

Plasma-Enhanced Synthesis of Maltodextrin–Polydimethylsiloxane Graft Copolymers

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ABSTRACT: Ether-extracted maltodextrin (MD) powder was surface functionalized under 13.56-MHz RF–SiCl₄-plasma conditions, and consecutively in situ aminated and grafted using dichlorodimethylsilane. Survey and high-resolution X-ray photoelectron spectroscopy, FTIR evaluations, fluorescence-labeling technique, SEM, and DTA/TG analyses prove the presence of a graft-copolymer layer on the modified starch-granule surfaces and the existence of a significantly changed surface morphology of the starch granules, as a result of the grafting reactions. The hydrophobic nature of the polydimethylsiloxane-grafted starch and its significantly changed thermal behaviors were also evaluated. Potential applications of modified maltodextrins are discussed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1120–1129, 2001

Key words: plasma; functionalized surface; maltodextrin; silicon tetrachloride; polydimethylsiloxane grafted

INTRODUCTION

Starch is a homopolymer of glucopyranose units composed of two different polymers based on 1,4 (linear amylose) and 1,6 (highly branched amylopectin) α -linkages. In most applications, the quasicrystalline structure of starch granules is altered and, depending on the technologies involved (e.g., chemical modification of starch, Table I),¹ the composing macromolecular structures are partly depolymerized.

Dextrins are oligosaccharides resulting from the partial degradation of starch (e.g., caloric energy-induced degradation, acid hydrolysis) that

can serve as low-molecular-weight model compounds for the evaluation of chemical reactivity of starch. Investigations targeting advanced applications of starch (or dextrins) include starch–plastic composites, starch–graft copolymers, and starch thermoplastics.^{2,3}

Starch and dextrins have many applications. Their use as a substitute for petrochemical-based plastics is one of the most attractive applications. The key requirements for starch-based biodegradable plastics are (1) to be processable through the molten state; (2) to be impervious to water or ambient moisture; and (3) to retain their integrity during normal use but readily degrade by microbial processes. To meet these requirements, starch has to be modified either chemically or physically, or both—including chemical modifications, changes in starch morphology, addition of plasticizers, and blending with other polymers.

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Table I Practiced U.S. Modifications of Corn/Maize Starch

I. Chemical modification
Derivatization
1. Monostarch substitution (etherification and esterification; includes polymer grafting)
2. Crosslinking (via distarch esterification)
Acid-thinning (hydrolytic depolymerization)
Dextrinization (depolymerization and transglycosylation)
Oxidation (bleaching and depolymerization)
Hydrolysis (to maltodextrins, glucose syrups, glucose, etc.; both acid- and enzyme-catalyzed)
II. Physical modification
Gelatinization (to produce pregelatinized starch)
Preparation of cold water swelling starch
III. Generic
Waxy maize starch
High-amylose maize starch

From BeMiller.¹

To prepare starch-plastic composites, granular or gelatinized starch is physically incorporated as a functional additive and filler into synthetic or natural polymers during polymer processing (e.g., foaming, extrusion, injection molding, or film blowing). Generally, 6–30% starch (by weight) can be added; but in some cases up to 60% starch was used.⁴ The major concerns of this method are to use dry starches and to efficiently combine the hydrophilic starch additive and the hydrophobic matrix polymers. The combination of starch with other biodegradable polymers, such as poly(hydroxybutyrate-cohydroxyvalerate; PHBV), a microbially produced polyester,^{5,6} is an example.

The hydroxyl groups on both the primary and secondary carbon atoms of starch and dextrin units offer vast opportunities for chemical modifications to incorporate into the polysaccharide structure new and useful properties. The most important reaction may be to graft thermoplastic polymer chains onto the polysaccharide backbones; the resulting copolymers are then formed into films or injection-molded items. The grafting reactions are developed by first generating free radicals on the starch backbones and then allowing these free radicals to initiate polymerization of common monomers, including acrylic acid and its derivatives,^{7–9} acrylamide,^{10,11} and vinyl acetate/alcohol,¹² and so forth.

Starch can also be processed under controlled high-pressure, temperature, and moisture conditions in an extruder or by injection molding, to

yield biodegradable thermoplastic products without the addition of petrochemical polymers.^{13–15}

Most of the conventional polysaccharide-modification reactions are based on wet chemistry techniques, which usually require large solvent quantities, expensive (energy intensive) separation processes, and they are environmentally hazardous. Cold-plasma technologies open up novel, efficient routes for the modification of natural polymeric raw materials, including polysaccharides.¹⁶ The main advantages of plasma technologies as compared with the conventional wet chemistry approaches are that they (1) are dry process; (2) can be developed in a large pressure range; (3) alter only the very top layers of the plasma-exposed surface, leaving the bulk properties of the substrates unchanged; and (4) are energy efficient.^{17–20} Because the energy levels of plasma species are comparable to the bond energies of common organic compounds, and organic compounds containing main-group elements, all gas-phase organic molecules and component molecules of condensed phase surfaces exposed to plasma species can conveniently be modified/functionalized under selected discharge parameters. The chemical nature of the plasma gases or surfaces that confine the discharge is less important for the plasma-induced reactions, and consequently even the most inert substrates, such as polyethylene, polytetrafluoroethylene, and quartz, can be modified/functionalized under cold-plasma conditions.

