

Preparation and Mechanical Properties of Poly(vinyl chloride)/Bamboo Flour Composites with a Novel Block Copolymer as a Coupling Agent

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ABSTRACT: To improve the interfacial adhesion between poly(vinyl chloride) (PVC) and bamboo flour in PVC/bamboo flour composites, a novel coupling agent, poly(styrene-co-maleic anhydride)-block-poly(styrene-co-acrylonitrile) [P[(SMA)-*b*-(SAN)]]], was synthesized through living free-radical polymerization in a one-pot reaction. P[(SMA)-*b*-(SAN)] was synthesized by a nitroxide-mediated polymerization technique in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl with azobisisobutyronitrile. The conversion of maleic anhydride (>99%) and styrene (>65%) was relatively high and yielded P[(SMA)-*b*-(SAN)] with a narrow molecular weight distribution (weight-aver-

age molecular weight/number-average molecular weight <1.38). PVC was blended with bamboo flours in the presence of the synthesized coupling agent with a two-roll mill. P[(SMA)-*b*-(SAN)] was added to the PVC matrix at a concentration of 55 or 20 wt %. As the content of P[(SMA)-*b*-(SAN)] in the wood-polymer composite increased, improved morphological and mechanical behaviors were observed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2654–2659, 2008

Key words: block copolymers; compatibility; compatibilization; composites; poly(vinyl chloride) (PVC)

INTRODUCTION

In recent years, academic and commercial focus on polymer composites with wood materials has increased.^{1–4} As early as the 1950s, researchers have tried to combine thermoplastics with woody materials because of the many advantages of wood-polymer composites (WPCs), such as high mechanical strength, low manufacturing cost, better dimensional stability, and low density. WPCs are defined as composite materials containing a polymer matrix mixed with natural woody components. Generally, the most popular thermoplastics in WPCs are polyethylene,⁵ polypropylene,⁶ and poly(vinyl chloride) (PVC).⁷ The woody filler in WPCs usually consists of ground wood waste, wood fiber, or flour.

Despite numerous advantages, WPCs have certain drawbacks, such as a poor interaction between the wood and polymer matrix and high sensitivities to moisture and heat.⁸ Most researchers have focused on these weak points to improve their properties. Most of the physical and mechanical properties of WPCs

depend on the interfacial adhesion between the woody materials and the polymer matrix. One method that has been used to solve this problem is to modify various coupling agents to provide a lower surface energy between the woody materials and the polymer matrix. Coupling agents play an important role in the improvement of interfacial adhesive strength in WPCs. Coupling agents in general can improve the compatibility¹ between hydrophilic-like wood and hydrophobic-like thermoplastics. Therefore, the development of suitable coupling agents is one of the key factors in the success of WPCs. Danyadi et al.⁸ and Hristov et al.⁹ prepared a polypropylene-based WPC with a maleic acid modified polypropylene coupling agent. Zhao et al.³ reported the effect of a coupling agent on PVC-based WPCs. Shah et al.¹⁰ investigated novel coupling agents that were composed of chitin and chitosan on PVC-based WPCs.

Living free-radical polymerization (LFRP) is one powerful method used for the synthesis of block copolymers.¹¹ There are three kinds of synthetic methods generally: nitroxide-mediated polymerization (NMP);¹² atom transfer radical polymerization,¹³ and reversible addition-fragmentation chain transfer polymerization.¹⁴ Block copolymers with controlled structures, molecular weight distributions, and end/functional groups can be prepared with these methods. The NMP technique has many of the attributes of a living system and can be successfully used to

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prepare a wide range of complex macromolecular architectures, including block copolymers.¹⁵

The goal of this study was to obtain a novel coupling agent, poly(styrene-*co*-maleic anhydride)-*block*-poly(styrene-*co*-acrylonitrile) [P[(SMA)-*b*-(SAN)]], with the NMP technique in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and azobisisobutyronitrile (AIBN). We also studied the effect of the coupling agent in a composite of PVC and bamboo flour.

