Surface Phosphonylation of Low-Density Polyethylene

JACQUELINE M. ALLAN,[1] R. LARRY DOOLEY,[2] SHALABY W. SHALABY[1]

[1]Poly-Med, Inc., Westinghouse Rd., Pendleton, South Carolina 29670

[2]Clemson University Bioengineering Department, Clemson, South Carolina 29634

ABSTRACT: Surface phosphonylation of thermoplastic polymers was previously demonstrated in both the liquid and gas phase. For the present study, the phosphonylation process was modified through the use of a two-chamber reactor and a dynamic oxygen flow in an effort to secure greater control of the gas phase reaction. Low-density polyethylene films were phosphonylated at both ambient and elevated temperatures for time periods ranging from 15 to 60 min. Subsequently, all films were analyzed by SEM, EDX, horizontal ATR-FTIR, surface roughness, and dynamic contact angle measurements. Analysis of the data indicates that after 15 min at ambient temperature, films do not phosphonylate to a degree that could be detected by the chosen methods. Phosphonylation was achieved at 30 and 60 min at ambient temperature, and at 60 min at 45°C. The data indicate that optimal conditions for gas phase phosphonylation in the described apparatus are 25°C for times greater than 15 min but less than 60 min. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1870–1875, 2000

Key words: polyethylene; phosphonylation; surface activation

INTRODUCTION

At the midpoint of this century, a method for the production of phosphonyl chlorides from aliphatic hydrocarbons was discovered simultaneously by Clayton, Soborovsky, and Graf.[3–5] These researchers found that the reaction of saturated hydrocarbons with phosphorus trichloride and oxygen results in phosphonylation of some of the carbon atoms in low molecular weight polyolefins such as paraffin and polyethylene grease. Subsequently, this scheme was applied for the bulk phosphonylation of higher molecular weight polymers.[6–12]

To a first approximation, saturated hydrocarbons give alkylphosphonyl chlorides by the overall reaction:[3]

$$R—H + 2PCl_3 + O_2 \rightarrow R—POCl_2 + POCl_3 + HCl$$
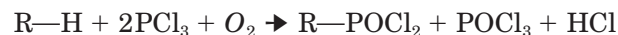
The intermediate poly(phosphonic dichloride) can easily be converted to a phosphonic amide, phosphonic ester, or, as shown below, a phosphonic acid:[3]

$$R—POCl_2 + 2H_2O \rightarrow R—PO(OH)_2 + 2HCl.$$

Production of polyolefin–phosphonic chlorides by this method is especially attractive, due to direct linkage of phosphorus to the polymer main chain by a P—C bond. The introduction of relatively small quantities of phosphorus to conventional polymers by this method can produce improvements in adhesion and dyeability as well as increases in hydrophilic properties and thermal stability.[13,14] However, phosphonylation as described above is carried out as a bulk polymer reaction and, therefore, effects notable changes in polymer properties, especially undesirable decreases in stiffness and percent elongation.[6,10]

Early efforts to surface modify polyethylene films included those of Bentjen and Sage.[5,16]

Bentjen and coworkers introduced phosphate groups, indirectly, to polyethylene surfaces through a hydroxy carboxylate functionality used as a spacer.[15] The phosphate (not phosphonate) groups were not directly linked to the polyethylene main chain as described in the present study. Sage and coworkers achieved polyethylene surface modification by exposure to oxygen, chlorine, and bromine gas under UV irradiation and by exposure to PCl$_3$ vapor.[16] However, direct phosphonylation with PCl$_3$ in the presence of oxygen as described in the present report was not addressed by these investigators.

Recently, Shalaby and coworkers developed methods for the surface activation of preformed polymeric articles using the above-described reaction.[1,2] Initially, the surface treatment scheme was devised as a liquid phase reaction in which a thermoplastic polymer was suspended in a phosphorus trichloride solution with a continuous flow of oxygen through the system.[1] A gas phase process was subsequently developed in which polymers were suspended directly over a reservoir of phosphorus trichloride in a static oxygen environment.[2] In each case, treatment resulted in the surface formation of polyphosphonic acids on thermoplastics without a concomitant change in bulk material properties.