This article describes grafting with polydimethylsiloxane (PDMS) of plasma-functionalized maltodextrin (MD) and discusses the potential applications of polysaccharide/polydimethylsiloxane graft copolymers.

EXPERIMENTAL

Materials and Methods

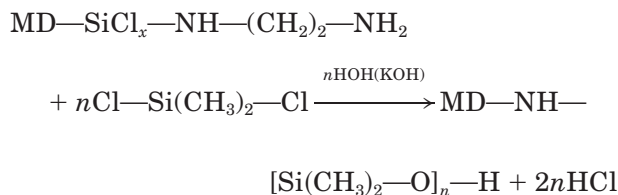
Oxygen used for the decontamination of the plasma reactor was obtained from Liquid Carbonic Co. Dichlorodimethylsilane (DCDS) (99%, bp: 70°C), silicon tetrachloride (99%, bp: 57.6°C), diethyl ether (ACS reagent, bp: 34.6°C), and ethylene diamine (ED) (99%, bp: 118°C) were purchased from Aldrich Co. Maltodextrin M040 was supplied by GPC. Fluorescamine employed for the identification of primary amine functionalities was purchased from Molecular Probes (Eugene, OR).

In all plasma treatments, Soxhlet-ether-extracted MD samples were used for minimizing the natural- and processing-origin hydrocarbon-type contamination. The 285-eV binding energy deconvoluted peak areas were monitored by high-resolution ESCA measurements.

Evaluation of primary amine functionalities has been performed by fluorescence labeling technique. The SiCl_4 -treated and in situ ED exposed MD substrates were sprayed 3 times consecutively with a fluorescamine solution (25 mg fluorescamine in 100 mL acetone) using a Gelman Chromist aerosol propellant, attached to a polypropylene bottle. The fluorescence of the substrates was revealed with the aid of a Black-Ray ultraviolet (UV) lamp, model: UBL 21 (UVP, San Gabriel, CA) and a FCR-10 photo camera (Fotodyne, Hartland, WI).

A typical grafting reaction of SiCl_x -plasma-functionalized and ED-aminated MD was carried out employing the following procedure: 10 g of functionalized MD was transferred into a Pyrex-glass beaker and mixed in an argon-filled glove-box environment with 5 mL of DCDS. Then 3-5 mL of 1 mol/L KOH solution was added in small portions as a catalyst under continuous stirring. During the addition of KOH solution, the hydrophilic MD-based, fluid-character mixture turned into a hydrophobic, yellow-colored mass with a viscous consistency, which made the mixing very difficult. Close to the end of the grafting procedure, the color of the copolymer became darker (brownish) and its viscosity slightly decreased.

The graft-copolymerization reaction was developed according to the following reaction mechanism:



The grafting reaction can also be performed directly from SiCl_x -plasma-functionalized MD-particle surfaces. However, the SiCl_x functionalities are extremely moisture sensitive and are converted under open laboratory conditions (e.g., removing the samples from the plasma reactor) into Si(OH)_x groups with significantly lower reactivity in comparison to their SiCl_x correspondents. By reacting in situ the SiCl_x functionalities with dia-

mine, moisture resistant primary amine end groups can be generated, which allow a significantly easier handling of the grafting step of the process.

The relative surface atomic concentrations and the nonequivalent C1s , O1s , N1s , and Si2p linkages of plasma-modified and -derivatized MD were carried out using a Perkin-Elmer Physical Electronics Phi540 small area ESCA system (Mg source; 15 kV; 300 W; pass energy: 89.45 eV; angle: 45°). Carbon (C1s), oxygen (O1s), silicon (Si2p), and nitrogen (N1s) atomic concentrations were evaluated and the nonequivalent positions of carbon linkages were analyzed. In order to correct surface-charge-origin binding energy shifts, calibrations were performed based on the well-known C1s , C—O (286.6-eV) peak of MD.

Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical linkages on the plasma treated MD. An ATI-Mattson, Research Series IR instrument was used for all measurements. All FTIR evaluations were performed under nitrogen blanket generated from a flow-controlled liquid nitrogen tank. Same amounts of samples and KBr were used for the preparation of IR pellets (0.6 g KBr and 0.001 g MD/modified MD samples; the components were thoroughly mixed and the pellets were prepared using identical die pressure). Data were collected in the 600–4000 cm^{-1} wavenumber region with 250 scans for each sample.

Surface morphologies of MD and grafted-MD particles were analyzed using SEM (JEOL JSM6100 SEM with EDS) investigations. SEM images were collected from gold-sputtered substrate surfaces.

The swelling characteristics (gelation) of MD and grafted-MD samples were visually evaluated by boiling for 5-min dispersions resulting from mixing of 3 g of MD or grafted-MD samples with 8 mL of distilled water.

