Development of a Bilayer Coating to Improve the Adhesion between Stainless Steel and In Situ-Polymerized Poly(methyl methacrylate)

Sergio A. Pellice, Diana P. Fasce, Roberto J. J. Williams

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), 7600 Mar del Plata, Argentina

ABSTRACT: A bilayer coating was developed that may be applied over a stainless steel surface to enhance the adhesive strength with *in situ*-polymerized poly(methyl methacrylate). The first layer was an epoxy based on diglycidyl ether of bisphenol A (DGEBA) crosslinked with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS). A prereaction and a fast cure were needed to avoid phase separation after the dip coating process. The second layer constituted of an organic–inorganic hybrid formulation synthesized by a sol-gel process. It was based on 2-hydroxyethylmethacrylate (HEMA), 3-methacryloxypropyltrimethoxysilane (MPMS), and tetraethoxysilane (TEOS). This layer provided silanol groups to react with the methoxysilane groups of the first layer and methacrylate groups to produce covalent bonds during the methyl methacrylate polymerization. Stainless steel plaques were successively coated with both layers (about 700 nm per layer), using a dip coating process. Both coated and uncoated plaques were bonded with a 0.55-mm thickness of a two-parts PMMA cement, using the standard geometry to perform single lap-shear strength tests. The average lap-shear strength increased from 3.4 ± 1.5 MPa for the uncoated metals to 9.7 ± 1.5 MPa for the plaques coated with the bilayer system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2351–2356, 2007

Key words: adhesion; coatings; damage zone; microlayers; shear

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is becoming successful in different fields of applications including water tunnels, wind protection, automotive parts, etc. In some of these applications a good adhesion between PMMA and a metal is required. This is particularly evident in the use of PMMA as a cement of the metal stem of hip prostheses.[1–3] It has been shown that debonding of the metal stem-PMMA interface is the initial event of loosening in cemented hip prostheses.[1–3]

Strong interfaces can be created through the use of coupling agents that increase the adhesion strength by chemical bonds.[4,5] They have been used to improve the strength of a metal-PMMA interface by first coating the metallic surface with a silica layer followed by a second layer containing an organosilane coupling agent (usually 3-methacryloxypropyltrimethoxysilane).[6–8] The organosilane covalently bonds to the silanol groups of the silica layer and to the PMMA-cement formulation through the copolymerization of methacrylate groups. The silica layer was generated by pyrolysis,[6] by sol-gel reactions at 340°C,[7] or by chemical vapor deposition.[8] In every case, an improvement of the adhesive strength of the joint was obtained.