The polyphosphonic acid surfaces so formed were then reacted with calcium containing solutions to produce calcium phosphate moities at the polymer surface.[1,17] Such surfaces approximate bioglass and hydroxyapatite, compounds with well-documented bone-binding properties.[18–21] Formation of calcium phosphates as bound moieties on present and proposed orthopedic polymers leads to the interesting possibility of direct fixation of orthopedic devices to bone without the need for an intermediate grouting material.

Previously, Shalaby and McCaig demonstrated the feasibility of gas phase surface phosphonylation of thermoplastics.[2] For the present research, the phosphonylation process itself was modified through the use of a two-chamber reactor and a dynamic oxygen flow in an effort to secure greater control of the gas phase reaction. Using this reaction scheme, this study seeks to determine the physico-chemical properties of low-density polyethylene activated by gas phase surface phosphonylation. Controlled surface activation of this model for orthopedic materials will allow for subsequent application to studies on bone binding and apposition to phosphonylated surfaces.

MATERIALS AND METHODS

Low-density polyethylene (LDPE) (Polymerland, Maumee, OH) was compression molded into films with an average thickness of $73 \pm 10 \mu$ using a Carver Model C laboratory press (Fred S. Carver, Inc., Wabash, IN). Prior to molding, the melt characteristics of the polymer were determined using a Perkin-Elmer DSC Model 6 (Perkin-Elmer, Norwalk, CT) to aid in establishing the proper melt cycle. Thin films were obtained by pressing 2.0-g LDPE pellets between 15 cm^2 stainless steel plates (Fred S. Carver, Inc., Wabash, IN), which were covered with aluminum-backed Bytac® adhesive (Norton, Akron, OH). The molding assembly was heated in the Carver press to 180°C for 15 min, at which point a load was applied at increments of 1 metric ton per minute to a final load of 11 metric tons. The press platens and molding assembly were then quenched to room temperature with running water.

The LDPE thin films were phosphonylated in the gas phase using a method initially developed by Shalaby and McCaig.[2] In an effort to simplify the experimental scheme, a two-chamber reactor was designed using standard laboratory glassware: a two neck boiling flask; gas inlet adapter; and adapted pressure filter (Kimble Kontes, Vineland, NJ). For phosphonylation, film samples were placed in the upper chamber, and the reactor was flame dried under reduced pressure and purged with oxygen (Holox Ltd., Greenville, SC). The oxygen flow rate through the reactor was set at 30 mL/min, and 5 mL phosphorus trichloride (PCl$_3$) (Aldrich, Milwaukee, WI) was added to the lower chamber. Phosphonylations were carried out for 15, 30, and 60 min after addition of PCl$_3$ at room temperature and for 60 min at 45°C. For reaction temperatures above ambient, the lower chamber was submerged in an oil bath which was heated using a Digi-Set-Temp (Laboratory Devices, Inc., Holliston, MA).

After phosphonylation, the films were removed from the reactor, immersed in distilled water, and sonicated in a Branson Model 3210 Ultrasonic Cleaner (Branson Ultrasonics Corp., Danbury, CT) for 60 min. Finally, the films were dried under reduced pressure at 37°C for at least 3 h and stored under argon (Holox Ltd., Greenville, SC).

In an effort to fully profile the physico-chemical properties of the phosphonylated films, several characterization techniques were employed. Initially, the surface was imaged by scanning elec-

tron microscopy (SEM) using a JEOL JSM-IC848 electron microscope (JEOL, Peabody, MA). Surface elemental analysis was obtained via electron dispersive X-ray (EDX) (JEOL) with semiquantitative assessment of the amounts of phosphorus and chlorine present in each film group. Horizontal attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Perkin-Elmer Paragon 1000 spectrophotometer (Perkin-Elmer) to elucidate binding modes of phosphonate groups to the thermoplastic surface.

