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Green Aqueous Surface Modification of Polypropylene for Novel Polymer Nanocomposites

Vijay Kumar Thakur[1], Danny Vennerberg[2], and Michael R. Kessler[1]*

[1]*School of Mechanical and Materials Engineering, Washington State University, Pullman, WA USA,*

[2] *Department of Materials Science and Engineering, Iowa State University, Ames, IA, USA*

* Corresponding Email: *MichaelR.Kessler@wsu.edu*

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Abstract

Polypropylene is one of the most widely used commercial commodity polymers; among many other applications it is used for electronic and structural applications. Despite its commercial importance, the hydrophobic nature of polypropylene limits its successful application in some fields, in particular for the preparation of polymer nanocomposites. Here, a facile, plasma assisted, biomimetic, environmentally friendly method was developed to enhance the interfacial interactions in polymer nanocomposites by modifying the surface of polypropylene. Plasma treated polypropylene was surface-modified with polydopamine (PDA) in an aqueous medium without employing other chemicals. The surface modification strategy used here was based on the easy self-polymerization and strong adhesion characteristics of dopamine (DA) under ambient laboratory conditions. The changes in surface characteristics of polypropylene were investigated using FTIR, TGA, and Raman spectroscopy. Subsequently, the surface modified polypropylene was used as the matrix to prepare SiO_2 -reinforced polymer nanocomposites. These nanocomposites demonstrated superior properties compared to nanocomposites prepared using pristine polypropylene. This simple, environmentally friendly, green method of modifying polypropylene indicated that polydopamine functionalized polypropylene is a promising material for various high performance applications.

Key Words: Polypropylene, green aqueous modification, dopamine, nanocomposites

Introduction

Certain polymers are the materials of choice in specific applications for which low density, efficient mechanical properties, low cost, good specific properties, low abrasiveness, or low environmental impact are required.[1-3] Because of their inherent advantages, some polymers are replacing traditional engineering materials in numerous fields, ranging from aircraft, electronics, packaging, appliances, to automotive applications to name a few.[4-7] Over the last few years, various polymers and their respective composites have attracted considerable scientific and technological interest.[8-11] Polypropylene is one of the most important commodity polymers produced on an industrial scale.[12-14] The intrinsic properties of polypropylene, such as its efficient mechanical properties, hardness, rigidity, good insulation properties, and thermal and chemical stability make it suitable for a number of applications. [13-16] However, its brittleness and hydrophobic nature limits the use of PP in particular applications.[17] Generally, compounding with different inorganic/organic materials improves the properties of PP. [17] In the recent past, considerable effort was made to modify the properties of PP matrices by reinforcing with nano-particles or by blending with other polymers.[13,15-16]However, the preparation of PP nanocomposites or the modification with other polymers still poses challenges because the backbone of PP has no functional/polar groups. [17] The difficulties in obtaining good homogeneous dispersions of nanomaterials within the polymer matrix prevent the preparation of nanocomposites with desired properties. Commonly used methods to prepare polymer nanocomposites include melt compounding, *in situ* polymerization, solvent-assisted processes, [18] and melt-blending, which is an inexpensive and environment-friendly method. [18] Several efforts were made to compatibilize PP with other materials using different compatibilizer, [17] such as maleic anhydride, resulting in modified PP (PP-g-MA), which was subsequently used as the matrix for nanocomposites.

However, the resulting nanocomposites exhibited only limited property improvements because of the significant polarity difference between matrix and nano-reinforcement. Therefore, the development of new PP polymer systems with suitable functional properties is of prime importance for various practical applications.

In the following, the effect of polydopamine modification on the properties of PP for novel nanocomposites was investigated. Dopamine is a synthetic mimic of mussel adhesive proteins (MAPs) that have attracted attention over the last few years.[19-21] Polydopamine (PDA) has been frequently used as a functional coating on various substrates because of its ability to adhere strongly to various kinds of surfaces, ranging from organic to inorganic, through the formation of hydrogen bonds, metal–ligand complexes, and quinhydrone charge-transfer complexes. [22-27] Lee *et al*., in their 2007 pioneer work[22], reported the surface modification of several materials, including polymers, noble metals, oxides, semiconductors, and ceramics by polydopamine (PDOPA) adhesive coatings.

In this work, plasma-assisted aqueous surface modification of polypropylene was used to incorporate suitable hydroxyl groups on the PP backbone for multifunctional applications in polymer nanocomposites. The prime focus of this work was to obtain better understanding of the underlying mechanisms ruling the dopamine surface coating of polypropylene. Using PP@PDOPA as the matrix, PP@PDOPA/ SiO_2 polymer nanocomposites were also prepared and their mechanical characteristics were investigated using tensile testing.

Experimental

Materials

All chemicals in the present work were used as received without any additional purification. Isotactic polypropylene (iPP) with a Mn = 67,000; Mw = 250,000 was purchased from Sigma Aldrich Chemical Company. Aerosil-OX50 fumed silica nanoparticles with an average particles size of 40 nm were obtained from Degussa (Essen, Germany). These particles exhibited a specific surface area of 50 m^2/g. Prior to their incorporation as reinforcement in pristine and polydopamine modified polypropylene matrices, these nanoparticles were dried in vacuum at 120 °C for 24 h unless otherwise stated. 3, 4-Dihydroxy-L-phenylalanine was purchased from Sigma−Aldrich Corporation (St. Louis, MO). Tris base (molecular biology grade) was obtained from Fischer Scientific (Hampton, NH).