Plasma Treatments

The implantation of SiCl_x functionalities onto starch-granule surfaces was carried out using a small-capacity rotating plasma installation (Fig. 1). The reactor is composed of a Pyrex-glass chamber (6) provided at both ends with ferrofluidic feedthroughs (14) which ensure the free rotation of the reaction chamber. The surfaces of the ferrofluidic sealing systems facing the interior of the reactor are protected by ceramic discs (10-mm thickness) against the plasma species. The rota-

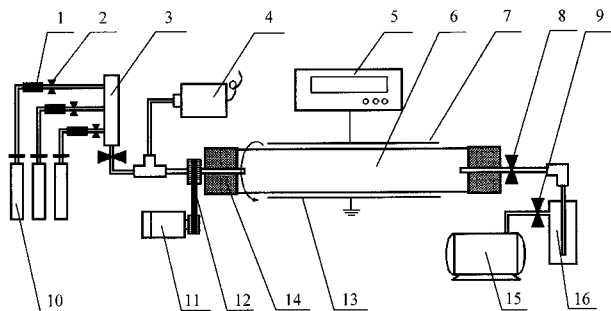


Figure 1 Rotating plasma reactor: 1, flow meters; 2, needle valves; 3, mixing chamber; 4, MKS vacuum gauge; 5, plasma power; 6, Pyrex glass chamber; 7, upper electrode; 8,9, valves; 10, metallic reservoirs; 11, electric motor; 12, coupling belt; 13, lower electrode; 14, ferrofluid sealing; 15, nitrogen trap; 16, vacuum pump.

tion of the plasma chamber is digitally controlled within the 0–50-rpm range with the aid of a driving unit composed of: electric motor (11), belt-coupling system (12), and angular speed controller. The plasma gases and vapors are supplied to the reactor through a mixing chamber (4) using flow controllers (1) and needle valves (2). The mechanical vacuum pump (16), liquid nitrogen trap (15), and the large-capacity valves (8,9) ensure the quick evacuation of the system. By operating properly the flow controllers and the valves, the desired flow rate and pressure, monitored by a MKS vacuum gauge (4), can be established in the reactor. The 13.56-MHz RF power is trans-

ferred to the reactor using two semicylindrical outside located copper electrodes (7,13).

In a typical experiment, the ether-extracted and vacuum-oven-dried MD powder is introduced into the reactor. The reaction chamber and the connecting supply lines are evacuated to base pressure. By operating the flow controllers and the corresponding needle valves, the required SiCl_4 vapor pressure and flow rate are created in the reactor. The rotation of the reactor is then started and the plasma ignited and sustained for the preselected reaction time. At the end of the plasma exposure, the gas-feed valves are closed and the system is evacuated to base pressure and the pressure is maintained for an additional 30 min. In the next step the chemical derivatization agent, ED, is introduced into the reactor under vacuum.

The following experimental conditions were employed during the plasma-functionalization of MD substrates: substrate: MD (40 g); plasma gas: SiCl_4 ; base pressure in the reactor: 80 mTorr; SiCl_4 vapor pressure in the absence of plasma: 180 mTorr; RF-power (13.56 MHz) dissipated to the electrodes: 100 W; plasma treatment time: 1 and 5 min.

RESULTS AND DISCUSSION

Figure 2 shows the ESCA survey diagrams and relative surface atomic concentrations of un-

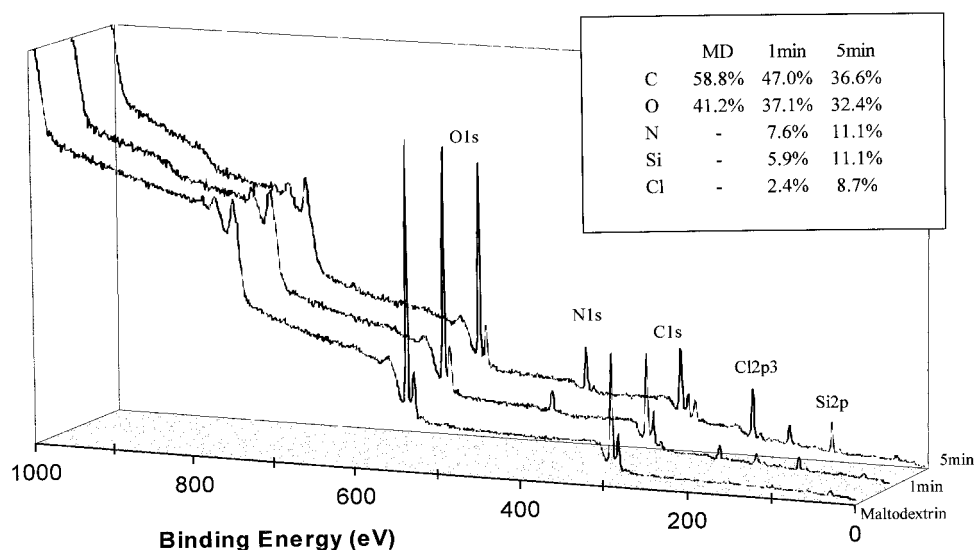


Figure 2 Survey ESCA results and the surface atomic concentrations for untreated maltodextrin (MD), 1-min and 5-min plasma-treated, then grafted MD.