In an effort to quantify surface variations for different reaction conditions, surface roughness and dynamic contact angles were measured. Surface roughness values were measured using a WYKO NT 2000 Profilometer (Veeco Corp., Tuscon, AZ). Roughness measurements were taken in vertical scanning interferometry mode at a magnification of 25×. The root-mean-square roughness, R_q, and average maximum height of the profile, R_z, were used to compare overall roughness of the different film surfaces.[22]

Advancing contact angles were measured using the Wilhelmy plate method in conjunction with the Young equation, $\theta = \cos^{-1}[F/(p \cdot \gamma_L)]$, where F is the force of the meniscus of the liquid at the film interface, p is the length of the interface (i.e., perimeter of the sample), and γ_L is the surface tension of the liquid.[23] Small film samples ($\sim$0.25 × 0.5 cm^2) were immersed in a liquid reservoir at a rate of 3 μ/min. The force was measured using a Cahn DCA 322 microbalance (Cahn Instruments, Inc., Cerritos, CA) as the liquid in contact with the specimen was raised. Films were tested in both HPLC grade water and methylene iodide (Aldrich, Milwaukee, WI) for comparison of behavior in polar and nonpolar solvents, respectively.

For all tests detailed above, five measurements were taken per group, with the exception of dynamic contact angles for which four measurements were taken. Statistical analysis was accomplished using SAS® System for Windows™ Release 6.12 (SAS Institute, Inc., Cary, NC). Fisher's least-significant difference procedure was applied to the data sets to determine statistically significant differences between groups at α = 0.05.

RESULTS AND DISCUSSION

Past gas phase phosphonylation experience using a single-chamber static reactor indicated that, while the set up was effective, the process could be difficult to regulate, and the resulting treatment was often times more severe than desired.[24] Design of a two-chamber dynamic reactor provided the process with the control it previously lacked. This system was implemented at the onset of these studies, and allowed for a more precise regulation of the phosphonylation reaction.

Initially, treated films were assessed using SEM; representative photographs are shown in Figure 1. The control polyethylene surface appears essentially smooth, with small artifactual lines formed during the molding process [Fig. 1(a)]. After 15 min phosphonylation time, the treated surface closely resembles the control [Fig. 1(b)], a first indication that the LDPE film surface did not phosphonylate to a detectable degree within the first 15 min of PCl$_3$ addition to the reactor. At 30 min, the surface is notably roughened [Fig. 1(c)], and at 60 min it is pitted [Fig. 1(d)]. This pitting suggests that the surface experiences local delamination at sites that are phosphonylated to an excess. After 60 min treatment at 45°C, the surface is markedly roughened [Fig. 1(e)]. The material experiences bulk phosphonylation and, therefore, does not exhibit the same pitting seen in the 60-min room temperature reaction.

EDX spectra of the control and treated surfaces indicate the absence of phosphorus and chlorine on the control and 15-min treatment groups, and the presence of these elements on all other surfaces. More revealing than the EDX spectra is the semiquantitative analysis computed from five such spectra for each treatment group. These average values and corresponding standard deviations are printed in Table I. For all cases, the amount of chlorine present is quite low—only a fraction of a percentage—indicating that samples were adequately hydrolyzed following phosphonylation.