Functionalization and Characterization of Polypropylene

Prior to plasma pre-treatment, polypropylene resin was dried in an oven at 50 °C to remove any moisture content. Subsequently, the dried polypropylene was deposited on a flat quartz plate inside the RF coil and treated with argon coupled plasma at room temperature (Harrick Plasma, model PDC-001, Ithaca, NY).[25] Radio frequency argon glow discharge plasma was generated using an inductively coupled plasma chamber operating at 13.56 MHz and 29.6 W. [25] Initially, the plasma chamber was evacuated to a base pressure of 0.001 Torr, which was increased to 0.5 Torr after gas feeding. After the stabilization of the process pressure inside the plasma chamber, radio frequency (13.56 MHz) discharge was created and the polypropylene was treated for a pre-set time of 8 min. [7,28]Immediately after the completion of plasma treatment, the treated polypropylene was

exposed to the atmosphere at room temperature (25 °C) for 30 min to facilitate the efficient formation of surface hydroperoxides and peroxides (Scheme 1). [25]

A dopamine solution was prepared using previously optimized concentration (2.0 g/l) by dissolving dopamine in distilled water. [25] Tris-HCl (10 mM) buffer solution (self-prepared in the laboratory) was used to adjust the pH (8.5) of the solution. Subsequently, polypropylene was added to this solution (250 mL, 10 mM Tris buffer). The suspension was then continuously stirred at 60 °C for a defined, optimized time period of 24 h in a heating mantle fitted with a reflux condenser to facilitate the polymerization reaction. After completion of the reaction, the suspension was centrifuged at 6400 rpm for 10 minutes and the resulting dark brown product was washed several times in copious amount of distilled water. The PP@PDOPA samples thus obtained were collected by filtration and dried to a constant weight in a vacuum oven at 50 °C for subsequent characterization. Pristine polypropylene and dopamine functionalized polypropylene PP@PDOPA samples were characterized using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and thermogravimetric analysis (TGA) (see corresponding descriptions in the Electronic Supplementary Information).

Preparation of Polypropylene/SiO_2 Nanocomposites

Nanocomposites with PP and PP@PDOPA matrices and SiO_2 reinforcement were prepared by melt mixing at 185 °C using a twin screw microcompounder from DACA Instruments, CA. Pristine and functionalized PP were kneaded for 10 min and then 1 wt.% SiO_2 nanoparticles was added. The residence time of melt in the barrel was maintained at 10 min to homogenize the melt. Subsequently the extruded polymer nanocomposites were pelletized and compression molded at 230 °C to prepare films with dimensions of 50 × 50 × 1 mm using a compression molding machine

from Wabash MPI, IN, USA. The tensile test samples having specimen length of 25mm and width of 1mm were prepared by stamping dog-bone shaped specimens from 1 mm thick films according to ISO 527 type 5A. During the testing of samples a crosshead speed of 50 mm/min was used. At least five measurements were conducted for each specimen and the results have been averaged to obtain a mean value.

Results and Discussion

Polypropylene Functionalization

The excellent physico-chemical properties of polypropylene, such as thermal stability, light weight, easy processing, low cost, high transparency, and chemical resistance make it a suitable material for a wide variety of applications. [29-31]However, polypropylene also exhibits less desirable properties, such as poor wettability and printability, and limited adhesion owing to its hydrophobic character.[32-34] Because these disadvantages limit the applications of polypropylene, a number of techniques have been used to modify its surface characteristics.[35-38] These methods include chemical treatment, electrochemical treatment, ultraviolet irradiation, corona discharge, electron bombardment, photo-irradiation, and plasma treatment.[39] Although chemical treatments, such as graft copolymerization, oxidation, and etching, are the most widely used methods to modify the surface of polypropylene, they require expensive waste disposal. In contrast to chemical treatments, polypropylene can be efficiently modified by plasma treatment that does not cause any environmental issues related to waste disposal. Plasma treatment creates a number of reactive species, including free radicals and ions, on the polymer's surface which can be used for further modification. [39-40]The advantage of treating polymeric materials using plasma modification is that

the reactions occur only on the surface and do not changes the polymer's bulk properties significantly. [39-40]

In this work, we tailored the surface properties of polypropylene by plasma assisted polydopamine functionalization. Dopamine was chosen because it is prone to oxidative self-polymerization that results in the formation of thin layers on various types of substrates, thus providing one-step surface functionalization. Recent studies indicate that plasma assisted modification of PP followed by exposure to air results in the formation of reactive species, such as hydroperoxide and peroxide, on the polypropylene surface. [28]These reactive functional groups then facilitate the effective surface functionalization of polypropylene by dopamine, see Scheme 1a and b.

It has been reported in the existing literature that the adhesion, proliferation and differentiation behaviors of polymer materials depend on their surface characteristics. [7, 28] Plasma treatment of polypropylene is limited to a depth of few microns and therefore does not cause significant changes in PP's molecular structure.[7, 28] When plasma pre-activated polypropylene is added to an aqueous solution of dopamine, the inherent adhesive properties of the dopamine molecules together with van der Waals interactions and hydrogen bonding between both the hydroperoxide and the surface peroxide of polypropylene and the amino groups of the dopamine molecules will result in significant adhesion between the polypropylene and the dopamine.[25-27] The mechanism of dopamine polymerization in a solution involves the oxidation of catechol in dopamine to quinone by alkaline pH-induced oxidation (Scheme 2). The polymerization of dopamine in solution for a requisite time results in the formation distinct polydopamine layer on polypropylene through a simple deposition process. [25-27]