The aim of this study was to analyze the possibility of improving the adhesion between *in situ*-polymerized PMMA and a stainless steel surface, using the bilayer concept but replacing the first silica layer by an epoxy/silane formulation. In principle, this should enable to make use of the excellent adhesion of epoxies to metals while providing alkoxysilane groups for the covalent bonding to the second layer. There is, however, a problem related to the incompatibility of typical epoxy formulations with the siloxane skeleton, leading to a phase separation.[9–11] It will be shown that by a convenient selection of process variables it is possible to avoid phase separation and generate a homogeneous epoxy/silane coating over a steel surface using dip coating. A second layer containing silanol and methacrylate groups and showing excellent wettability with the first layer was then generated. The improvement of
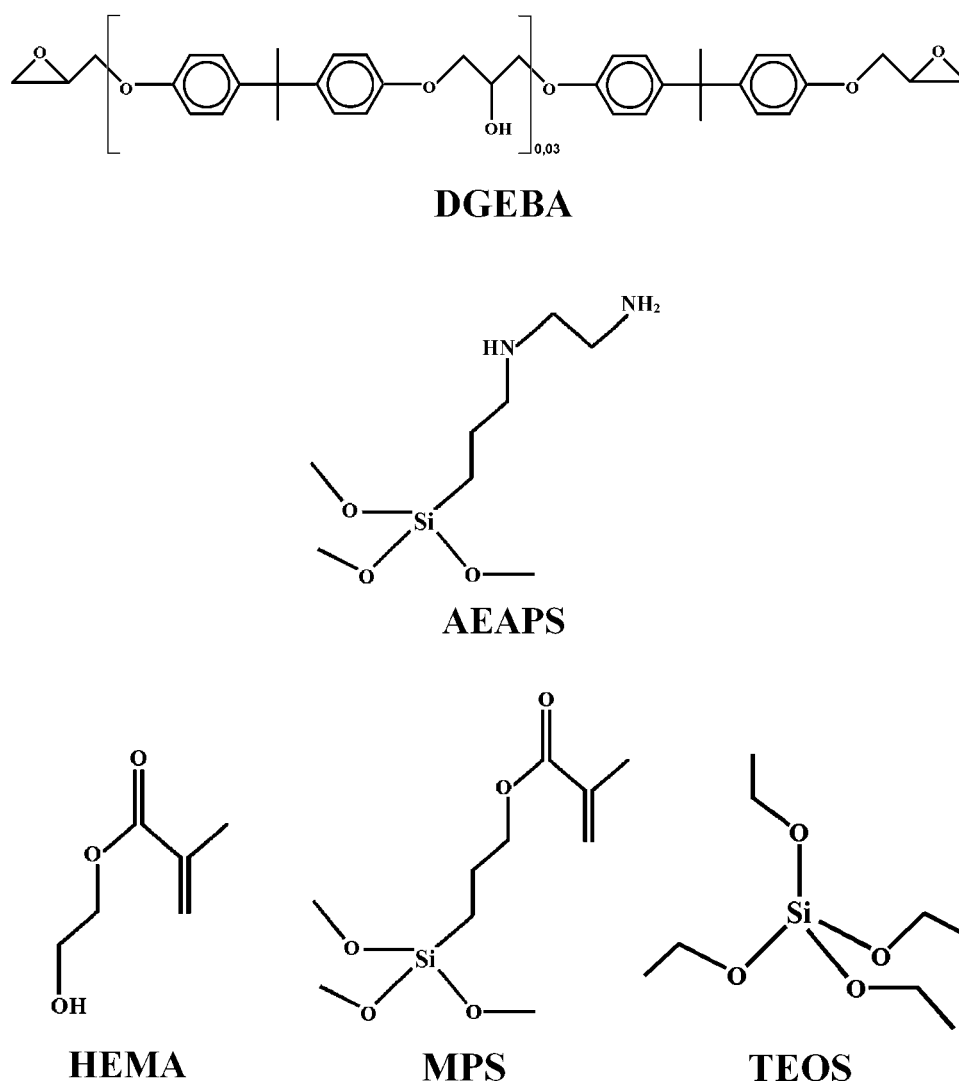
Figure 1 Chemical structures of the monomers used to generate the bilayer coating.

the adhesive strength of a stainless steel-PMMA interface using the bilayer coating was analyzed with single lap-shear strength tests. A commercial PMMA-cement was polymerized at 37°C to mimic the possible use of the bilayer coating in metallic prostheses inside the human body. Obviously, to explore further this possibility would require testing important factors such as biocompatibility issues, hydrolytic stability, and fatigue resistance.

EXPERIMENTAL

Materials

Stainless steel plaques (AISI 304L) (110 × 25 × 1.45 mm^3) were degreased with a commercial detergent and ultrasonically cleaned with isopropanol. The commercial PMMA cement (Subiton, Buenos Aires, Argentina) was based on a formulation of two parts of a powder (87.6% poly(methyl methacrylate), 10% BaSO$_4$ and 2.4% benzoyl peroxide) and 1 part of a

liquid (98.8% methyl methacrylate, 1.2% N,N-di-methyl-p-toluidine and 20 ppm hydroquinone). The epoxy/silane hybrid coating was based on the reaction of diglycidylether of bisphenol A (DGEBA, Ciba MY790, Basel, Switzerland; epoxy equivalent weight equal to 174 g/mol), with N-(2-aminoethyl)-3-amino-propyltrimethoxysilane (AEAPS, Aldrich, Buenos Aires, Argentina; 97% purity). The precursor sol for the second layer was synthesized employing 2-hydroxyethylmethacrylate (HEMA, Aldrich, 97%), 3-methacryloxypropyltrimethoxysilane (MPMS, ABCR, Karlsruhe, Germany, 98%), and tetraethoxysilane (TEOS, ABCR, 98%). Chemical structures of the different monomers are shown in Figure 1. Isopropanol was employed as solvent and a 0.1N nitric acid solution was used as a catalyst and as a source of water for the hydrolysis and polycondensation. A partial polymerization of C=C bonds was performed using 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich, 98%) as initiator.
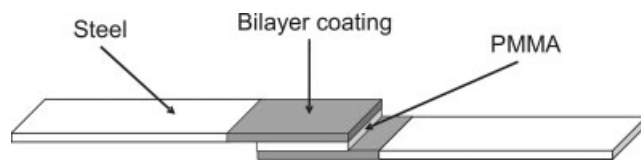
Figure 2 Joint prepared to perform lap-shear strength tests.