EXPERIMENTAL

Materials

Styrene (St; Aldrich, Wisconsin, USA) and acrylonitrile (AN; Aldrich, Wisconsin, USA) were purified by activated Al₂O₃ to remove stabilizers. Maleic anhydride (MA; Aldrich, Wisconsin, USA), AIBN (Samchun Pure Chemical, Gyeonggi-do, Korea), and TEMPO (Aldrich, Wisconsin, USA) were used without further purification. A high-pressure reactor (250 mL) equipped with heating/cooling units, a thermocouple, a thermocontroller, and a pressure gauge were manufactured for this study. Wood samples were supplied by Woojin Co., Ltd. (Gyeonggi-do, Korea). The wood component was a bamboo flour with an average size of 100 mesh. PVC was supplied from LG Chemical (Seoul, Korea). Dioctylphthalate (DOP; Song won Industrial Co., Ltd., Ulsan, Korea) was used as a plasticizer.

Synthesis of P[(SMA)-*b*-(SAN)]

Polymerizations were carried out as follows: The feed molar ratio [St]/[MA]/[AN]/[AIBN]/[TEMPO] was calculated to be 375 : 25 : 100 : 1 : 2.4. In a typical reaction, the high-pressure reactor (250 mL) was charged with 0.375 mol of St, 0.025 mol of MA, 0.001 mol of AIBN, and 0.0024 mol of TEMPO. After degassing with three times freeze-pump-thaw cycles, the reactor was heated to 125°C. After 80 min of reaction, the reactor was cooled to room temperature, and then, 0.1 mol of AN degassed separately was added. Polymerization continued by the heating of the reactor to 125°C. After 6 h of polymerization, the polymer product was recovered from the solution by precipitation under methanol; the product was then dried *in vacuo* at 80°C for 24 h.

Preparation of the PVC/bamboo flour composites

A laboratory-scale two-roll mill equipped with heating units was used to prepare WPC sheets. The bamboo flour samples were dried at 80°C for over 24 h in a convection oven to reduce moisture. PVC (45 wt %), bamboo flour (55 wt %), dioctylphthalate (15 phr), and P[(SMA)-*b*-(SAN)] (5–20 wt %) were placed into small buckets and then mixed with a

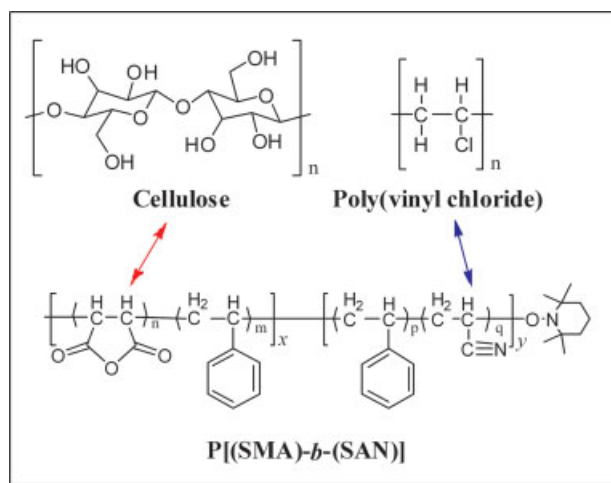
supermixer for 10 min. The mixed compounds were the put into a laboratory-scale two-roll mill. The mixing time in the two-roll mill was 10 min at 170°C¹⁶ with a rotor speed of 60 rpm. The thickness of the WPC sheets were fixed at a gab-length volume of 2 mm.

Characterization

The conversion of each monomer was determined by gas chromatography (GC; Shimadzu GC-2010, Kyoto, Japan). The chemical structure of P[(SMA)-*b*-(SAN)] was determined by ¹H-NMR spectroscopy (Bruker Avance, FT NMR 400 MHz, Rheinstetten, Germany, chloroform-*d*), Fourier transform infrared (FTIR) spectroscopy (Bio-Rad Excaliber series, California, USA) with a KBr pellet, and elemental analysis (EA; CE Instruments, EA-1110, Wigan, UK). The molecular weight and molecular weight distribution [weight-average molecular weight (M_w)/number-average molecular weight (M_n)] of the polymer were measured with gel permeation chromatography (Younglin Acme 9200, Seoul, Korea, Reflective index (RI) detector, tetrahydrofuran eluent, 1 mL/min) with Waters HR1, HR2, and HR5SE columns at 40°C. The calibration curve was obtained with PS standard samples (Showa Denko, Shodex Standard SM-105, Tokyo, Japan). The thermal properties of the samples were investigated by differential scanning calorimetry (DSC; Mettler Toledo DSC 821e, Switzerland, scanning rate = 20–250°C at 20°C/min) and thermogravimetric analysis (Mettler Toledo SDTA 851e, Switzerland, 75- μ L alumina crucible, 20–550°C at 20°C/min) under a nitrogen atmosphere. The morphological and mechanical properties of the WPCs were investigated with scanning electron microscopy (SEM; Jeol JSM-6400, Tokyo, Japan, coated with a gold, 20 kV) at different magnifications and with a universal test machine (Hounsfield H100KS, Surrey, UK) at a crosshead speed of 10 mm/min. The tensile specimen was prepared following ASTM D 638 with a sample cutter.