Characterization of Plasma Assisted Functionalized Polypropylene

The structural changes on the polypropylene surface that resulted from polydopamine functionalization were determined by FTIR, Raman, and TGA techniques. The FTIR spectra of untreated PP and polydopamine treated PP (PP@PDOPA) are shown in Fig. 1. The FTIR spectrum of pristine polypropylene polymer exhibited the characteristic peaks at 2947, 2920, 2833, and 1451 cm^{-1}. These peaks correspond to asymmetric CH_3, asymmetric $–CH_2–$, and symmetric CH_2 stretching vibration and methylene deformation in the polypropylene polymer.[7] The peaks at 805 cm^{-1} correspond to CH_2 rocking, C-C chain stretching, and C-CH stretching; those at 900 cm^{-1} correspond to CH_2 rocking and C-CH_3 stretching; those at 975 cm^{-1} correspond to CH_3 rocking and C-C chain stretching; those at 1225 cm^{-1} correspond to CH_2 twisting, C-C chain stretching, and CH bending; and those at 1385 cm^{-1} correspond to CH_3 symmetric bending and CH_2 wagging. On the other hand, the FTIR spectrum of PP@PDPA exhibited a new strong OH stretching peak centered at 3430 cm^{-1}. This peak may be attributed to the intermolecular bonding at the surface of the modified polypropylene. From the spectra it is clear that the polydopamine functional groups dominated the IR spectrum of PP@PDOPA. The strong peak at 1615 cm^{-1} of PDOPA@PMMA was assigned to the overlap of C=C resonance vibrations in the aromatic ring and N–H bending, confirming the successful polymerization of dopamine onto the PP surface.[19-21] Other peaks in the range of 1230 to1500 cm^{-1} were attributed to phenolic O–H deformations coupled or decoupled with C–C ring stretching and phenolic C–O stretching. [25-27] Comparative study of the IR spectra of pristine PP and PP@PPDOPA demonstrated a significant difference in their intensity over the studied range, indicating the strong presence of the OH and NH_2 groups of polydopamine on the surface of PP.

Raman spectra (Figure 2) were used to confirm the successful surface functionalization of PP. Figure 2 shows that the dopamine functionalized PP exhibited significant changes in peak intensity, indicating strong interactions between the plasma modified PP and the dopamine molecules. The Raman spectrum of pristine PP showed the characteristic bands between 811 cm^{-1} and 2100 cm^{-1}. [41]The band at 811 cm^{-1} corresponds to C-C stretching and CH_2 rocking; the band at 841 cm^{-1} corresponds to CH_2 rocking; the band at 972 cm^{-1} corresponds to C-C stretching and CH_3 rocking; the band at 998 cm^{-1} corresponds to CH_3 rocking; the band at 1151 cm^{-1} corresponds to C-C stretching and C-H bending; the band at 1168 cm^{-1} corresponds to C-C stretching, CH_3 rocking, and C-C wagging; the band at 1220 cm^{-1} corresponds to C-C stretching, CH_3 C-H wagging, and CH_2 twisting; the band at 1435 cm^{-1} corresponds to C-H_2 bending; and the band at 1458 cm^{-1} corresponds to CH_2 bending. [41]

The Raman spectra of polydopamine modified polypropylene (PP@PDOPA) showed that after polydopamine polymerization of the PP surface, the structural characteristics of polypropylene were strongly dominated by polydopamine. [25-27] In addition, the intensity of the polypropylene bands considerably decreased upon polydopamine modification, indicating the successful functionalization of polydopamine onto PP. The spectra of PP@PDOPA showed the presence of two protuberant characteristic bands at 1351 cm^{-1} and 1570 cm^{-1} that were attributed to the deformation of the catechol group in the polydopamine molecules. These results match earlier results published on polydopamine polymerization. [25-27]

Figure 3 shows the thermogravimetric analysis (TGA) curves of pristine PP, dopamine, and PP@PDOPA samples obtained in nitrogen atmosphere. The thermal stability of the investigated samples was determined in terms of percentage weight loss. In general, the thermal stability of all samples (pristine PP, dopamine, and PP@PDOPA) decreased with increasing

temperature. Pristine PP underwent initial thermal degradation between 270 and 410 °C, followed by a slight weight loss stage between 410 and 480 °C. Pristine dopamine was thermally stable without any significant change in weight up to 217 °C. Dopamine degraded in two stages: initial degradation occurred between 227 and 300 °C, and the second degradation occurred between 300 and 500 °C. This degradation behavior was attributed to the degradation of the catechol moiety and the decomposition of the amide group and the alkyl spacer, respectively. [25-27] PP@PDOPA showed thermal degradation behavior similar to that of pristine dopamine. The initial degradation temperature of PP@PDOPA was lower than that of pristine dopamine, while the final degradation temperature was higher than that of polypropylene. The steady weight loss between 250 and 430 °C for PP@PDOPA was attributed to the weight loss encountered during dopamine degradation. From the thermal calculations it can be concluded that the PP@PDOPA contains nearly 2 – 5 wt. % of dopamine, further confirming the successful functionalization of polypropylene. [25-27]