At 15 min phosphonylation time, the surface does not show phosphorus above the amount detected in the control film, again an indication that the LDPE film does not phosphonylate to a detectable degree in this time period. At 30 min treatment, the film surface is composed of approximately 10% phosphorus. Polyphosphonic acids obtained after hydrolysis are highly hydrophilic, and previous research has shown that these moieties dissolve in water at phosphorus contents in excess of 10%.[25] Therefore, the fact that at 60 min treatment time the phosphorus content decreases to 6% is of no surprise; isolated surface hydrocar-
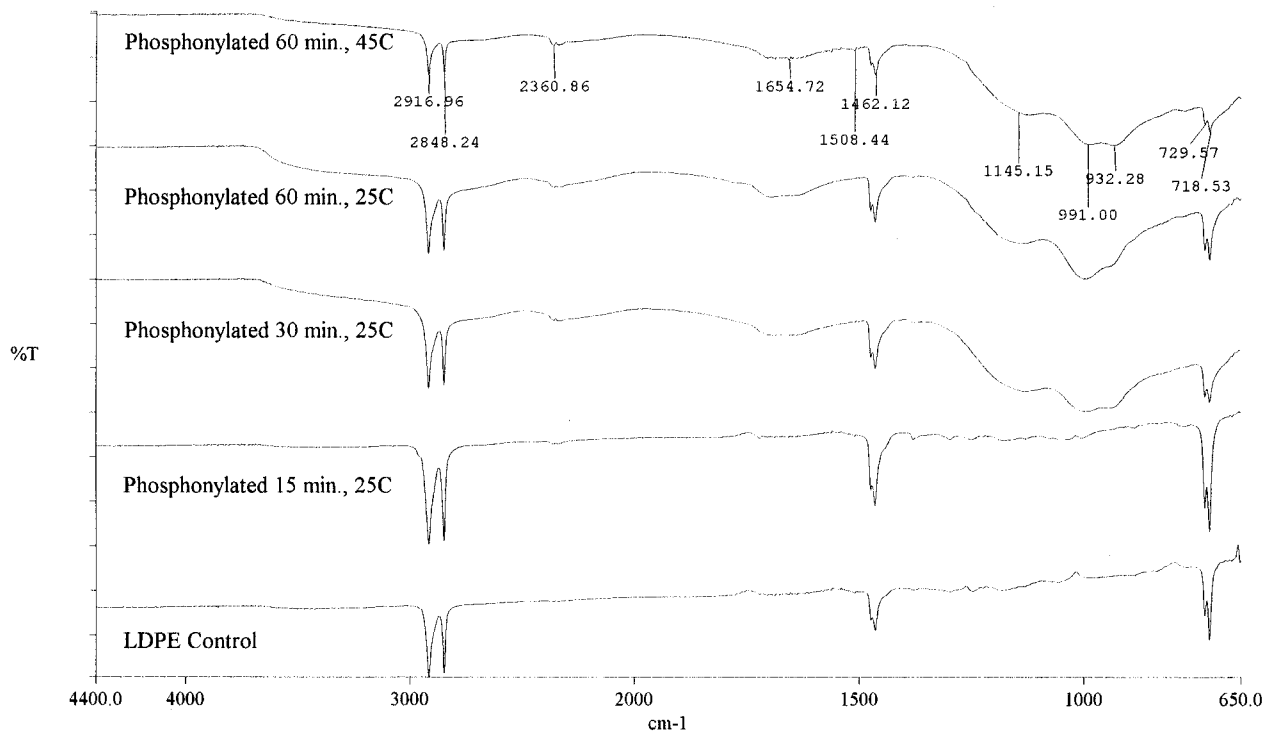
Figure 1 Figuire SEMs of phosphonylated LDPE.

bon chains are excessively phosphonylated, and pulled from the bulk during hydrolysis. Solubilization of over phosphonylated surface molecules upon hydrolysis is consistent with pitting of this film group seen using SEM. Finally, the highest phosphorus incorporation, i.e., 13%, is achieved for 60 min phosphonylation at 45°C, indicating that the material is phosphonylated well below the surface without the concomitant solubilization of overphosphonylated surface molecules.