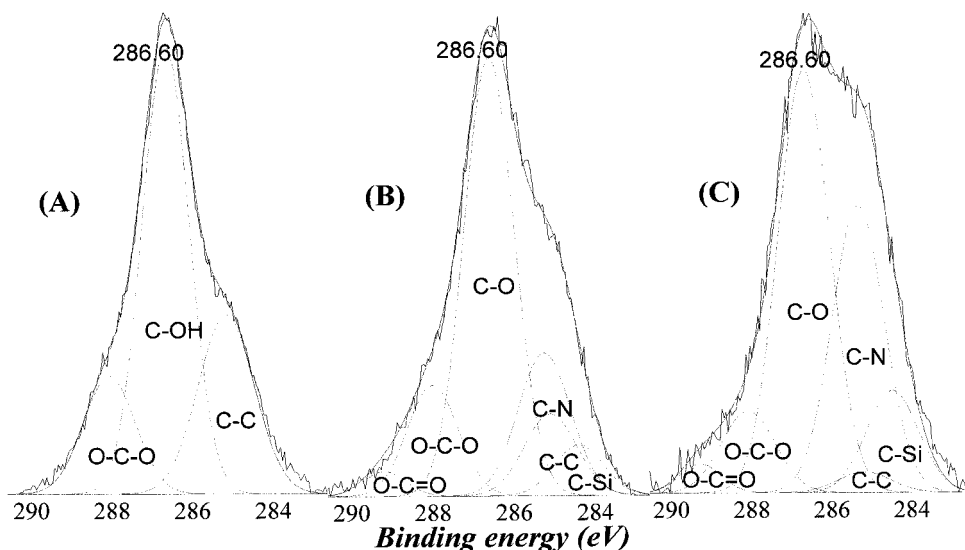
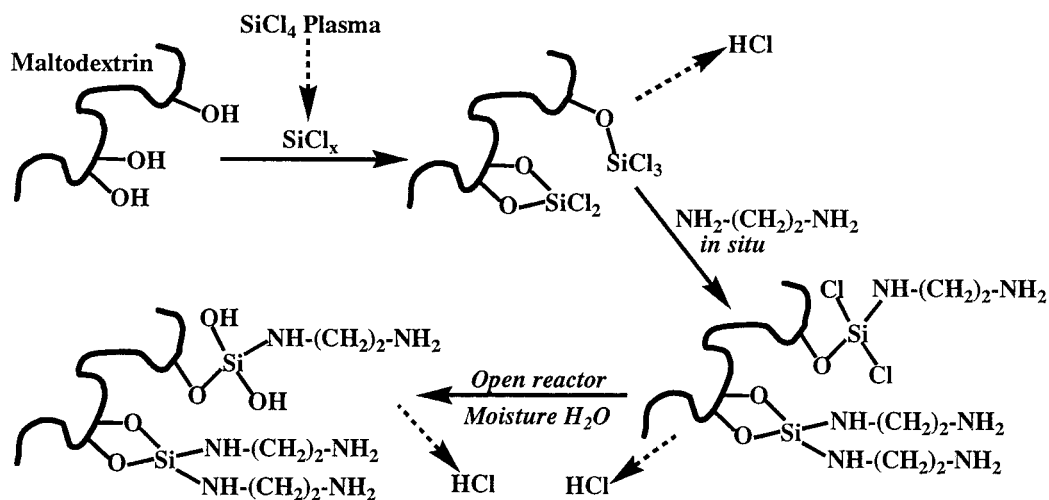


Figure 3 C1s high-resolution (HR) ESCA results of (A) untreated MD; (B) 1-min plasma-treated and subsequently aminated maltodextrin (MD); and (C) 5-min plasma-treated and subsequently aminated MD.

treated MD, 1-min and 5-min SiCl_4 -plasma-treated, and subsequently ED-aminated, MD substrates. The high-resolution (HR) ESCA diagrams of C1s are presented in Figure 3. The C1s ESCA data indicate that in addition to the characteristic C—O (286.6 eV) and O—C=O (288-eV) binding energy peaks of MD, the presence of C—Si (284.4-eV), C—C (285-eV), C—N (285.6-eV), and very small surface area O—C=O (298.2-eV) binding energy peaks can also be noted in the diagrams of the 1-min (S1) and 5-min (S5) plasma-treated and aminated substrates. The relative ratio of C—OH/

O—C—O peak areas of S1 (3.9; Fig. 3) is slightly higher as compared with that of unmodified MD (3.6; Fig. 3), whereas the same peak area ratio of S5 has a significantly higher value (5.8; Fig. 3). This might be explained by the development of plasma species-induced (SiCl_x) functionalization reaction mechanisms with the generation of C—O— SiCl_x linkages. The binding energy values of C—O linkages originating from C—OH, C—O—C, and C—O—Si are practically identical, and this can explain the gradually increased C—O/O—C—O ratios of modified MD samples



