The Nature and Location of SEBS–MA Compatibilizer in Polyethylene–Wood Flour Composites

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ABSTRACT: A maleic-anhydride-grafted styrene–ethylene—butylene–styrene (SEBS–MA) triblock copolymer has been used as a compatibilizer in low-density polyethylene–wood flour (LDPE–WF) composite system. The location of compatibilizer was studied using transmission electron microscopy (TEM). The unsaturated parts of the copolymer were stained with osmium tetraoxide (OsO_4) to enhance contrast between the different phases. TEM micrographs indicated that part of the compatibilizer was located at the interface between the wood particles and PE matrix and that wood was also stained by the OsO_4. The nature of the interface between the wood surface and the SEBS–MA was studied using Fourier transform infrared spectroscopy (FTIR). The results indicated that MA reacts with wood through esterification and hydrogen bonding and also possibly through interaction between the styrene and wood. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 201–209, 1998

Key words: wood flour–polymer composite; compatibilizer; transmission electron microscopy; Fourier transform infrared spectroscopy

INTRODUCTION

Natural fibers such as wood and cellulose fibers can be used as reinforcement or fillers in common polyolefins. Wood and cellulose fibers have several advantages compared to inorganic fillers, including low price and density, high stiffness, nonabrasiveness, and they are biodegradable and recyclable. However, despite the advantages mentioned above, the use of cellulose-based materials as reinforcement or filler for polyolefins has only recently gained acceptance. The possible reasons for this are difficulties in processing and that the resulting composites usually have reduced toughness and poor stress transfer efficiencies resulting from the incompatibility between the polar and hydrophilic filler and the nonpolar and hydrophobic characteristics of polyolefins.[1–6]

Interfacial adhesion between cellulose-based reinforcements or fillers and thermoplastics has been the focus of a large amount of research during the last 10 years. Different types of coupling agents or compatibilizers have been tested in such composite systems.[1–12] Styrene–butadiene–styrene (SBS) block copolymer used as compatibilizer in low-density polyethylene–wood flour (LDPE–WF) composite systems had a positive effect on the composite's mechanical properties and the adhesion between the wood and LDPE matrix. However, results indicate that the compatibilizer effect of SBS was quite weak because complete coupling between phases was not achieved.[6] The SBS copolymer location in the composite was studied in transmission electron microscopy (TEM)
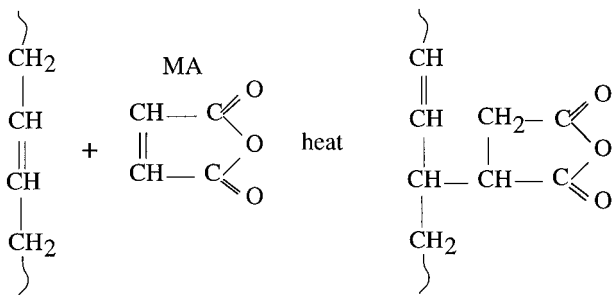
Figure 1 Schematic description of the grafting of SEBS with MA.

and was found to be located at the interfacial region between the LDPE matrix and the wood particles.[13] Previous work[10–12] has shown that maleic-anhydride-grafted styrene–ethylene—butylene–styrene (SEBS–MA) triblock copolymers have a stronger compatibilizing effect between wood flour and polyethylene and polypropylene. The composite's mechanical properties, such as tensile and impact strength, were improved with a small amount of SEBS–MA. Electron microscopy studies have also confirmed significantly improved adhesion at the filler–matrix interfaces.

The SEBS–MA triblock copolymer has a bridging effect between different organic fillers and the olefin matrix. Several authors have shown that maleated or unsaturated elastomers are capable of forming an interphase around the filler particle and therefore improve the interfacial adhesion between phases.[14–17] SEBS is an hydrogenated form of a SBS block copolymer to which maleic anhydride can be grafted on to the unsaturated part of the ethylene–butylene (EB) chain.[18–20] The nature of the EB part of the block copolymer is equivalent to a random copolymer of ethylene and butylene. A complete hydrogenation of double bonds may not be achieved or even desired as the unreacted double bonds are useful as reactive sites for further chemical modification. This can be utilized for modifying SEBS with MA; hydrogenated butadiene polymers that contain residual unsaturation of the order of 0.5–20% are readily reacted with MA. Figure 1 shows the schematic description of the reaction of maleic anhydride with the unsaturated part of the SEBS.[18–20]