Polypropylene/ SiO_2 Nanocomposites

Polymer-based nanocomposites, prepared using organic/inorganic nanomaterials as reinforcement, potentially offer a number of advantages over conventional composites, including improvements in mechanical and physical properties at low loading levels (wt./vol.%). [45]Several nanomaterials, such as carbon nanotubes (CNT), $BaTiO_3$, TiO_2, Al_2O_3, SiO_2 and graphene, have been used to prepare nanocomposites with both thermosetting to thermoplastic matrices.[42-48] However, nanomaterials often have to be modified with suitable functional groups to make them compatible with polypropylene. In some cases compatibilizers are also added in the polymer

matrices to increase the dispersion of nanoparticles in the polymers.[49-50] Lee et al have studied in detail the effect of different reaction conditions such as screw speed and screw configuration on the dispersion of nanosilica in the polypropylene matrix. It was observed from the study that high shear stress, sufficient residence time, and high fill ratio in the melting section of the screw facilitates the nanosilica dispersion in the polypropylene matrix. In this study, the effects of maleated polypropylene (PP-g-MA) compatibilizer on the degree of SiO_2 dispersion was also investigated. The addition of PP-g-MA has been found to reduce the number of large aggregates and facilitates the more efficient stress transfer. [49] The structure and physical properties of nanosilica reinforced polypropylene and thermoplastic olefin were also studied by Liu and Kontopoulou. In this study, the effect of incorporation of maleated propylene on the dispersion of nanoparticles in the polypropylene matrix as well as effect of surface modification of SiO_2 nanoparticles was studied. The addition of PP-g-MAn into PP was found to reduce large SiO_2 aggregates within the polymer matrix and facilitate the good dispersion of the filler. The surface modification of silica nanoparticles also resulted in the efficient dispersion of nanoparticles in a PP-g-MAn/ PP matrix than untreated SiO_2.[50]

In the present work, an alternative approach was used, modifying the surface characteristics of polypropylene for various end applications. To validate the effectiveness of the method, polymer nanocomposites were prepared using fumed SiO_2 nanoparticles at 1 wt. % loading as reinforcement of pristine and polydopamine functionalized PP matrices (see Figure 4). These polymer nanocomposites were then subjected to tensile strength analysis, see Figure 5 (a,b). Figure 5 (a,b) shows that the tensile strength and young's modulus of polypropylene/ SiO_2 nanocomposites increased by a significant margin after modification with polydopamine, which was attributed to better interfacial attraction between polymer matrix (PP@PDOPA) and SiO_2

nanoparticles.[26]This interfacial attraction resulted in the improved mechanical properties owing to the efficient transfer of mechanical loads from the PP@PDOPA to the SiO_2 nanoparticles.

Conclusions

In the present work, dopamine (a synthetic mimic of mussel adhesive protein) was used to modify the surface characteristics of polypropylene for polymer nanocomposites applications. Plasma assisted functionalization of polypropylene was accomplished in an aqueous medium without employing any harmful chemicals. The surface functionalization of polypropylene was confirmed by different characterization techniques, namely thermogravimetric analysis, FTIR, and Raman spectroscopy. The results confirmed that dopamine has the potential for the successful functionalization of polypropylene. In addition, polymer nanocomposites prepared using modified polypropylene exhibited improved mechanical strength. The present work suggests that surface modification of polypropylene with polar functional groups employing dopamine is a promising technique and is expected to lead to the production of novel polymer nanocomposites with enhanced properties.

Supporting Information

Characterization of the pristine polypropylene and dopamine functionalized polypropylene (PP@PDOPA) samples using FTIR, Raman and thermogravimetric analysis. Preparation of films by melt mixing using a twin screw microcompounder

"This information is available free of charge via the Internet at http://pubs.acs.org/."