Scheme 1

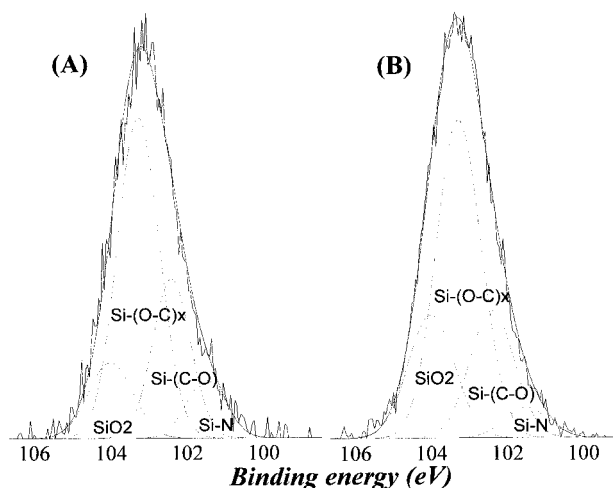


Figure 4 $\text{Si}2p$ high-resolution (HR) ESCA results of (A) 1-min plasma-treated and subsequently aminated maltodextrin (MD); (B) 5-min plasma-treated and subsequently aminated MD.

during the plasma exposure. The increased silicon and nitrogen relative surface atomic concentrations (Fig. 2, inset data) also substantiate the conclusion that C—O—Si—N linkages are produced as a result of plasma-induced surface modification and in situ amination reactions.

The $\text{Si}2p$ nonequivalent HR binding energy regions of 1-min and 5-min SiCl_4 -plasma-modified and subsequently aminated MD, exhibit the presence of a very high surface area Si—(O—C)_x (103.3 eV) peak [Fig. 4(A,B)], in addition to the

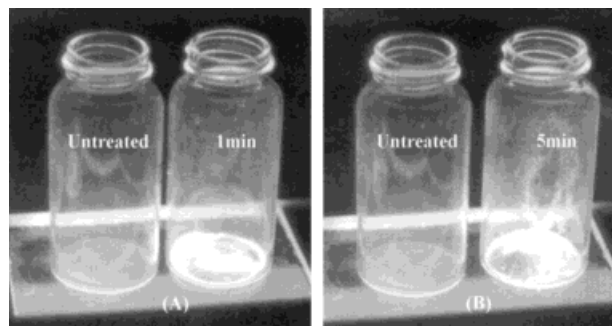


Figure 5 Fluorescamine-labeled samples: (A) Untreated and 1min-plasma-treated maltodextrin (MD); (B) untreated and 5-min plasma-treated MD.

presence of low surface area Si—C/Si—N (101.5-eV), Si—C—O (102.4-eV), and SiO_2 (104-eV) peaks. This is in good agreement with the HR $\text{C}1s$ data and allows us to suggest that the SiCl_4 -plasma-induced surface functionalization mechanism of MD were developed mainly through the formation of C—O—SiCl_x functionalities, not by involving —C—SiCl_x groups, according to the possible mechanism shown in Scheme I.

The presence of primary amine groups on the functionalized MD substrates, resulting from the in situ gas-phase reaction of ED with the SiCl_4 -plasma-treated MD, was evidenced by fluorescamine labeling technique (FA). Figure 5(A,B) shows the fluorescence images of FA-labeled MD, and 1-min and 5-min plasma-treated, consecutively aminated, and FA-labeled MDs. The intense brightness of the

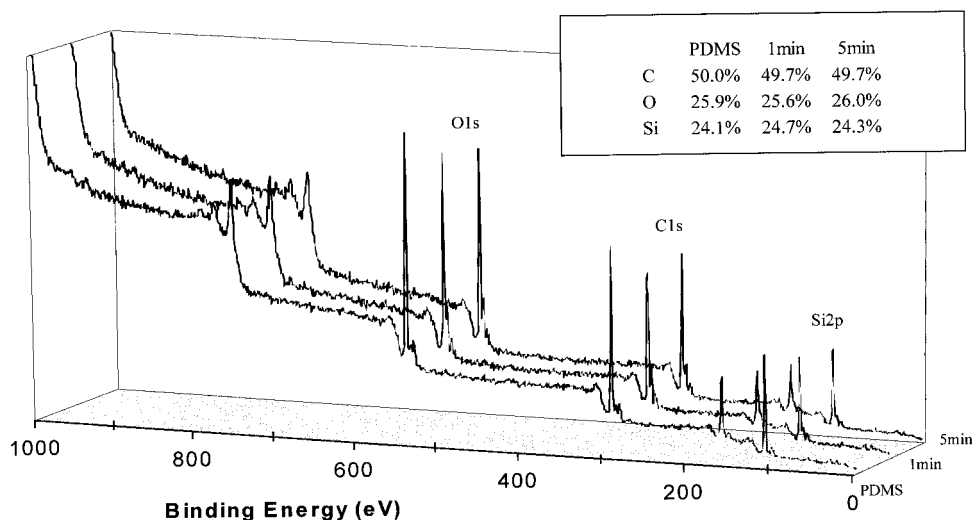


Figure 6 Survey ESCA results and the surface atomic concentrations for polydimethylsiloxane (PDMS); 1-min plasma-treated and grafted MD; and 5-min plasma-treated and grafted maltodextrin (MD).