The location of the compatibilizer has been studied in the following two ways: directly and indirectly. The indirect methods use the face that if the compatibilizer can improve composite properties such as maximum tensile or impact strengths, then the compatibilizer is expected to be located at the interface region between the re-inforcing particles and the polymer matrix. The direct methods, such as microscopic studies, look for improved adhesion or evidence of the compatibilizer. Several investigations of the interfacial region between reinforcement and polymer matrix have been made by using TEM.[13,15,21,22]

Previous work with PE–WF composites has shown that the SBS copolymer compatibilizer is located at the interfacial region between WF surfaces and the PE matrix and also distributed in the PE matrix.[13] SBS was also found to be located at the interface between the matrix and the filler in PP–talc composites.[15] In a polypropylene–cellulose fiber (PP–CF) composite system, a maleated polypropylene (MAPP) used as compatibilizer was found to be located at the interface between the CF and the PP matrix. The reason for the MAPP being located at the interface, forming an interphase between the PP and CF, is thought to be the difference in polarity between the wood filler and the matrix polymer. Because of this, it is more likely that MAPP molecules with polar acid anhydride groups will move toward to the polar surface of the CF during the kneading.[21] Other researchers have studied CF–polyester composites where the CF surface was treated with a methylolmelamine resin. As would be expected, the results showed that the melamine resin was located at the interface between the CF and matrix.[22]

Using spectroscopy studies, chemical bonding and reactions can be detected and may also give information about interfacial molecular interaction. The nature of the adhesion in PP–CF composites when MAPP was used as a compatibilizer has been studied by Fourier transform infrared (FTIR) spectroscopy. The findings show that the MAPP is bonded to the cellulose fibers through ester linkages[4,7] and hydrogen bonds.[4]

A previous report[12] concerning PE–WF–SEBS–MA composites confirmed that the SEBS–MA was located at the interfaces between the wood particles and the polyethylene matrix. The composites tested with small amount of compatibilizer showed improved impact and tensile strength and elongation at break but had a negative effect on the stiffness compared to unmodified composites. Figure 2 shows that the composite's maximum tensile strength was reached with only 4 wt % (percent by weight) of SEBS–MA addition. The influence of SEBS–MA on the composite's tensile modulus is shown in Figure 3. The modulus shows a notable drop between 0 and 2 wt % SEBS–MA addition; after that, it is almost constant.[12] Several authors have suggested
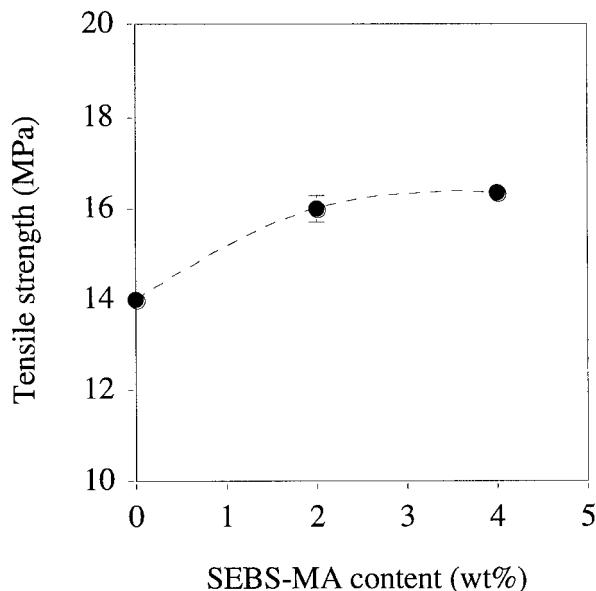
Figure 2 Maximum tensile strength of the LDPE–WF composites as a function of the SEBS–MA content.

that the elastomer additive, which forms interphases around more stiff particles, will decrease the composite's stiffness more than elastomers that are distributed in the matrix.[14–17] The dynamic mechanical properties of SEBS—MA–WF systems also showed possible interaction between the EB–MA part of the copolymer and the wood.[12] Scanning electron microscopy (SEM) fractography showed significantly improved adhesion between the wood and polymer matrix in compatibilized systems compared with composites without SEBS–MA.[12] However, a high-resolution study of the interfacial region is needed to better understand the role played by copolymer compatibilizers in PE–WF composites.