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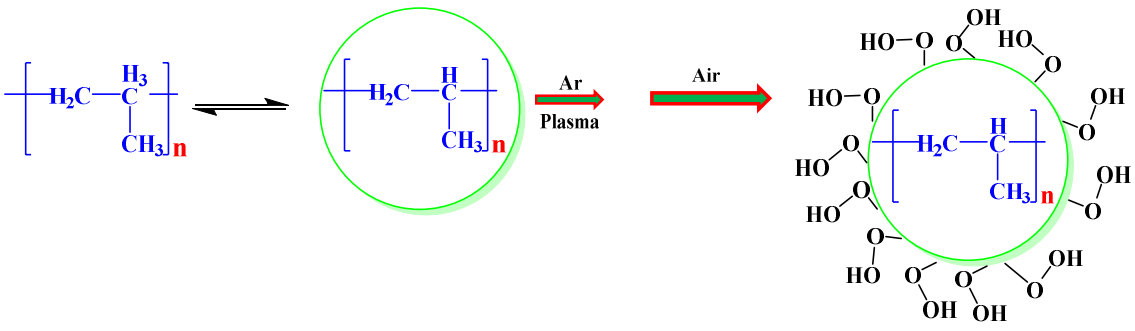
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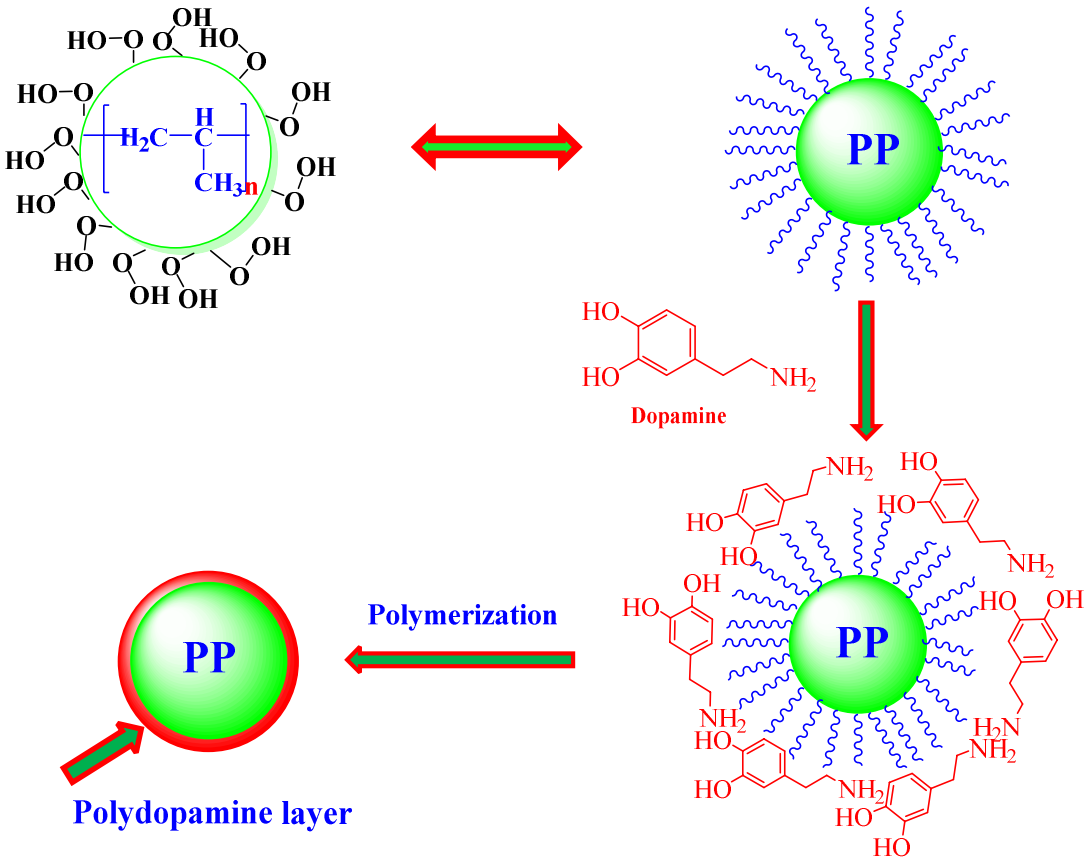
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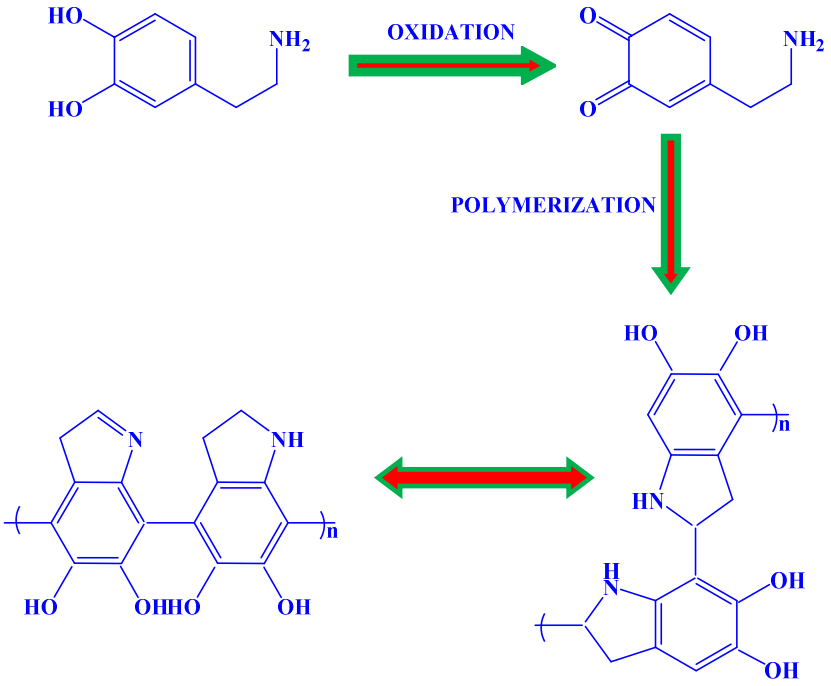
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Scheme 1(a): Plasma modification process of polypropylene (PP)



Scheme 1(b): Functionalization of polypropylene (PP) with polydopamine (PDOPA)[27]



Scheme 2: Polymerization of dopamine to polydopamine[27]