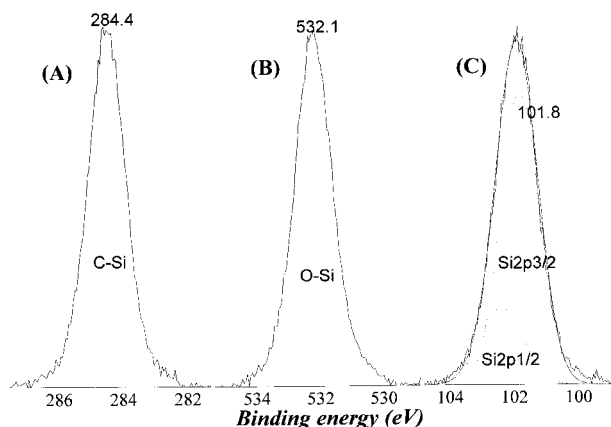


Figure 7 High-resolution (HR) ESCA spectra of polydimethylsiloxane (PDMS): (A) $C1s$; (B) $O1s$; and (C) $Si2p$.

modified substrates, as compared with MD, clearly indicates the presence of primary amine functionalities on the MD substrate surfaces.

The survey ESCA diagrams of standard PDMS graft and of ether-extracted, MD/PDMS graft copolymers resulting from 1-min and 5-min plasma treatments and subsequent amination reactions (1-MD-PDMS and 5-MD-PDMS), and the corresponding relative surface atomic concentrations are presented in Figure 6. It can be observed that the similarity between the relative surface atomic concentration of PDMS and that of the copolymers is remarkable. The nonequivalent $C1s$ carbon and $O1s$ oxygen functionalities, exhibited by the HR ESCA diagrams of PDMS and graft-copol-

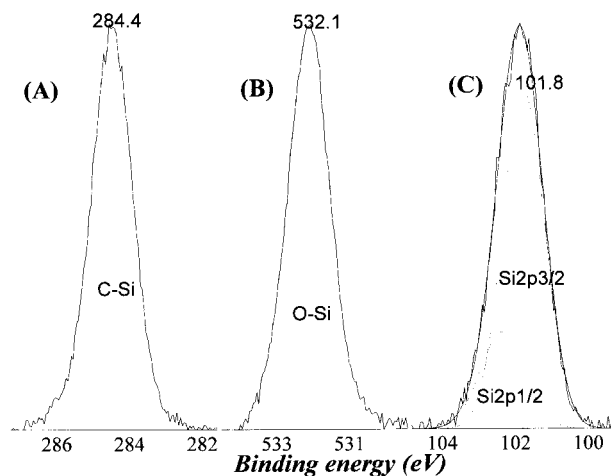


Figure 8 High-resolution (HR) ESCA spectra of 5-min plasma-treated and grafted maltodextrin (MD): (A) $C1s$; (B) $O1s$; and (C) $Si2p$.

ymers [Figs. 7(A,B), 8(A,B)], show only the presence of symmetrical C—Si (284.4 eV) and O—Si (532 eV) binding energy peaks, characteristic for PDMS structures. The $Si2p$ HR diagrams of PDMS, and 1-MD-PDMS and 5-MD-PDMS are also similar; the deconvoluted diagrams [Figs. 7(C), 8(C)] indicate the existence of $Si2p_{1/2}$ (102.4 eV) and $Si2p_{3/2}$ (101.8 eV) binding energy components.

Differential FTIR measurements of ether-extracted 1-MD-PDMS and 5-MD-PDMS polymers, performed by subtracting the IR spectrum of MD

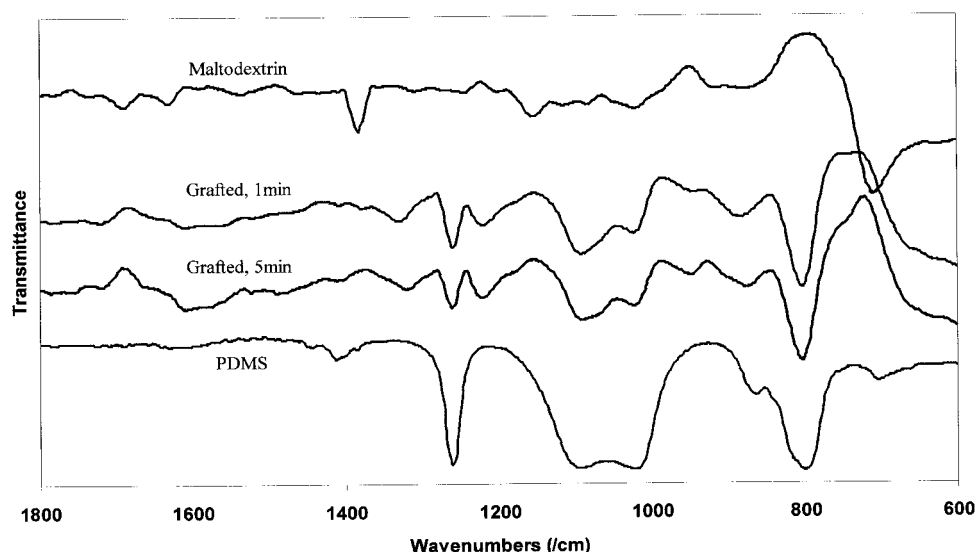


Figure 9 Subtraction FTIR spectra of untreated maltodextrin (MD), grafted MD (1-min and 5-min plasma-treated), and polydimethylsiloxane (PDMS).