Horizontal ATR-FTIR spectra of representative control and phosphonylated films are shown in Figure 2; these spectra validate the above stated observations. That is, at 15 min phosphonylation time, the horizontal ATR-FTIR spectrum

is identical to that of the control, with no evidence of phosphonylation. For all other groups, spectra indicate apparent surface modification with the same characteristic peaks present for 30, 60, and 60 min at 45°C treatments. Spectra of phosphonylated surfaces collected in this research are in close agreement with those obtained by other researchers.[1,2,15,26,27] The P—O—H group has four characteristic frequencies: 2525 to 2725, 2080 to 2350, 1600 to 1740, and 917 to 1040 cm^{-1}.[26,27] As seen in the figure, the first of these frequencies appears as a slight shoulder on the spectra, while the last three are readily apparent. Coupled with the identification of phosphorus at the surface, these spectra provide conclusive evidence that phosphonic acid moieties exist on the surfaces phosphonylated for more than 15 min.

Average surface roughness measurements and corresponding standard deviations are shown in Table II. The film treated for 15 min essentially shows the same roughness as the control, once again indicating that it was not phosphonylated to a detectable degree. For 30- and 60-min phosphonylation times at room temperature, the surface roughness values are similar to each other, and are both notably rougher than the control. Phosphonylation does, therefore, cause a physical

Table I Elemental Surface Analysis of Phosphonylated LDPE

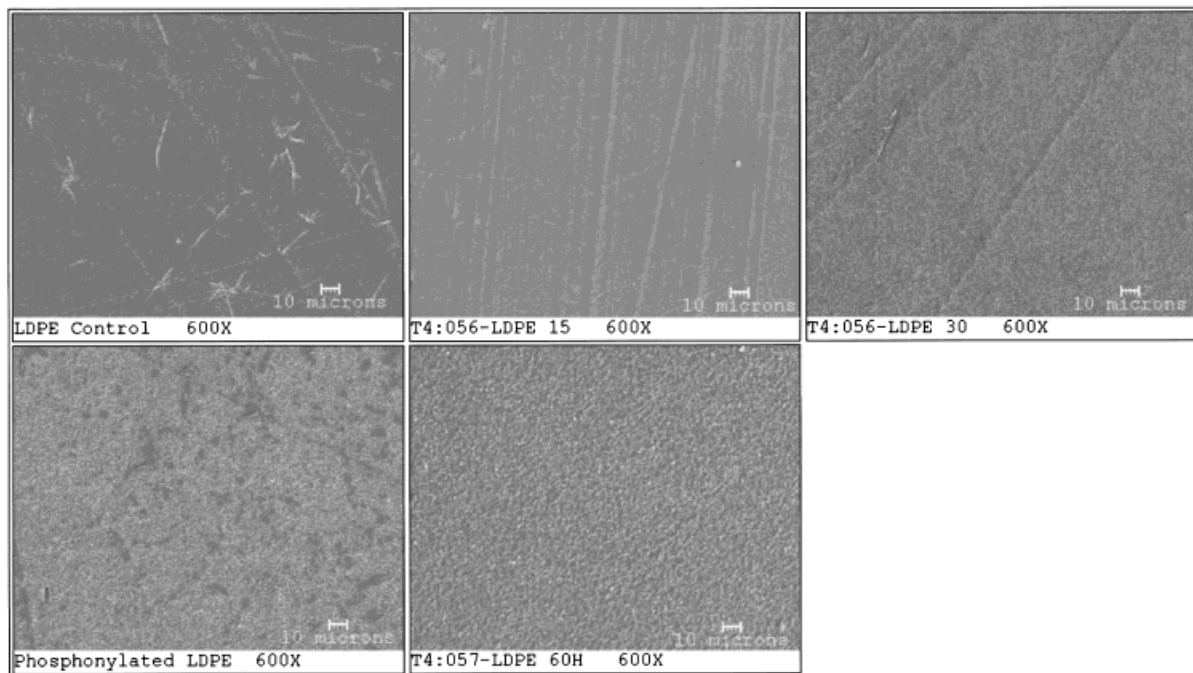| Reaction Time (min)	Reaction Temp. (°C)	%P (avg. ± SD)	%Cl (avg. ± SD)
0	—	0.20 ± 0.01	0.04 ± 0.07
15	25	0.26 ± 0.04	0.04 ± 0.03
30	25	9.50 ± 1.39	0.22 ± 0.03
60	25	6.13 ± 0.68	0.27 ± 0.02
60	45	13.65 ± 0.49	0.35 ± 0.04