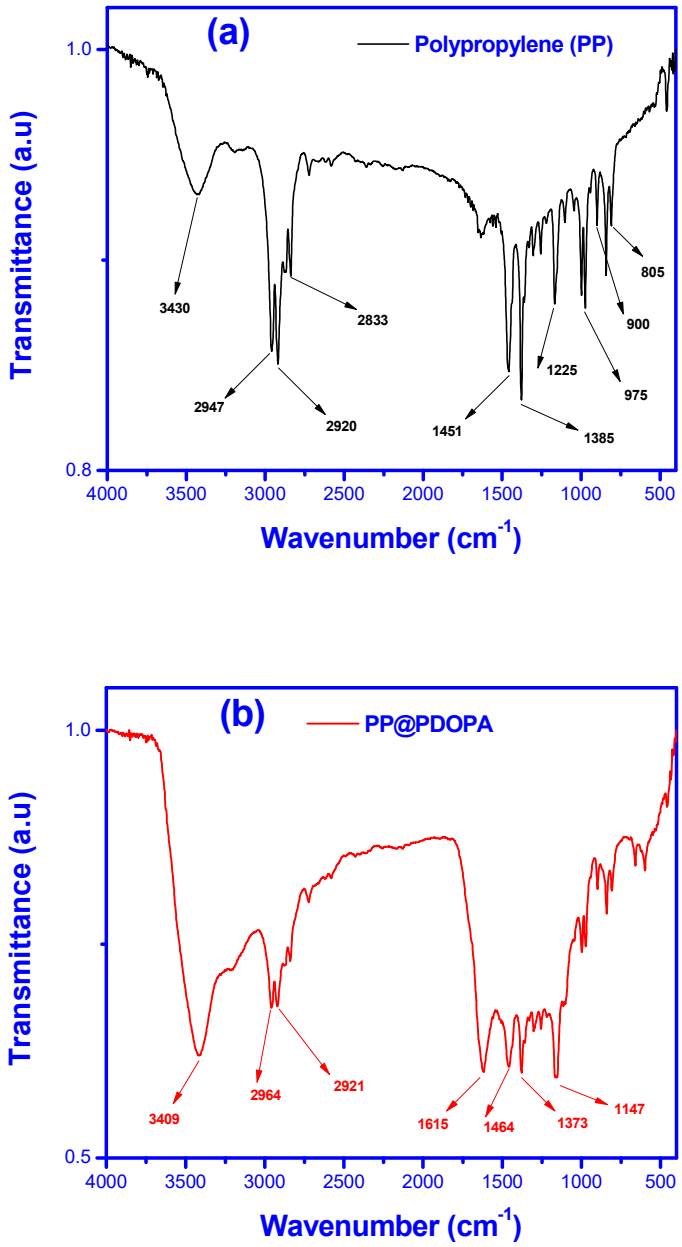


Figure 1 FTIR spectra of (a) pristine polypropylene (PP) and (b) PP@PDOPA

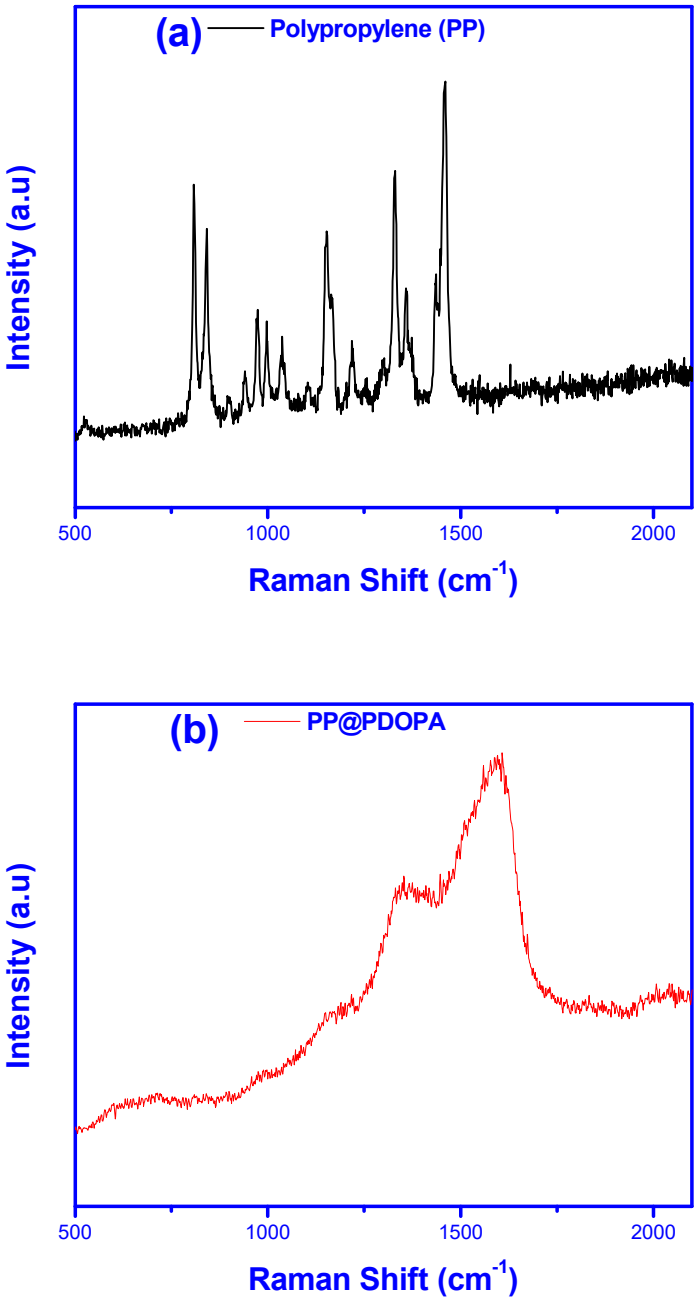


Figure 2 (a) Raman spectra of (a) pristine polypropylene (PP) and (b) PP@PDOPA