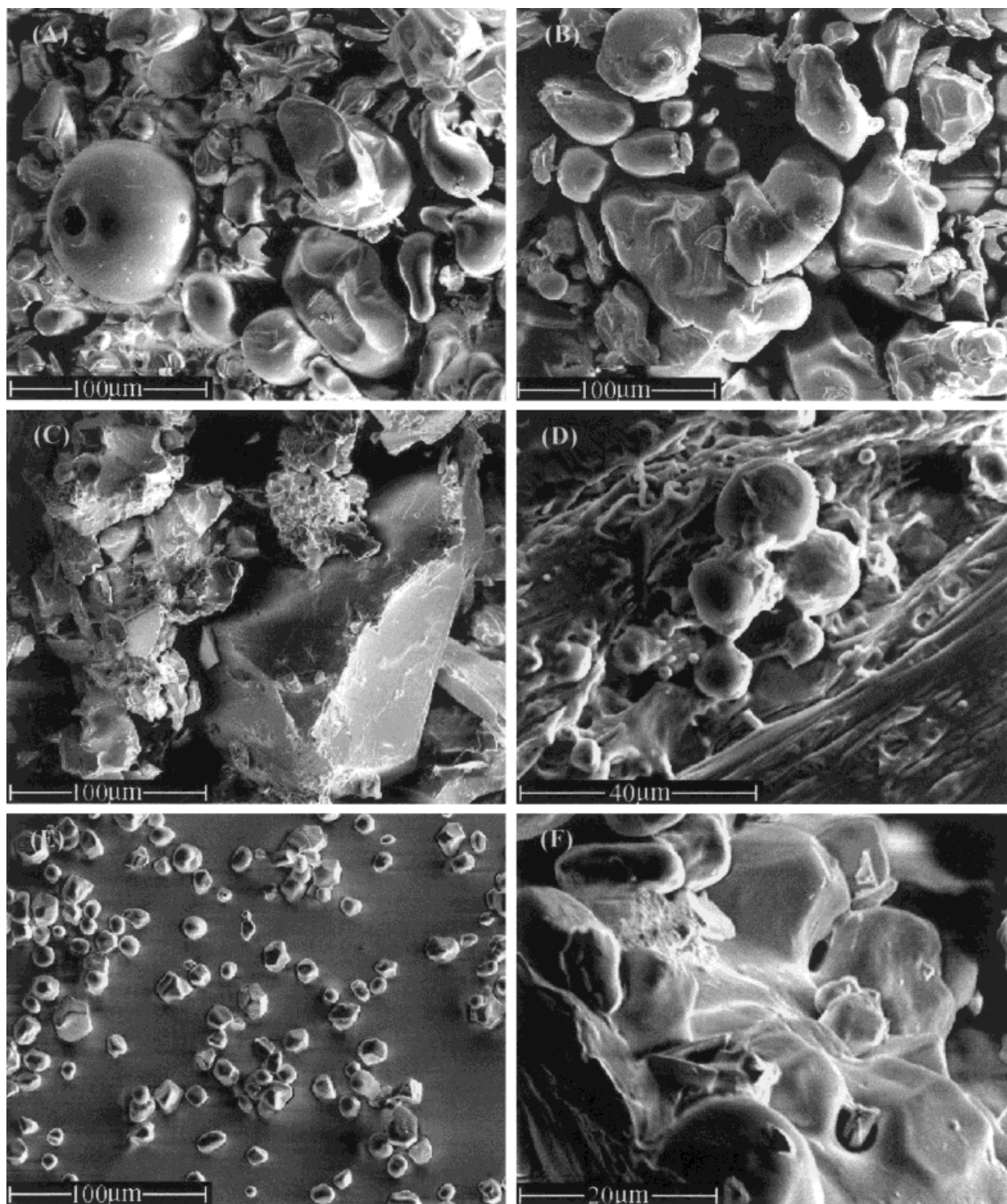


Figure 10 SEM images of (A) untreated maltodextrin (MD); (B) 5-min plasma-treated MD; (C) polydimethylsiloxane (PDMS)-grafted MD; (D) granules of PDMS-grafted MD; (E) untreated starch; and (F) plasma-treated and PDMS-grafted starch.

from the IR spectra of the graft-copolymers (Fig. 9), exhibit all characteristic absorptions of PDMS, including Si—CH₃ stretching (800 and 860 cm⁻¹), Si—CH₃ rocking (1020 cm⁻¹), Si—O stretching (1095 cm⁻¹), CH₃ rocking from Si(CH₃)₂ (1259 cm⁻¹), CH stretching from CH₃ (2904 cm⁻¹ and 2962 cm⁻¹). The IR data substantiate the earlier ESCA findings that the surfaces of MD granules have successfully been grafted with PDMS structures. For comparative reasons, starch granules have also been plasma-treated and grafted under similar experimental conditions to the modification and grafting of MD.