Characterization techniques

Near-infrared spectroscopy (NIR) was used to follow the reaction of DGEBA with AEAPS. An FTIR (Genesis II, Mattson, Madison, WI), provided with a heated transmission cell (HT-32, Spectra Tech, Thermo Fisher Scientific, Waltham, MA) with quartz windows (32 mm diameter) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T = \pm 1°C$), was employed. The sample was placed in a polyethylene bag inserted between the quartz windows (polyethylene did not exhibit absorption peaks in the spectral range of interest). The reaction was carried out at 50°C following the area of the absorption peak at 4528 cm^{-1} (assigned to the conjugated epoxy CH$_2$ deformation band with the aromatic CH fundamental stretch), with respect to the area of a reference band at 4620 cm^{-1} (assigned to a combination band of the aromatic conjugated C=C stretch with the aromatic CH fundamental stretch).[12,13] Fourier Transformed infrared spectroscopy (FTIR 1760X, Perkin-Elmer, Wellesley, MA) was used to study the evolution of the concentration of C=C bonds during the organic polymerization of the sol synthesized for the second layer. Micro-droplets were placed between KRS5 crystals (TlBr/TlI) and the scans were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} and acquisition of 1 cm^{-1} in transmission mode. The conversion of C=C groups was determined from the ratio between the areas of the C=C peak at about 1630 cm^{-1} and the C=O peak at 1700–1735 cm^{-1}.

Phase separation produced during formation of the epoxy/silane layer was observed using scanning electron microscopy (SEM, Philips 505, Eindhoven, Holland), after coating with a fine gold layer.

Thicknesses of the first layer and of the bilayer coating were measured with a profilemeter (Talystep, Taylor Hobson, Leicester, England).

Preparation of joints for single lap-shear strength tests

Joints for single lap-shear strength tests (Fig. 2) were prepared with dimensions indicated in the ASTM D 3164-92a standard. The overlapping area was 25 × 15 mm^2 and the PMMA cement layer had a thickness of 0.55 mm. Once the PMMA cement was applied the desired thickness was fixed by a spacer

and a slight pressure was applied holding both plaques with a clamp. The assemblies were placed in an oven at 37°C for 7 days before performing the mechanical test. A total of 10 joints were prepared, five for uncoated steel plaques and another five for plaques coated with the bilayer system.

Single lap-shear strength tests

Single lap-shear strength tests were performed at 20°C with a universal testing machine (Instron 4467, Norwood, MA), at a rate of 1.27 mm/min. The shear strength was calculated as the ratio between the maximum force and the bonding area. Debonded surfaces were inspected to analyze the failure mechanisms.

RESULTS AND DISCUSSION

The epoxy/silane layer

As DGEBA is a difunctional monomer (two epoxy groups per molecule, Fig. 1) and AEAPS is a trifunctional comonomer (three amine hydrogens per molecule, Fig. 1), their reaction in stoichiometric proportions leads to a polymer network, with a theoretical gel conversion of 70.7%.[14] However, methoxy groups of AEAPS may react with the hydroxyl groups generated in the epoxy-amine reaction leading to Si—O—C bonds with elimination of methanol. Intermolecular reactions of this type produce a decrease in the gel conversion. When monomers were dissolved in a convenient solvent the reaction advanced slowly at room temperature. Depending on the solvent and the initial concentration either precipitation of polymeric species or the formation of a homogeneous gel was observed. Dip coating could be carried out from the homogeneous solution during the pregel period. However, the resulting coating became opalescent after a few minutes due to a phase separation process induced by solvent evaporation.

Different ways were investigated to produce homogeneous coatings. The technique that was finally adopted consisted in producing a fast gelation of the material after dip coating so that phase separation was kinetically avoided by the rapid formation of a polymer network in a medium containing a high solvent concentration. The fast gelation was the result of two factors: (a) prereaction of DGEBA-AEAPS, (b) introduction of the coated stainless steel plaque in an oven at 120°C immediately after the dip coating process, to produce a fast polymerization.