RESULTS AND DISCUSSION

The development of polymer/wood flour (WF) composites is limited because of poor interfacial adhesion between the hydrophilic woody part and the hydrophobic polymer matrix. Therefore, for the development of a novel coupling agent for a PVC/WF composite system, P[(SMA)-*b*-(SAN)] was synthesized by LFRP, especially NMP. Scheme 1 shows the chemical structure of P[(SMA)-*b*-(SAN)] and the possible chemical associability of the copolymer with the PVC matrix and bamboo flour. Covalent or hydrogen bonding and a strong proton-acceptor effect of the —Cl group between the prepared copolymer and the cellulose of bamboo flour or —Cl of PVC was exhibited, which resulted in strong adhesion at the interfaces.



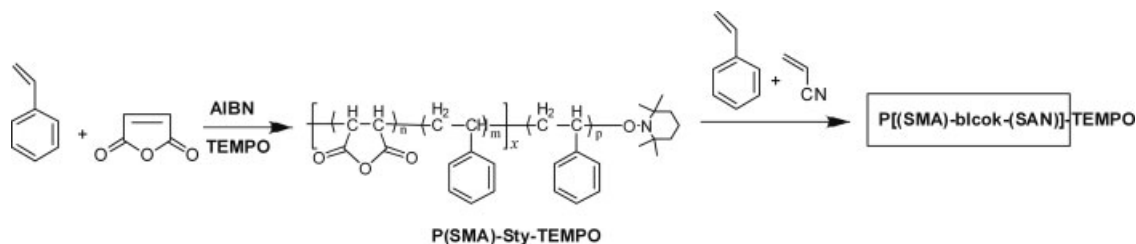
Scheme 1 Chemical structure of P[(SMA)-*b*-(SAN)] and a possible interaction between the coupling agent and cellulose of the wood/PVC resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The block copolymer, P[(SMA)-*b*-(SAN)], was synthesized by the NMP technique with TEMPO and AIBN at 125°C for 6 h. The synthetic pathway of P[(SMA)-*b*-(SAN)] is shown in Scheme 2. In general, it is known that the order of polymerization of each of the monomers is an important factor in LFRP.^{17,18} To synthesize the block copolymer, poly(styrene-*co*-maleic anhydride) endcapped with 2,2,6,6-tetramethylpiperidin-1-oxyl [P(SMA)-TEMPO] was synthesized first. This block allowed for the improvement of the compatibility of the wood cellulose (Scheme 1).

Figure 1 shows the monomer conversions of the P(SMA)-TEMPO unit determined by GC according to different polymerization times at 125°C. Eighty-five percent of MA was consumed within 20 min, and more than 99% of MA was consumed at a reaction time less than 80 min. Approximately 65% of the St monomer was consumed at 4 h, where the St monomers were consumed linearly with polymerization time. These results mean that poly(styrene-*co*-maleic anhydride) [P(SMA)] was first synthesized within 80 min, and then, the remaining St block could form after the P(SMA) block, which resulted in a P(SMA)-TEMPO unit.