Figure 2   Horizontal ATR-FTIR spectra of control and phosphonylated LDPE films.

change in the polymer surface, as also noted from the SEMs, in addition to the known chemical modification. Also, while excessively phosphonylated molecules of the 60-min treatment group delaminate from the surface, the overall surface roughness does not change substantially due to this process. Finally, for 60 min treatment at 45°C, both the average roughness and peak-to-valley height are substantially greater than those of other treatment groups, which is consistent with the theory that the treatment is effected toward the bulk material and not limited to the surface.

Dynamic contact angle measurements must be considered in conjunction with the physico-chemical differences of the surfaces described above;

the average contact angles and corresponding standard deviations are listed in Table III. As expected, water proved to be the superior probe liquid for discriminating differences in the treated and untreated surfaces, while methylene iodide was none too revealing. This is due to the fact that phosphonylation renders the polymer surface hydrophilic, and water, a polar liquid, is quite responsive to this change, while methylene iodide, a nonpolar liquid, is not. Therefore, treatments are discussed in terms of their advancing dynamic contact angle in water.

Consistent with the aforementioned note that 15-min treatment time was insufficient to effect a change of the polymer surface, the contact angle

Table II   Surface Roughness Measurements of Phosphonylated LDPE

Reaction Time (min)	Reaction Temp. (°C)	R_q (nm) (avg. $\pm$ SD)	R_z (μm) (avg. $\pm$ SD)
0	—	75.59 $\pm$ 4.61	1.40 $\pm$ 0.33
15	25	78.02 $\pm$ 20.88	1.23 $\pm$ 0.30
30	25	127.19 $\pm$ 20.48	1.90 $\pm$ 0.27
60	25	130.43 $\pm$ 23.85	1.81 $\pm$ 0.46
60	45	201.42 $\pm$ 12.75	2.81 $\pm$ 0.19

Table III   Contact Angle Measurements of Phosphonylated LDPE

Reaction Time (min)	Reaction Temp. (°C)	Water (°) (avg. $\pm$ SD)	Methylene Iodide (°) (avg. $\pm$ SD)
0	—	96.81 $\pm$ 1.48	69.32 $\pm$ 1.39
15	25	93.49 $\pm$ 1.12	78.45 $\pm$ 2.95
30	25	52.19 $\pm$ 2.08	67.15 $\pm$ 2.28
60	25	56.36 $\pm$ 6.06	66.47 $\pm$ 4.44
60	45	50.70 $\pm$ 1.81	64.02 $\pm$ 2.27

in water of this group is virtually the same as the control film. As the surface is phosphonylated, it becomes hydrophilic, which results in a significant decrease of the contact angle measured in water for 30- and 60-min treatment times at room temperature as well as the 60-min treatment at 45°C. Meanwhile, among the three phosphonylated groups, there is essentially no difference between the measured contact angles, even though the roughness data and elemental analysis point to dissimilarities in these surfaces. Of all the analyses conducted on these films, surface roughness and dynamic contact angle measurements are the most surface sensitive for assaying only the outermost layers of the surface. Elemental analysis using EDX is somewhat less sensitive, probing one to two microns into the material. The above-noted trends in the data coupled with knowledge of the analytical techniques suggest that, in the present scenario, the dynamic contact angle is most sensitive to the chemical characteristics of the film and less so to its physical structure. Although elemental analysis revealed differences in degree of phosphonylation that dynamic contact angle does not, this can be attributed to the fact that EDX probes a deeper layer of the film. At the film surface, the three surface phosphonylated materials are, most probably, similar in chemical structure, thereby accounting for the similar contact angles.