The following procedure was used. A nonstoichiometric formulation of DGEBA (0.75 mol) and AEAPS (2 mol) was reacted in bulk at 50°C and the epoxy peak at 4528 cm^{-1} was followed by near-infrared spectroscopy. Figure 3 shows the epoxy band and
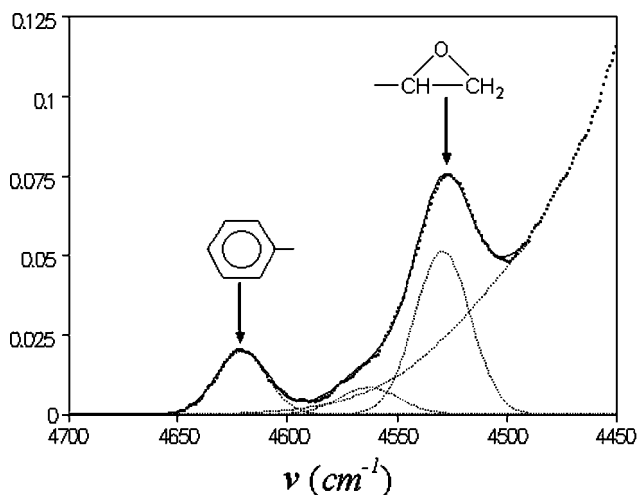
Figure 3 Epoxy and reference bands in near-infrared spectra.

the reference band at 4620 cm^{-1} for a partially reacted sample. After 3 h a conversion of epoxy groups higher than 95% was attained (calculated as the ratio of the areas of the epoxy and the reference bands). Gelation did not occur due to the high excess of amine over epoxy groups. The remaining amount of DGEBA (2.25 mol) necessary for the stoichiometric balance was added, and the resulting product was dissolved in tetrahydrofuran (THF) to obtain a 15 wt % solution.

Stainless steel plaques were immersed in this solution and extracted at 25 cm/min. Immediately after extraction the plaques were placed in an oven at 120°C for 1 h, to complete the epoxy-amine reaction. This procedure led to homogeneous and transparent coatings. When the plaques were kept for several minutes at room temperature before placing them in the oven, solvent evaporation produced a phase separation as shown in Figure 4.

The thickness of the epoxy/silane layer obtained under these conditions was close to 700 nm. The methoxysilane groups might be partially converted to silanol groups by reaction with ambient humidity during storage. But this is not important because both methoxysilane and silanol groups react with silanol groups of the second layer to generate Si—O—Si covalent bonds between both layers.

Second layer

The formulation used to generate the second layer was empirically adjusted to obtain an excellent wettability of the stainless steel substrate precoated with the first layer.

The following procedure was finally adopted. In a first step, a solution of TEOS, MPMS, and HNO$_3$ 0.1N in isopropanol at an equivalent concentration

of 0.15 g SiO$_2$/cm^3, was prepared, with a molar ratio TEOS (0.6 mol): MPMS (0.1 mol): water (1.35 mol). Hydrolysis and condensation reactions were produced at 50°C for 3 h in a closed reactor to give a sol functionalized with methacrylic groups. In a second step, HEMA (0.30 mol) and AIBN (0.004 mol) were added to the precondensed sol together with an extra amount of isopropanol to reach an equivalent concentration of 0.04 g SiO$_2$/cm^3. The solution was held at 65°C in a closed reactor for 5 h. During this period a free-radical copolymerization of methacrylic groups of HEMA and MPMS took place. This produced the partial covalent bonding of HEMA to the sol a fact that led to an excellent wettability of the precoated substrate. As it was necessary to keep a significant fraction of unreacted methacrylic groups available to react with methyl methacrylate during formation of the adhesive joint, the free-radical copolymerization of HEMA and MPMS was followed by FTIR as described in the experimental section. After 5 h at 65°C the conversion of methacrylic groups was close to 25%. At this time the resulting sol was cooled to room temperature significantly reducing the free-radical polymerization rate.