The surface morphologies of MD, SiCl₄-plasma-treated MD, and graft copolymers, evidenced by SEM evaluations (Fig. 10), also indicate that the globular granule formations of MD and plasma-treated MD have been replaced by chunky morphologies and coated granule structures, as a result of the grafting processes. At higher magnification, it can be clearly observed that the chunky structures of the grafted MD [Fig. 10(C)] incorporate granular and coated morphologies [Fig. 10(D)]. The fact that the granular morphologies of MD were not changed notably during the plasma exposure, allows us to suggest that the functionalization reactions involved only the surface layers of the MD granules. The absence of cleaved interfaces in the SEM images of the grafted substrates substantiates the conclusion that the MD granule surfaces were successfully grafted with PDMS structures. Intense coating of both MD [Fig. 10(C,D)] and starch [Fig. 10(F)] particles produced by plasma-enhanced surface modification and grafting can be observed.

Comparative DTA/TG data resulting from MD and grafted MD samples indicate a very different thermal behavior for the two substrates [Fig. 11(A,B)]. The thermal decomposition initiation temperature of MD is ~280°C and that the decomposition rate is very high during the first process (280–320°C) and significantly slower during the second stage (320–600°C). At 300°C, 75% of MD is lost and an more than 80% weight loss is recorded at 600°C. The DTA and DTG diagrams of MD indicate the presence of an endothermal process of ~300°C, which corresponds to the fast thermal degradation process exhibited by the TG diagram. The grafted MD substrates show three distinctive weight-loss processes (100–150°C; 200–300°C; 300–600°C). The first process is a relatively fast endothermal event and it is characterized by a weight loss of 20%, while the second and the third decomposition zones indicate

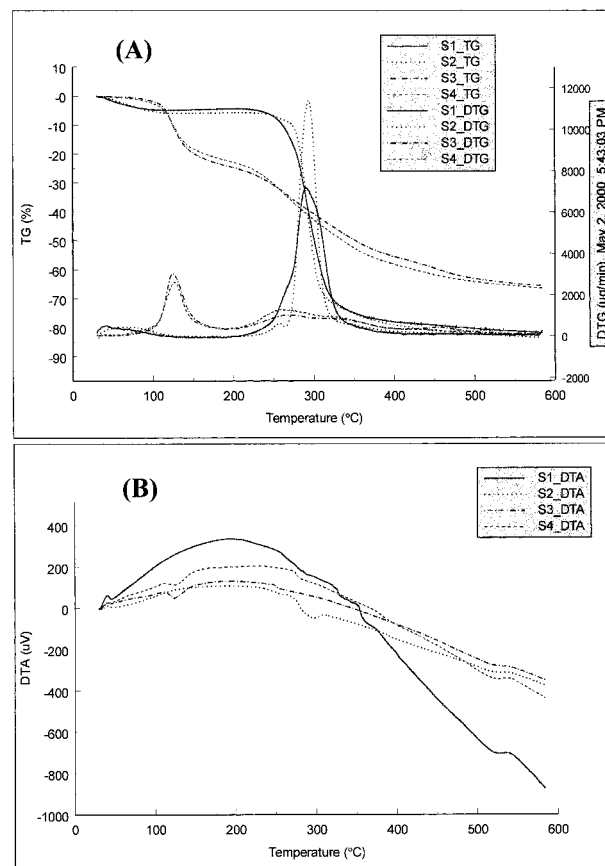


Figure 11 TG/DTG (A) and DTA (B) curves of maltodextrin (MD) (S1), starch (S2), plasma-treated and grafted MD (S3), and plasma-treated and grafted starch (S4).

the presence of significantly slower weight-loss mechanisms. At 300°C, the weight-loss of grafted MD is only 45%; at 600°C, 30% of the sample is still retained. The very different thermal behaviors of virgin and grafted MD substrates emphasize the copolymer nature of the grafted MD.

The protecting PDMS layer grafted onto MD granule surfaces is responsible for the modified characteristics of MD. The resulting graft copolymers have a hydrophobic character; they do not result in gelation (swelling) in boiling water, and the iodine test indicates negative results.

The presence of a PDMS-based hydrophobic structure on the MD granule surfaces and the new characteristics of graft copolymers make these materials very attractive as active fillers in PDMS-based composite materials.

CONCLUSIONS

Maltodextrin and starch were functionalized under SiCl₄-RF-plasma conditions and consecu-

tively grafted with polydimethylsiloxane. The plasma-enhanced implantation of SiCl_x functionalities was followed by in situ reaction with ethylene diamine for the generation of stable primary amine functionalities. Maltodextrin and starch granules bearing the primary amine groups were involved in graft copolymerization reactions using dimethyldichlorosilane and KOH as catalyst.

Survey and HR ESCA analysis, FTIR investigations, and fluorescence labeling technique demonstrated the presence of SiCl_x and Si-NH_2 functionalities on the maltodextrin and starch granule surfaces, and the existence of a polydimethylsiloxane structure in the resulting copolymers.

Ether-extracted (for the removal of homopolymeric structures) graft copolymers were characterized by differential thermal analysis and scanning electron microscopy. It was demonstrated that the thermal behavior of graft copolymers is significantly different as compared with that of maltodextrin and starch, and the electron microscopy images evidenced the presence of a transition layers between the polysaccharide granule surfaces and polydimethylsiloxane matrix. It is suggested that maltodextrin-, starch-, and polydimethylsiloxane-based block copolymers might find their applications as reinforcing components in silicon-rubber materials.

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