Before the formation of the PS block, 0.075 mol of AN monomer was added to the reactor, which led to the formation of the poly(acrylonitrile-*co*-styrene) block. The styrene-*co*-acrylonitrile (SAN) block ensured the interaction of the compatibilizer with the PVC matrix (Scheme 1). Fukuda et al.¹⁹ also reported the synthesis of well-defined PS-*b*-P(SAN) block copolymers, and Li et al.²⁰ reported the synthesis of SAN-*b*-isoprene (IP) and IP-*b*-St-IP-*b*-SAN-IP block copolymers. Figure 2 shows the FTIR and ¹H-NMR spectra of P[(SMA)-*b*-(SAN)]. Characteristic peaks of the polymer, such as the aromatic C—H stretching peak around 3010–3100 cm⁻¹, the aliphatic C—H stretching peak around 2800–2993 cm⁻¹, the strong C≡N stretching peak of the —(SAN) unit at 2244 cm⁻¹, the —(C=O)O— of the —(SMA) unit around 1615 cm⁻¹, and the C—H bending at 1460 cm⁻¹, were clearly observed. The ¹H-NMR spectra also exhibited the aromatic protons of St at δ = 6.4–7.7 ppm as a multiplet; the methylene and methine protons of the block copolymer overlapped at δ = 1.25–3.4 ppm; and the α-methyl protons of —C—CN were assigned around δ2.45 ppm,²¹ which suggested the successful synthesis of P[(SMA)-*b*-(SAN)]. EA results were as follows: C: 71.85%, H: 7.25%, O: 16.18%, and N: 4.72%; these were comparable to the calculated values of C: 74.69%, H: 7.98%, O: 12.06%, and N: 5.28%, respectively. The glass-transition temperature was determined to be 110°C by DSC. The onset temperature for decomposition was determined to be 383°C with thermogravimetric analysis.

Figure 3 shows the number of molecular weights (M_n 's) and polydispersity (M_w/M_n) of P[(SMA)-*b*-(SAN)]-TEMPO at different reaction times. In general, in the LFRP mechanism, monomers can only add to the growing polymer radical between successive activation and deactivation reactions.^{22–24} This behavior gives some unique experimental results compared to those of conventional free-radical polymerization; such as a linear increase in the molecular weight depending on the reaction time and a narrow polydispersity below $M_w/M_n = 1.5$ universally. As shown in Figure 3, the molecular weights increased linearly with increasing reaction time, and also, the polydispersities were in the range 1.2–1.4. These



Scheme 2 Synthetic pathway for the preparation of the block copolymer via NMP at 125°C.

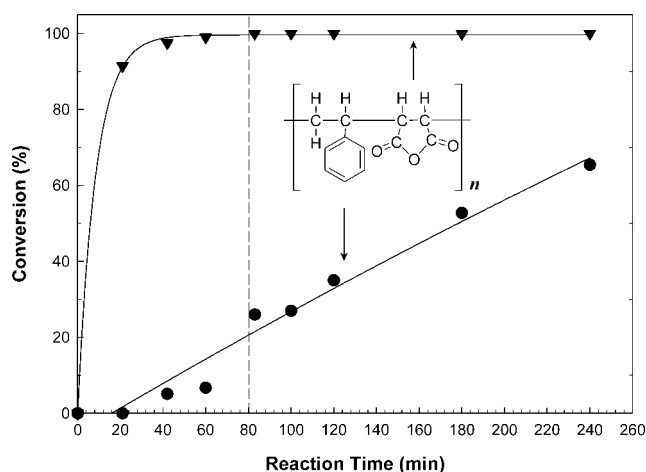


Figure 1 Conversions of St and MA with the reaction time needed to prepare P(SMA)-TEMPO at 125°C for 4 h with AIBN.

results imply that the P[(SMA)-*b*-(SAN)]-TEMPO was polymerized by the LFRP technique.