SBS has been studied as a possible compatibilizer in PE–WF composites where mechanical properties were improved with the addition of SBS.[6] SBS is a weaker compatibilizer than SEBS–MA, but the polybutadiene is in an unsaturated form, and it can therefore be stained more easily with osmium(VIII)oxide (OsO_4). The SBS was found to locate at the interface between the wood and LDPE matrix having a cylindrical morphology and an interface thickness of approximately 0.1 μm.[13] It is expected that the morphology of composite systems would be similar regardless of the material used (SBS or SEBS–MA).

In this study, transmission electron microscopy (TEM) was used to investigate the composite morphology with the aim of locating the compatibilizer in the PE–WF composites and especially to study the interfacial region between the wood and PE matrix. FTIR spectroscopy has been used to study the nature of the interaction mechanism between the SEBS–MA and the wood filler.

MATERIALS AND METHODS

Materials

The following commercially available materials were used.

Matrix

The linear low density polyethylene (LLDPE) was NCPE 8065 (NESTE Chemicals, Scandinavia, Stenungsund, Sweden), with a density of 924 kg/m^3 and an MFI (190°C, 2.16 kg) of 65 g/10 min.

Compatibilizer

The compatibilizer was maleated styrene–ethylene—butylene–styrene triblock copolymer (SEBS–MA) Kraton FG 1901X (Shell Chemicals Company, Houston, Texas, USA) with a PS content of 28% by weight, functionality of 2% by weight as bound maleic anhydride, and a density of 910 kg/m^3.

Filler

The filler was softwood sawdust (*Pinus silvestris*) with a density of 450 kg/m^3 and a cell wall density
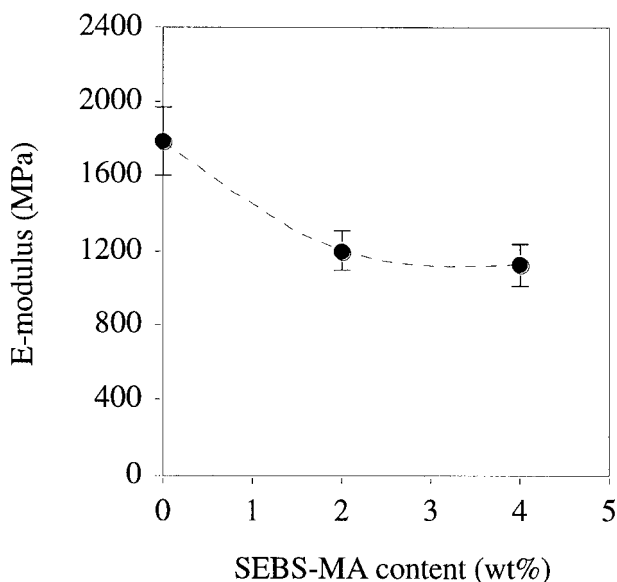

Figure 3 Effect of the SEBS–MA compatibilizer content on the composite's stiffness.

of 1500 kg/m^3. The shape of the particles were fractured fiber bundles.

Processing

The WF was sieved for particles less than 1 mm and then cleaned with acetone. The WF was then filtered and oven-dried for 48 h at 105°C.

The composite samples for mechanical testing and TEM study were injection-molded in a conventional machine, Arburg 320 M 750-210, into test bars (ASTM D 638) having a cross section of 13 × 4 mm and a length of 217 mm. The melt temperature was 180°C, the injection speed was 40 cm^3/s, and the pressure was 230 bar. The WF filler content was constant at 30 wt %, and the SEBS−MA compatibilizer content was 5 wt %.

The samples for the FTIR spectroscopy study were mechanically blended in a Brabender mixer at 100 rpm and at a temperature of about 180–190°C. The mixing was continued until a constant torque was reached; this took about 5 min. One batch of blend was, at most, 30 g. After blending, the materials were pressed in a laboratory press to form 0.5–2-mm-thick plates. The press temperature was 200°C, and the pressure about 10 MPa.

Electron Microscopy

A high-resolution study of the composite interphase was made using a Jeol 2000EX STEM−TEM instrument. The samples were taken from injection-molded test bars and pressed to form 1-mm-thick plates. Small pieces, about 1 × 2 × 12 mm, were then embedded in low-viscosity acrylate. The embedded specimens were sectioned with a diamond knife using an LKB Ultratome V to give a specimen thickness less than 150 nm. After that, the samples were stained with OsO$_4$ vapor for about 2 h in order to give good contrast for the unsaturated part of the EB−MA blocks in the copolymers.