Stainless steel plaques that had already been precoated with the epoxy/silane layer were immersed in the resulting solution and extracted at 25 cm/min to generate the second layer. Drying of the second layer was performed at room temperature. Its thickness was also close to 700 nm. An excellent adhesion of the second layer over the first one was observed, leading to uniform and transparent bilayer coatings with both layers of approximately the same thickness.
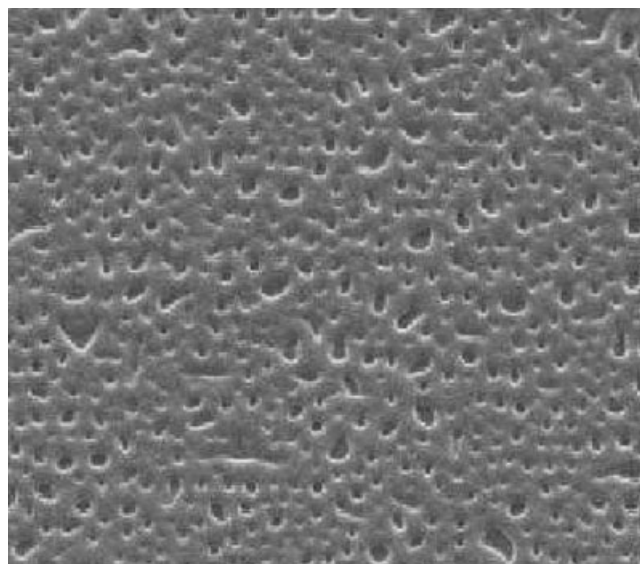
Figure 4 SEM micrograph of an epoxy/silane layer kept during 4 min at room temperature after the dip coating process, and placed in an oven at 120°C during 1 h. The width of the micrograph is 20 μm.
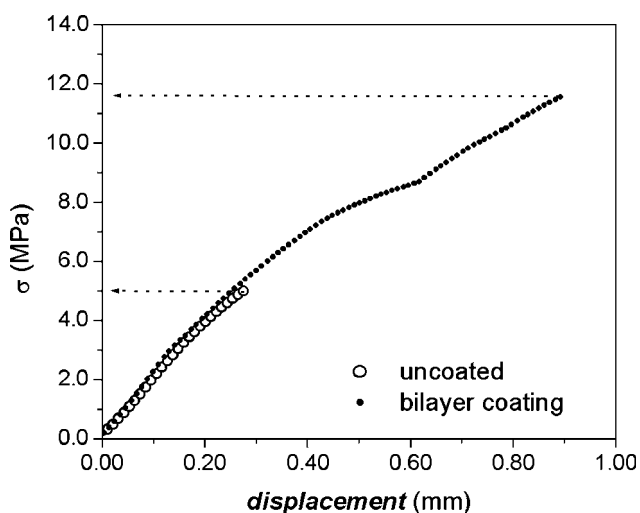
Adhesion strength

Joints with the PMMA cement were prepared using both coated and uncoated steel plaques (five joints of each class), as described in the experimental section. In the case of coated plaques, a copolymerization of methyl methacrylate with methacrylic groups of the second layer is expected. The occurrence of this reaction must be reflected in an improvement of the adhesion strength.
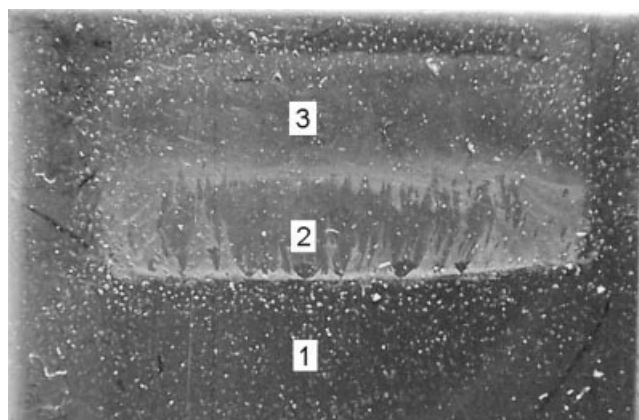
A comparison of two particular single lap-shear strength tests, one for uncoated plaques and the other one for coated plaques, is shown in Figure 5.

A significant increase in the adhesion strength for the joints prepared with coated plaques is observed. A discontinuity in the derivative of the force with respect to displacement was always recorded for coated plaques. This sudden increase of this derivative could be correlated with features present in debonded surfaces. Average values of single lap-shear strength were 3.4 ± 1.5 MPa for the uncoated plaques and 9.7 ± 1.5 MPa for the plaques coated with the bilayer system.