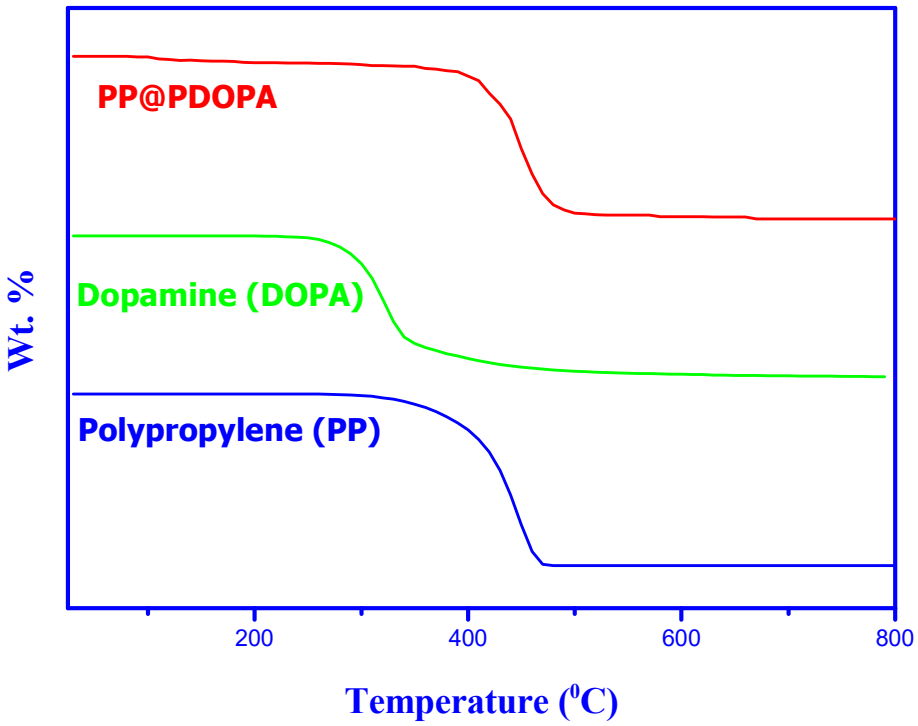


Figure 3 TGA of pristine polypropylene (PP), dopamine, and PP@PDOPA

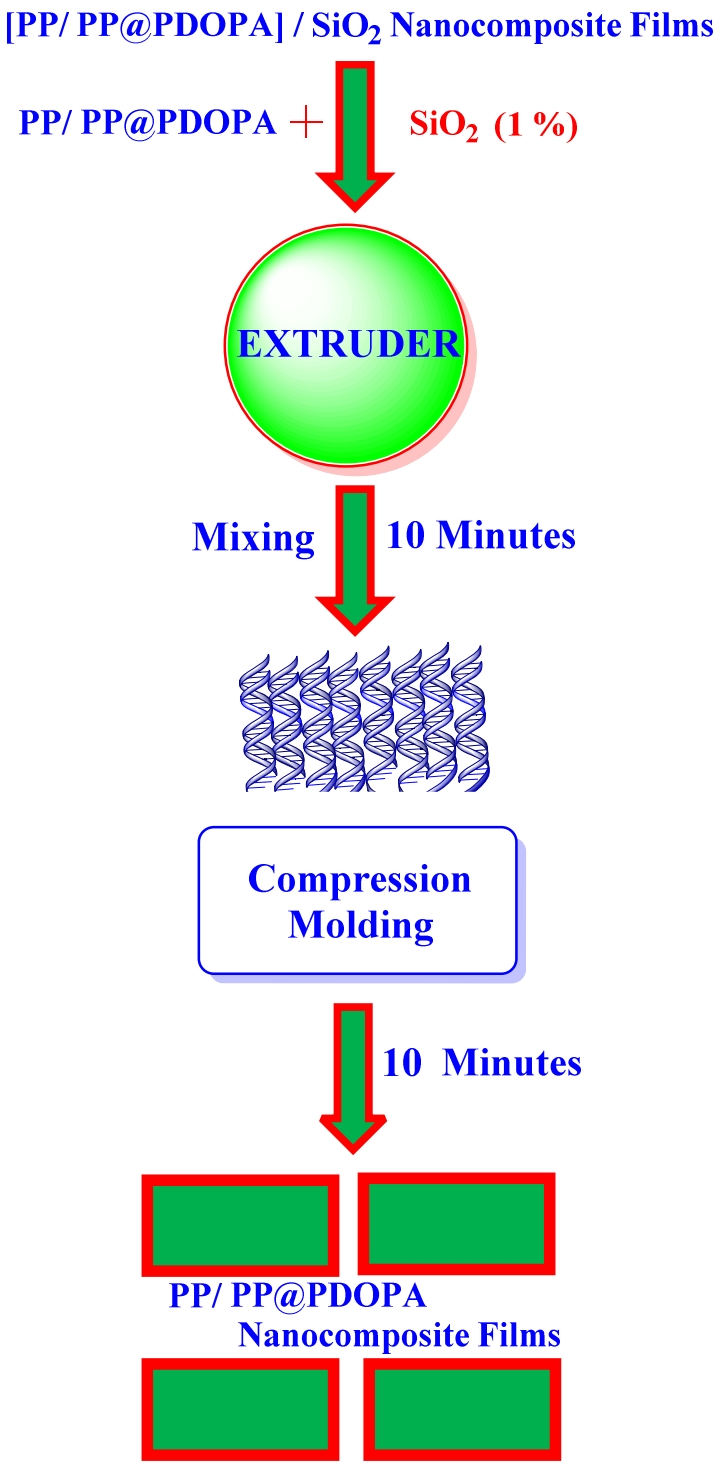


Figure 4 Schematic for the preparation of (PP/PP@PDOPA)/SiO_2 polymer nanocomposites.