Infrared and Raman Spectroscopy

Raman spectra were recorded using a Perkin−Elmer PE 1760X FTIR spectrometer equipped with a near-infrared (NIR) Raman bench. In the Raman experiment, the scattering was excited with intensity-stabilized (0.1% rms) 1064 nm emission from a Spectron SL 301 neodymium-doped yttrium aluminium garnet (Nd : YAG) laser, and the scattered light was collected with a 180° backscattering geometry lens. The spectra presented are typically 100 accumulations at 4-cm^{-1} resolution, using an indium gallium arsenide (In Ga As) detector and an integral preamplifier. The interference filters used to reject light at the excitation wavelength allowed collection of Stokes Raman scatter greater than 200 cm^{-1} shift. The laser reference frequency was set to 9396 cm^{-1} in all experiments, and the mirror drive speed was set at 0.1 cm^{-1}.

For the IR measurements, spectra were collected by the diffuse-reflectance technique using a Perkin−Elmer 2000 FTIR spectrometer and a PE DRIFT accessory. Oven-dried spectroscopic grade potassium bromide was used as diluent, and, typically, 100 scans at 4-cm^{-1} resolution were collected for each sample. Diffuse reflectance spectra were plotted as the Kubelka−Munk function, which is suitable for quantitative analysis. The samples were pulverized using a diamond paper disk and diluted with oven-dried spectroscopic-grade potassium bromide.

RESULTS AND DISCUSSION

Morphology of Composites

Scanning electron microscopy studies have confirmed that adhesion between the LDPE matrix and WF particles is improved when SBS and SEBS−MA are used as a compatibilizer.[6,10,12] SEBS−MA has been found to act as a better compatibilizer than SBS, but both are expected to locate at the interface between WF particles and LDPE matrix. It is difficult to see if SEBS−MA or SBS occurs at the WF surfaces in SEM micrographs, and, therefore, a higher-resolution TEM was used to study the interfaces in the LDPE−WF−SBS system.[13] The SBS compatibilizer was stained with OsO$_4$ to distinguish it from the LDPE matrix. As a result of the study, the SBS was found to locate at the interface between the PE and wood and also in the PE matrix. OsO$_4$ is a useful staining agent for unsaturated polymers and is expected to stain the double bonds in the SEBS−MA, the unsaturated part of EB block, and double bonds in MA. An earlier high-resolution study with TEM−EDXA showed that maleated polypropylene (MAPP) was located at the interface between cellulose fiber and PP matrix, forming an interphase and acting as a compatibilizer.[21]

Figure 4 shows the transmission electron micrograph of an LDPE−WF composite with SEBS−MA (5 wt %) as compatibilizer. It can be seen
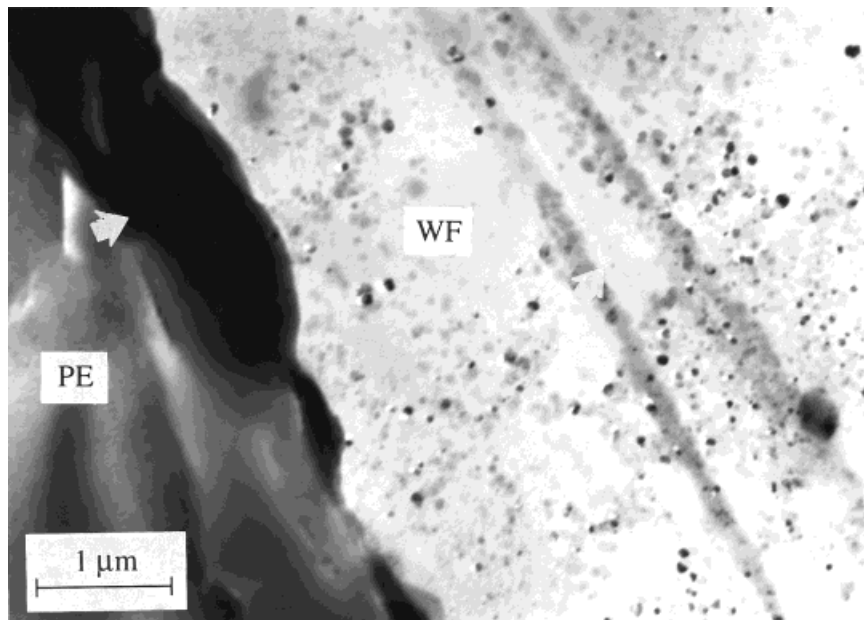
Figure 4 Transmission electron micrograph of LDPE–WF composite with 5 wt % SEBS–MA as compatibilizer.