CONCLUSIONS

Using a two chamber, dynamic flow system, phosphonylation of LDPE can be regulated to control the extent and uniformity of surface modification. Under the prevailing reaction conditions, LDPE films do not phosphonylate to a detectable degree at 15 min using the above-noted characterization methods. Within 30 min, the surface phosphonylates, and at 60 min, the surface overphosphonylates at localized sites with concomitant surface pitting observed. Phosphonylation at 45°C results in phosphonylation of the material as a bulk as opposed to a treatment limited to the surface. Overall, gas phase phosphonylation of LDPE is best regulated at 25°C, with reaction times greater than 15 min but less than 60 min providing the most uniform surface treatment.

REFERENCES

1. Shalaby, S. W.; Rogers, K. U.S. Pat. 5,558,517 (1996).
2. Shalaby, S. W.; McCaig, S. U.S. Pat. 5,491,198 (1996).
3. Clayton, J. O.; Jensen, W. L. J Am Chem Soc 1948, 70, 3880.
4. Soborovsky, L. Z.; Zinovyev, Y. M.; Englin, M. A. Dokl Akad Nauk SSSR 1949, 67, 293.
5. Graf, R. Chem Ber 1952, 85, 9.
6. Schroeder, J. P.; Sopchak, W. P. J Polym Sci 1960, 47, 417.
7. Hotton, B. W.; Johnson, F. O. U.S. Pat. 2,837, 480 (1958).
8. Kuznetsov, E. V.; Devitaeva, R. S. Tr Kazansk Khim Tekhnol Inst 1962, 30, 63.
9. Leonard, E. C.; Loeb, W. E.; Mason, J. H.; Wheelwright, W. L. J Appl Polym Sci 1961, 5, 157.
10. Rafikov, S. R.; Chelnokova, G. N.; Ergebekov, M. E.; Ershova, T. V. Vysokomolekul Soedin 1965, 7, 65.
11. Sumita, Y.; Seko, M.; Misumi, T.; Ogawa, S. Jpn. Pat. 7197/61.
12. Yyolles, S. U.S. Pat. 2,829,137 (1958).
13. Sander, M.; Steininger, E. J Macromol Sci Rev Macromol Chem 1968, 2, 57.
14. Corbridge, D. E. C. In Studies in Inorganic Chemistry: Phosphorus an Outline of Its Chemistry, Biochemistry and Technology; Elsevier: New York, 1990, p. 653.
15. Bentjen, S. B.; Nelson, D. A.; Tarasevich, B. J.; Rieke, P. C. J Appl Polym Sci 1992, 44, 965.
16. Sage, D., et al. Angew Makromol Chem 1976, 54, 151.
17. Cambell, C. Doctoral Thesis, Clemson University, Clemson, SC (1996).
18. Hench, L. L.; Paschall, H. A. J Biomed Mater Res Symp 1973, 4, 25.
19. Hench, L. L.; Ethride, E. C. In Biomaterials: An Interfacial Approach; Academic Press: New York, 1982, p. 71.
20. Holmes, R. E.; Hagler, H. K. J Oral Maxillofac Surg 1987, 45, 421.
21. Geesink, R. G.; de Groot, K.; Klein, C. P. Clin Orthop 1987, 225, 147.
22. Schey, J. In Encyclopedia of Materials Science and Engineering; Bever, M. B., Ed.; The MIT Press: Cambridge, MA, 1986, p. 4806.
23. Lloyd, T. B.; Dwight, D. W. In Characterization of Polymers; Tong, H.; Kowalczyk, S. P.; Saraf, R.; Chou, N. J., Eds.; Butterworth-Heinemann: Boston, MA, 1994, p. 156.
24. Allan, J. M. Masters Thesis, Clemson University, Clemson, SC (1994).
25. Isbell, A. F.; Wadsworth, F. T. J Am Chem Soc 1956, 78, 6042.
26. Rafikov, S. R.; Chelnokova, G. N.; Yergebekov, M. Ye.; Yershova, T. V. Polym Sci USSR 1965, 7, 67.
27. Weiss, R. A.; Lenz, R. W.; MacKnight, W. J. J Polym Sci 1977, 15, 1409.