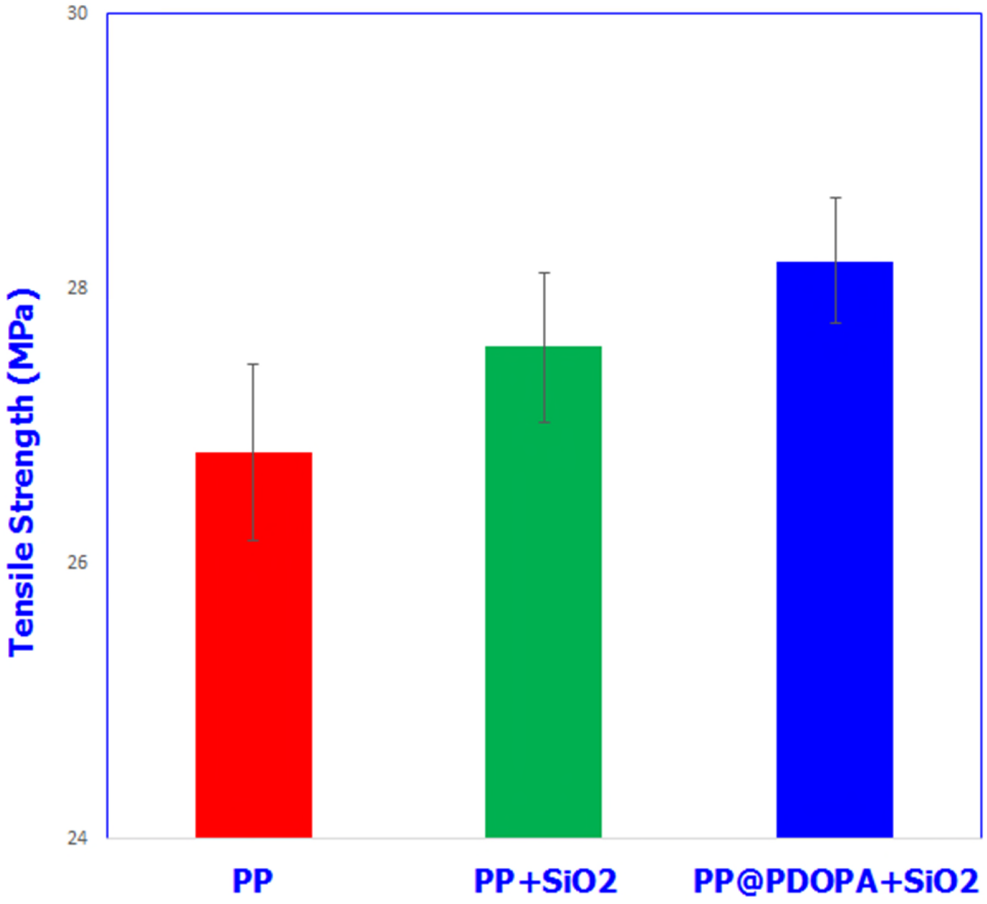


Figure 5 (a): Tensile strength results for PP, PP-SiO_2, and PP@PDOPA-SiO_2 polymer nanocomposites.

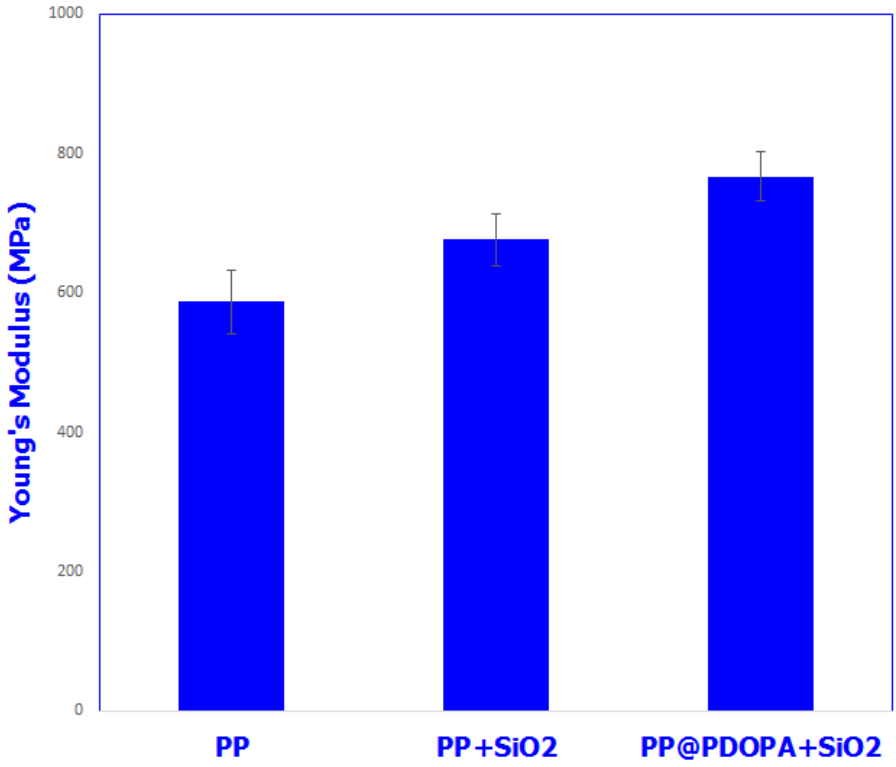
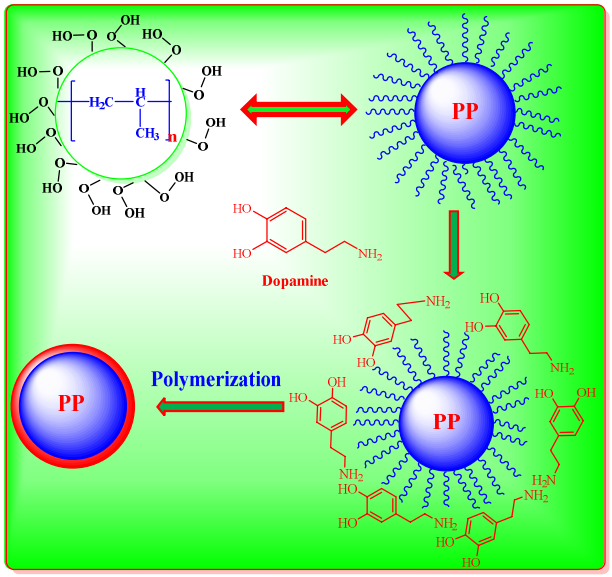


Figure 5 (b): Young's modulus results for PP, PP-SiO_2, and PP@PDOPA-SiO_2 polymer nanocomposites.

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