from the micrograph that the lighter area is the wood cell wall and that the darker area is the LDPE matrix. It is also possible to distinguish the middle lamellae in the wood cell wall. The area between the WF and PE is black and is believed to be the SEBS–MA compatibilizer. The micrograph indicates that the interphase is not continuous. It is difficult to discern the structure of the SEBS–MA copolymer, but black dots can be seen in both the interface between the PE and WF and in the wood cell wall. It has been reported that the woody cell wall may also have components that can be stained with OsO_4.[21] However, the wood cell wall was not stained in the previous study when SBS was used.[13] One more possibility is that the SEBS–MA is taken from the interphase to the cell wall with the knife during sectioning. The SEBS–MA seems to be located at the interfacial region rather than in the PE matrix. It should be noted that the SEBS–MA content is lower compared to the previous study[13] when the SBS content was 30 phr (per hundred resin) and was also found to be dispersed in the PE matrix. Figure 5 shows a higher magnification of the interface region. It can be seen from the micrograph that the interphase thickness is not uniform; the thinnest part is approximately 0.1 μm, but it is difficult to measure the thickness because it is hard to know in which orientation the cell wall is sectioned. Figure 6 shows higher magnification of the

interface region when the sample is not stained as much in the micrographs in Figures 4 and 5. The SEBS–MA interphase between the WF and LDPE can be seen more clearly; the interface region is darker than the polymer matrix, and small dots are distributed from the interface to the wood cell wall. The OsO_4 is expected to be located at the double bonds in the maleic anhydride, in a possible ester bond. If the polystyrene (PS) content is 28 wt %, then it is expected to form a cylindrical structure in the EB matrix. However, the previous DMTA study[12] of the SEBS–MA copolymer indicated that the styrene content in the SEBS–MA is probably higher. If the styrene content in the SEBS–MA is higher than 28 wt % then the structure of copolymer can be one of cylindrical or spherical EB domains in the PS matrix. Therefore, the dark dots shown in the micrograph could be EB–MA particles embedded in polystyrene matrix. The micrographs in this study agree with the earlier TEM study made on the PP–CF composite system where MAPP was used as compatibilizer.[21] In the micrographs, the MAPP was shown as black areas around the CF. The energy-dispersive X-ray analysis (EDXA) of the OsO_4 distribution showed that the OsO_4 stained MAPP was located mainly at the interface region between CF and PP and not in the PP matrix.[21]

The mechanical properties of the composites give indirect information about the interface be-
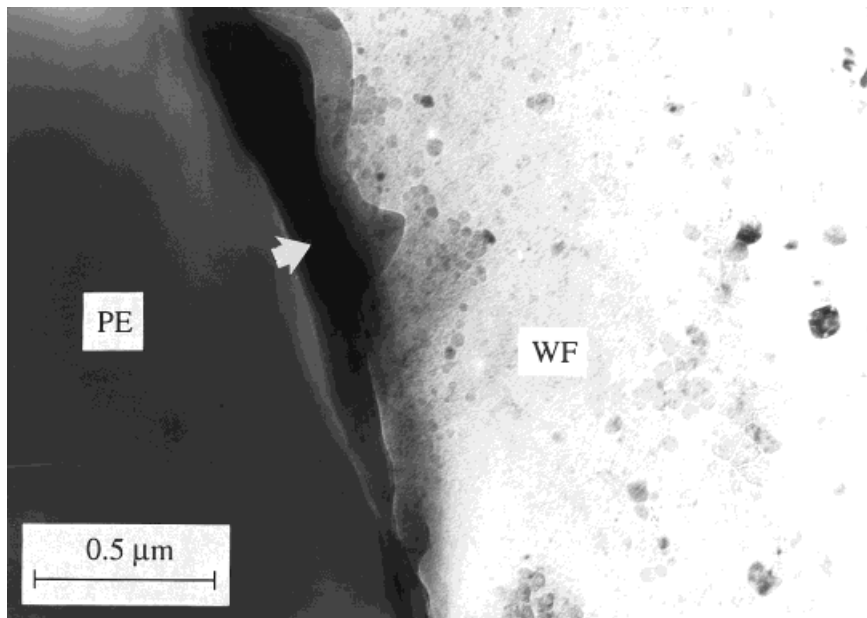
Figure 5   Transmission electron micrograph of LDPE–WF composite with 5 wt % SEBS–MA content, the interfacial region between wood particle, and PE matrix.

tween the WF and LDPE matrix.[12] Mechanical properties and TEM results lead to the conclusion that the SEBS–MA is located at the WF interface.

