in the spectrum of BPCPA and at about 950 and 941 cm^{-1} in the spectrum of BPCPMA, ascribed to the vinylic C-H out-of-plane bending vibrations, disappeared in the spectra of the coproducts. The disappearance of the bands and formation of completely homogeneous structure without any phase separation, revealed in SEM studies, confirmed the success of the graft copolymerization of the monomers onto polypropylene.

3.3. Characterization of the products

¹H-NMR spectra of the monomers and the intermediate products, ABA, MBA, ABC, and MBC, in the synthesis of the monomers were obtained with a Bruker-Spectrospin Avance DPX 400 Ultra-shield ¹H-NMR spectrometer with a frequency of 400 MHz in dimethyl sulfoxide-d₆, using tetramethylsilane (TMS) as an internal reference.

DSC measurements of the monomers, the intermediate products of the monomer syntheses, homopolymers, and the graft coproducts were performed with a Shimadzu DSC-60 Differential Scanning Calorimeter at a heating rate of 10 °C/min under nitrogen atmosphere.

The TGA analyses of poly(BPCPA), poly(BPCPMA), and the graft coproduct samples were carried out with a PerkinElmer Pyris 1 TGA Thermogravimetric Analyzer in air and nitrogen atmosphere in the temperature range from 25 °C to 600 °C with a heating rate of 10 °C/min.

Tensile properties of PP and the graft coproducts were determined with a LLYOD LR5K Mechanical Tester at room temperature. The test samples were prepared by microinjection molding at 230 °C with thickness of 3 mm, width of 7 mm, and gauge length of 62 mm. Crosshead speed in testing was 5 cm/min. The tensile strengths and moduli were directly obtained from the stress-strain curves by the provided software of the instrument. A minimum of five specimens were tested for each composition.

The impact strengths of the test samples prepared, as for tensile tests, were determined by the Coesfeld Material Test Pendulum Impact Tester at room temperature.

Morphological properties of tensile and impact fractured surfaces of the graft coproducts were studied by using a scanning electron microscope, JEOL 6390-LV, operated at 20 kV with a resolution power of 3 nm.

3.4. Computational details

In this comprehensive study, computations belonging to the monomers of BPCPA and BPCPMA are used to describe the crucial changes in the mechanical performances of the PP with the grafting of homopolymers. In the calculations, the Gaussian 09 program³⁵ is used with a molecular visualization program.³⁶ The statistical thermodynamic energies and functions of the optimized structure are determined by means of the B3LYP method based on Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional of DFT at the 6-311++G (d,p) level of theory.

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