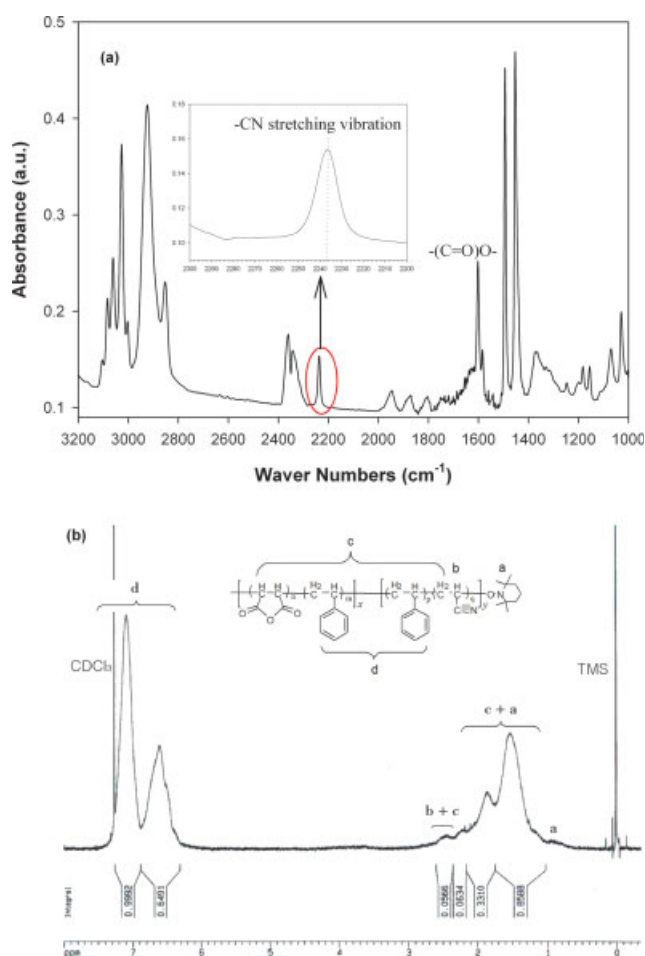


Figure 2 Characteristic peaks of the (a) FTIR and (b) ^1H -NMR spectra of P[(SMA)-*b*-(SAN)]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

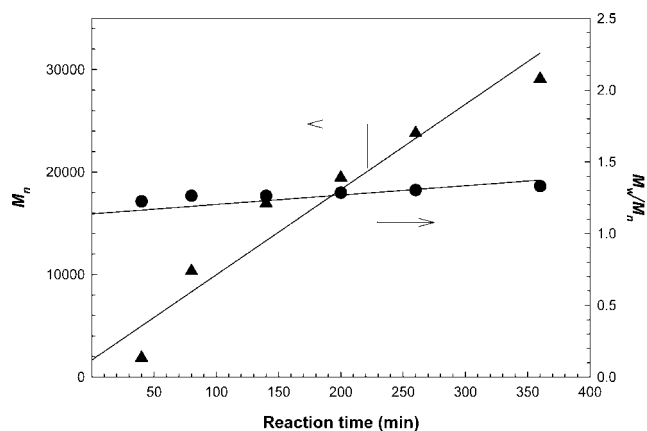


Figure 3 Dependence of M_n and polydispersity (M_w/M_n) on the reaction time for the preparation of P[(SMA)-*b*-(SAN)]-TEMPO at 125°C for 6 h with AIBN.

Generally, wood is a natural polymeric material composed mainly of cellulose, hemicellulose, lignin, and other materials. The chemical composition of bamboo is similar to that of wood. A number of research articles have reported the effect of coupling agents in WPCs.^{3,9,25–27} Compatibility between the hydrophilic woody part and the hydrophobic thermoplastic is a key factor in the improvement of the interfacial energy in WPCs. The compatibility can be described as a linking of two materials by mechanical and/or chemical means. In general, mechanical adhesion is described as the physical interlocking of materials, whereas chemical adhesion alludes to the interactions between molecular species. These chemical interactions play an important role in the improvement of interfacial bonding between components in WPCs.

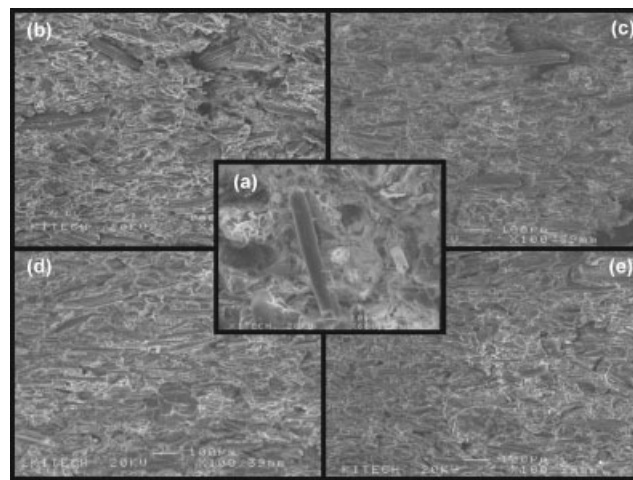


Figure 4 SEM images of the PVC/bamboo flour composites at different concentrations of the coupling agent: (a) without P[(SMA)-*b*-(SAN)] and (b) 5, (c) 10, (d) 15, and (e) 20 wt % P[(SMA)-*b*-(SAN)].