Infrared and Raman Spectroscopy

FTIR spectroscopy was used to investigate the nature of the adhesion between WF and SEBS–MA.

Spectras of pure wood particles, SEBS–MA, and a blend of SEBS—MA–WF (60/40 wt %) were compared in order to study the nature of the interaction. Raman spectroscopy was mainly used to obtain spectra from the ring stretching region less affected by nearby carbonyl absorptions.
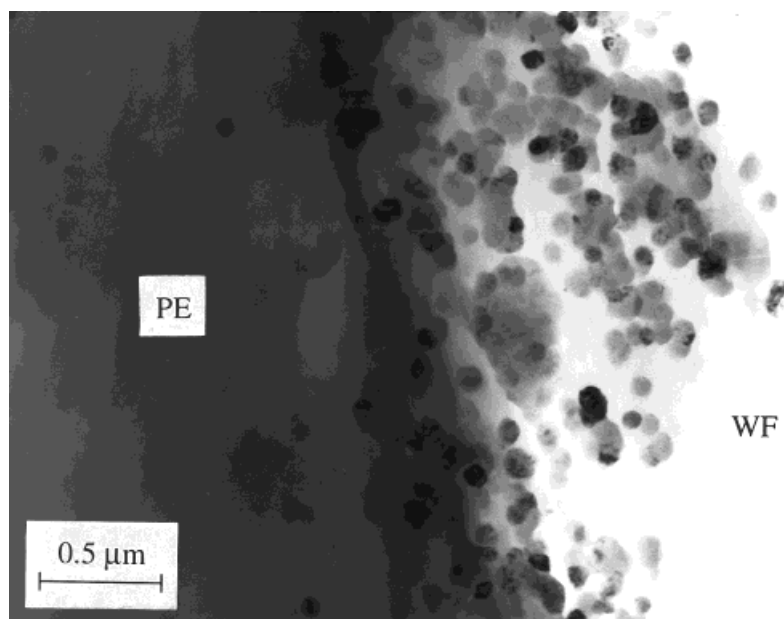
The IR spectrum of the SEBS–MA is shown in

Figure 6   Transmission electron micrograph of LDPE–WF composite with 5 wt % SEBS–MA content and higher magnification of the interfacial region between wood particle and PE matrix.
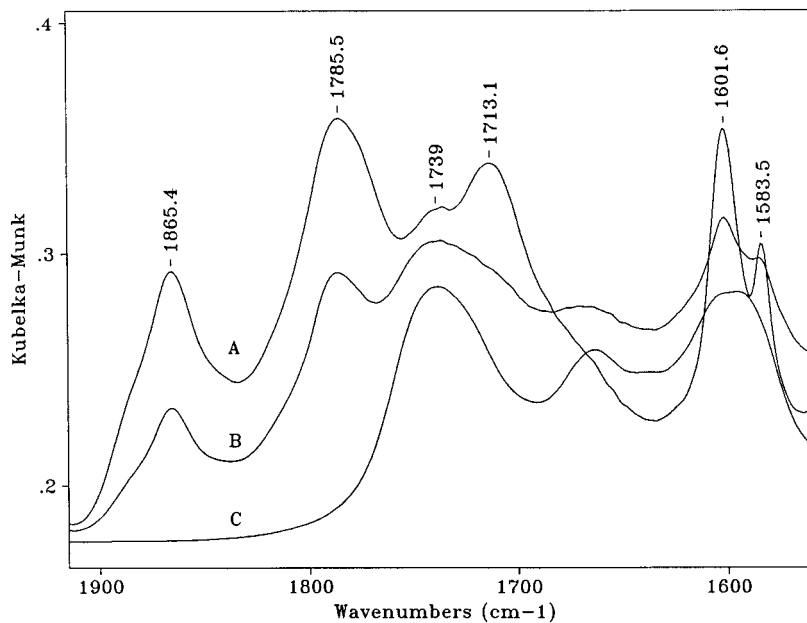
Figure 7 FTIR spectra of (A) SEBS–MA, (B) SEBS–MA with 40 wt % WF, and (C) WF.