Figure 6 shows an upper view of the debonded area next to the metal surface. As shown by finite element analysis,[15] higher stresses are developed at the boundary region (region 1 in Fig. 6), which should be the first to debond. Inspection of this area showed that failure occurred mostly by debonding of the PMMA cement from the second layer although some small portions of the cement remained attached to the surface. When the debonding area progressed towards the joint center an arrest of the debonding front was observed followed by a change in the failure mechanism. This point is associated with the sudden increase in the derivative of the force with respect to displacement. Debonding continued by stretching and tearing the coating layer (region 2 in

Figure 6 Photograph of the debonded surface on the metal side (a view of the whole debonded area, 25×15 mm^2).

Fig. 6), followed by catastrophic failure (region 3 in Fig. 6). In spite of the complex mechanical behavior the bilayer coating provides an effective enhancement of the interfacial adhesive strength.

CONCLUSIONS

A bilayer coating was developed to improve the adhesive strength between stainless steel and *in situ*-polymerized PMMA. The first layer was based on an epoxy/silane formulation to make use of the excellent adhesion of epoxies to metals and to provide alkoxysilane groups for the covalent bonding to the second layer. Conditions leading to a fast gelation of the polymer network immediately after dip coating, were selected to obtain a homogeneous layer. The second coating provided silanol groups to react with the alkoxysilane groups of the first layer and methacrylic groups to produce covalent bonds during the polymerization of methyl methacrylate. To improve the wettability of the precoated stainless steel substrate with the second layer it was necessary to introduce HEMA and to advance the free-radical copolymerization of methacrylic groups to a conversion close to 25%. Stainless steel plaques either coated with the bilayer system or uncoated, were bonded with a 0.55-mm thickness of PMMA cement using the standard geometry to perform single lap-shear strength tests. The average lap-shear strength increased from 3.4 ± 1.5 MPa for the uncoated plaques to 9.7 ± 1.5 MPa for the plaques coated with the bilayer system.

Figure 5 Comparison of single lap-shear strength tests for uncoated and coated steel plaques.

References

1. Jasty, M.; Maloney, W. J.; Bragdon, C. R.; Haire, T.; Harris, W. H. J Bone Joint Surg 1990, 72, 1220.
2. Anthony, P. P.; Gie, G. A.; Ling, R. S. M.; Howie, C. R. J Bone Joint Surg 1990, 72, 971.
3. Jasty, M.; Maloney, W. J.; Bragdon, C. R.; O'Connor, D. O.; Haire, T.; Harris, W. H. J Bone Joint Surg 1991, 73, 551.

4. Plueddemann, E. P. In Fundamentals of Adhesion, Chapter 9; Lee, L. H., Ed.; Plenum: New York, 1991.

5. Miller, J. D.; Ishida, H. In Fundamentals of Adhesion, Chapter 10; Lee, L. H., Ed.; Plenum: New York, 1991.

6. Caeg, C.; Leinfelder, K. F.; Lacefield, W. R.; Bell, W. J Prosthet Dent 1990, 64, 37.

7. Yerby, S. A.; Paal, A. F.; Young, P. M.; Beaupré, G. S.; Ohashi, K. L.; Goodman, S. B. J Biomed Mater Res 2000, 49, 127.

8. Fischer, H.; Wirtz, D. C.; Weber, M.; Neuss, M.; Niethard, F. U.; Marx, R. J Biomed Mater Res 2001, 57, 413.

9. Cabanelas, J. C.; Serrano, B.; Gonzalez-Benito, J.; Bravo, J.; Baselga, J. Macromol Rapid Commun 2001, 22, 694.

10. Prolongo, S. G.; Cabanelas, J. C.; Baselga, J. Macromol Symp 2003, 198, 203.

11. Cabanelas, J. C.; Prolongo, S. G.; Serrano, B.; Bravo, J.; Baselga, J. J Mater Proc Technol 2003, 143/144, 311.

12. Poisson, N.; Lachenal, G.; Sautereau, H. Vib Spectrosc 1996, 12, 237.

13. Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J Macromolecules 2002, 35, 6324.

14. Flory, P. J Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.

15. Pereira, A. B.; de Morais, A. B. Int J Adhes Adhesives 2003, 23, 315.