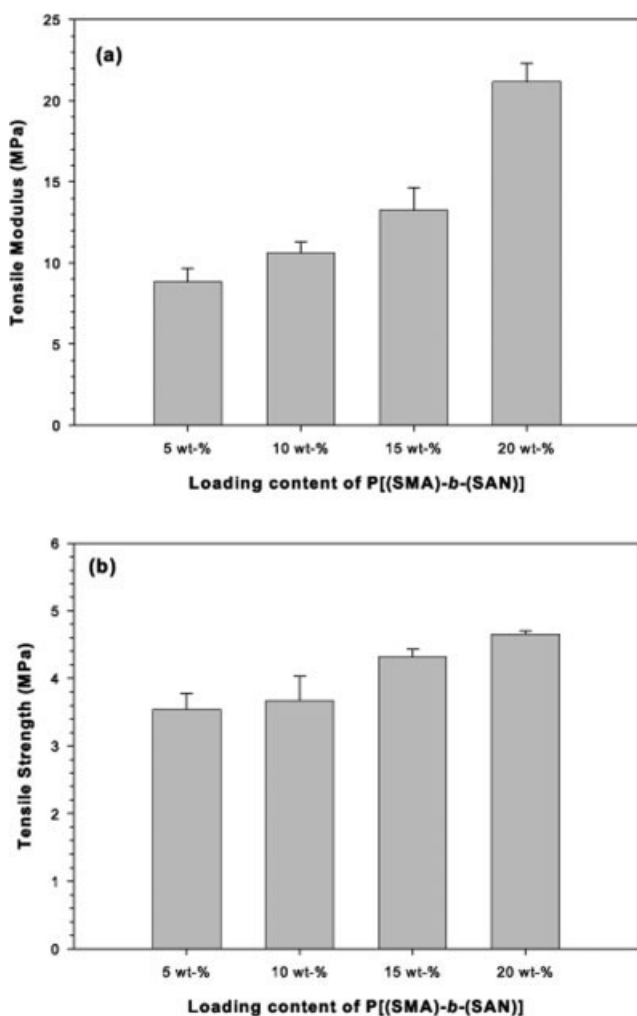


Figure 5 Influence of the content of the coupling agent in the PVC/bamboo flour composite on the (a) tensile modulus and (b) tensile strength.

The coupling agent facilitates the affinity between WF and the PVC matrix by lowering the interfacial tension. Coupling agents are classified into organic, inorganic, and organic-inorganic groups. Organic coupling agents include functional groups of isocyanate, anhydride, amide, imide, acrylate, chlorotriazine, epoxide, cyanate, and so on. Polymeric coupling agents have been widely examined for their effectiveness in WPCs, and they serve more like compatibilizers between the wood phase and the polymer matrix.⁷

Figure 4 shows typical SEM images of the fractured PVC/bamboo flour composites. For the composite without P[(SMA)-b-(SAN)], the WF was easily pulled out from the PVC matrix, as shown in Figure 4(a), which lowered the mechanical properties of the WPCs because of inferior interfacial bonding between the WF and PVC. Figure 4(b-e) shows improved interfacial interaction between the WF and PVC as the content of P[(SMA)-b-(SAN)] increased.

With higher concentrations of P[(SMA)-b-(SAN)] in the composite, the interfacial boundaries between the WF and PVC were narrowed, and the dispersion of WFs into the PVC matrix was improved.

Figure 5 shows the result of tensile testing of the PVC/bamboo flour composites as a function of the concentration of P[(SMA)-b-(SAN)] in the composite. The tensile modulus of the resultant composites increased dramatically at 15 wt % P[(SMA)-b-(SAN)]. The tensile strength also improved with increasing P[(SMA)-b-(SAN)] content.

CONCLUSIONS

A novel coupling agent, P[(SMA)-b-(SAN)], was successfully synthesized via the NMP technique in a one-pot reaction. The conversions of MA (>99%) and St (>65%) were relatively high, yielding P[(SMA)-b-(SAN)] with a narrow molecular weight distribution ($M_w/M_n < 1.38$). From the SEM images, the boundaries between the WF and PVC gradually narrowed with increasing amount of P[(SMA)-b-(SAN)], which was also evidenced by the better dispersion of WF into the PVC matrix. The mechanical properties were also improved with more P[(SMA)-b-(SAN)], which clearly indicated the compatibilizing effect of the block copolymer in the bamboo flour/PVC composite.

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