Figure 7. Absorption bands at 1865 and 1786 cm^{-1} are characteristic of the cyclic anhydride,[23] whereas the IR band at 1713 cm^{-1} and bands at 1602 and 1584 cm^{-1} are typical frequency positions for maleic acid carbonyls and aromatic ring stretching vibrations, respectively. The IR spectrum of the SEBS–MA therefore shows evidence

of both grafted MA and maleic acid. The presence of maleic acid is further confirmed by the spectrum of the polymer in the OH stretching region, namely, 3700–3000 cm^{-1} (see Fig. 8, spectrum A). Absorptions at 3648 and 3616 cm^{-1} are clear indications of free (nonhydrogen-bonded) OH stretching vibrations. It is interesting to note that
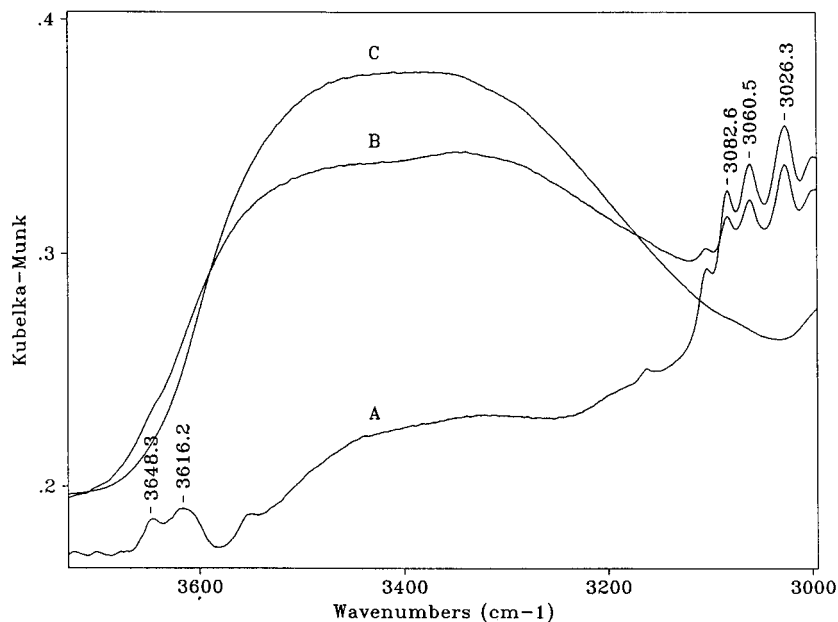

Figure 8 FTIR spectra of (A) SEBS–MA, (B) SEBS–MA with 40 wt % WF, and (C) WF.
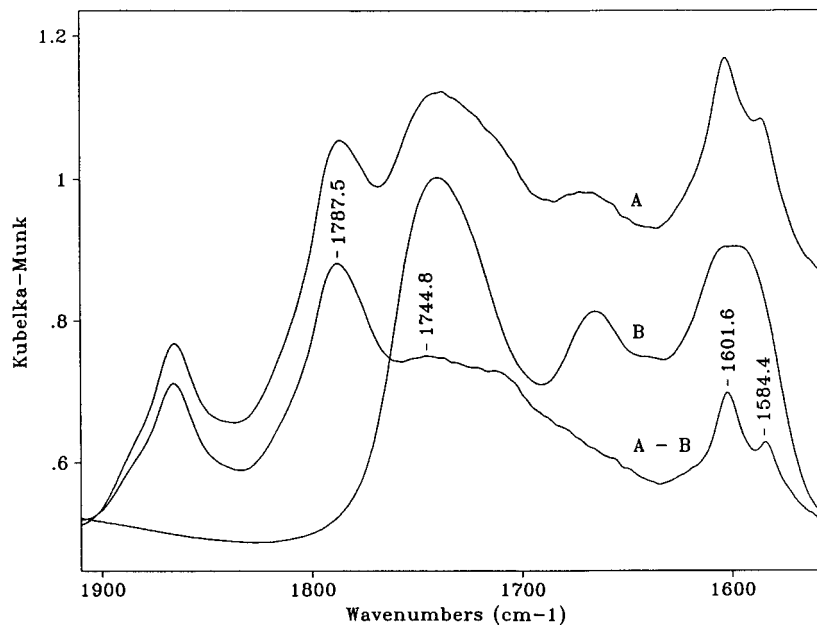
Figure 9 FTIR spectra of (A) SEBS–MA, (B) SEBS–MA with 40 wt % WF, and (A-B) is the difference spectrum.

these free hydroxyl functions are hardly detectable in the spectrum of the SEBS—MA–WF composite. In Figure 7, the spectrum of the SEBS—MA–WF composite shows that unreacted MA can still be observed. In order to investigate the possi-

ble formation of ester bonds when anhydride reacts with OH functions in wood, the spectrum of WF was subtracted from the SEBS—MA–WF spectrum. Unfortunately, the vibrational frequency of these ester carbonyls appear in the
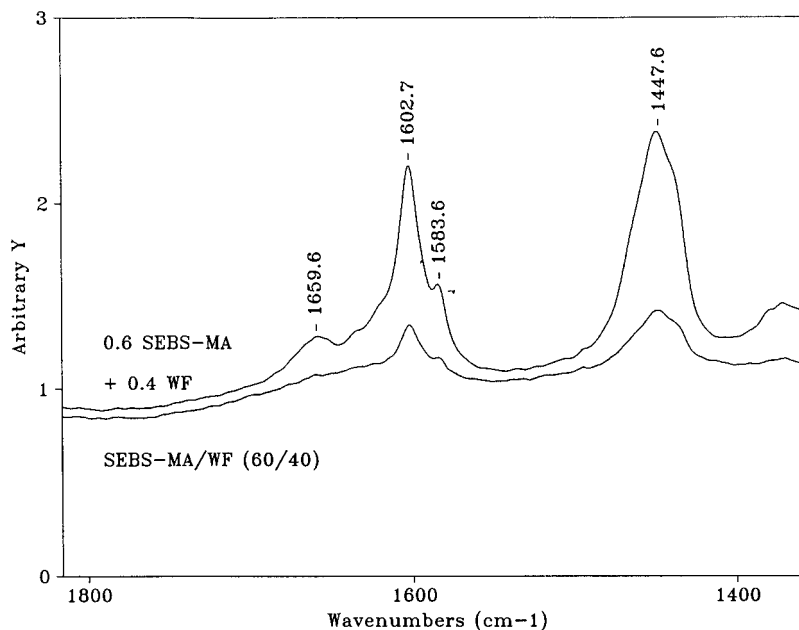

Figure 10 Raman spectra of SEBS–MA–WF (60/40) and SEBS–MA + WF showing changes in the intensity at 1584 and 1448 cm^{-1} when WF is added to the SEBS–MA. The spectra of pure SEBS–MA and WF have been multiplied by a factor of 0.6 and 0.4, respectively. Spectra are shifted along the intensity scale.

same spectral region as the carbonyl groups of the wood itself. The result of the subtraction is shown in Figure 9. This difference spectrum indicates a residual intensity at 1745 cm^{-1} as well as an IR absorption band at 1713 cm^{-1} originating from the C=O entity of a carboxylic acid function. The improved mechanical properties of the investigated composite materials are expected to originate in reaction or molecular interaction between the SEBS–MA copolymer and wood flour. It is also interesting to note the spectral change in the aromatic ring stretching region following mixing of SEBS–MA and WF. According to Figure 10, the intensity of ring stretch typical for monosubstituted benzene ring at 1584 cm^{-1} is reduced in the Raman spectrum of SEBS—MA–WF (60/40) in comparison with the intensity of this line in the computed spectrum of 0.6 SEBS–MA + 0.4 WF. A similar reduction in line intensity is observed at 1448 cm^{-1} where semicircle stretching of monosubstituted benzene rings and C—H in plane bending appears. The difference obtained using the computed spectrum as subtrahend spectrum results in broad bands centered at 1584 and 1448 cm^{-1}, indicating slightly different line widths (not shown in Figure 10). These spectral changes may be taken as an indication of molecular interaction involving the phenyl entity of SEBS–MA.

CONCLUSIONS

TEM studies indicated that the SEBS–MA was located at the interface region between the LDPE matrix and the wood particles. The structure of the SEBS–MA copolymer also indicated that the styrene content was higher than the manufacture reported.

The FTIR spectroscopy showed that the MA is partially bonded to the wood through esterification but that some nonactivated MA remains at the interface. The results also indicated hydrogen bonds between OH groups on the wood surfaces and the MA. Raman spectroscopy also indicated possible interaction between the styrene part of the copolymer and the wood.

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