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Modification of properties of rayon fibre by graft copolymerization with acrylic monomers

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Abstract The change in rayon fibre properties due the grafting polymerization of methyl metacrylate (MMA) and butyl acrylate (BA) was investigated. The formation of rayon-g-PMMA or PBA was confirmed by FTIR spectroscopy, X-ray analysis, and TGA. The adhesion to PMMA and epoxy resin matrixes was determined using the microdrop technique. The PBA or PMMA grafting on the fibre led to lower mechanical properties than the ungrafted rayon fibre. However, the grafted rayon had better thermal properties than the ungrafted rayon and a shift of the decomposition temperature of the rayon was observed. The PMMA grafted to rayon improved the interfacial adhesion when PMMA was used as matrix (microdrop technique). The grafted polymer (PBA or PMMA) restricted the ''wetting'' of the fibre when epoxy resin was used as matrix and lowering the adhesion in comparison with ungrafted rayon fibre.

Introduction

The use of cellulose fibres as fillers or as reinforcement of polymeric matrices has increased lately [1–5]. These materials are inexpensive and they are obtained from renewable natural sources. They have other advantages such as low density, flexibility in their processing, little equipment wear and biodegradability in comparison with glass fibre, which is still the most commonly used reinforcement [6, 7]. Cellulose fibres have been frequently used in thermoset matrices but their uses in thermoplastic matrices has been limited by the incompatibility between the fibre and matrix [8, 9]. It is known that the hydrophilic nature of cellulose fibres prevents adhesion to hydrophobic thermoplastic matrices [8].

However, the fibre-matrix adhesion and dispersion of the fibres during composite processing can be improved by grafting a polymer onto the fibre surface [10]. Such polymer must shown compatibility or some degree of miscibility with the matrix. The initiation by free radical is one of the most commonly used methods for grafting vinylic monomers onto cellulose. Such free radicals are produced by the reaction of the cellulosic chain with redox systems. In this reaction, oxidation of anhydroglucose units occur along the cellulosic chain and macrocellulosic radicals are generated on the fibre's surface. These reactions modify the properties of cellulose fibre [11–13], and it is necessary to evaluate these changes after grafting.

The use of rayon fibre, kind of regenerated cellulose, as reinforcement in thermoplastic or thermoset composites has not been investigated thorough [1, 14–16] and its applications are limited to tire manufacture. In this work we are studied the change in mechanical, thermal and surface properties of rayon fibre due the grafting with acrylic monomers.

Experimental

The rayon fibre used was from Akzo nobel as a long multifilament fibre, which were soxhlet extracted with

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toluene previous the grafting reactions. Reagent-grade methyl methacrylate (MMA) and butyl acrylate (BA) from Aldrich were distilled at reduced pressure to remove the inhibitor. Cerium-and-ammonium nitrate (CAN) from Aldrich was used as initiator.

To carry out the grafting reactions, 0.5 g of rayon fibre (about 25 cm) was mounted over a HDPE square as support and it was introduced in an Erlenmeyer flask with 25 ml of distilled water and closed with a rubber septa; the oxygen in the flask was displaced with nitrogen 0.5 g of MMA or BA monomer was introduced in the flask and placed on a rotatory shaker at room temperature. After 10 min, the initiator (CAN dissolved in 1.5 ml of HNO_3 1N) was added to the flask to start the reaction. After 3 h of reaction, the grafted rayon was washed with 250 ml water and dried to constant weight in an oven at 70 °C. To remove the homopolymer (PMMA or PBA) formed in the reaction, the fibres were soxhlet extracted with acetone during 24 h, dried and weighted. The grafting parameters were calculated as reported in previous work [17].

ATR FTIR spectroscopy was used to analyze the surface of the rayon and grafted rayon with a Nicolet 460 Protégé Magna IR spectrophotometer coupling with a Techna Spectre Microscopy. The infrared spectra were obtained in a 4,000–700 cm^{-1} range with a resolution of 4 cm^{-1}. Thermogravimetric analysis of the samples were carry out in a Perkin Elmer TG7 thermogravimetric balance, using a heating rate of 10 °C min^{-1} and a temperature range of 50–550 °C under nitrogen atmosphere. WAXS studies were performed on fibres by using a goniometer Siemens (model Kristalloflex) containing a CuKα target X-ray tube operated at 35 kV and 25 mA. Monochromatization was achieved by Bragg's diffraction from graphite crystal. The diffraction intensity was recorded with a proportional counter coupled with a discriminator–integrator system. The 2θ angle was scanned from 2–60 at a rate of 2θ/min. Tensile test for the grafted and ungrafted rayon fibre were performed in a microtensile-tester equipped with a computer-controlled actuator and a 250-g load cell. An initial length (L_0) of 4.16 mm and a cross head to 1.2 mm/min were used. The cross section area of the fibre was obtained from the apparent diameter measurements performed prior to tensile test. These measurements were carried out with an optical microscope (American Optical model 21) equipped with a micrometric scale.

To analyze the change on the fibre's surface due the grafting, the microdrop technique was used. In this technique, one drop of polymer (thermoplastic or thermoset) is formed on the fibre surface and the force necessary to removed it is measured [18]. To obtain the PMMA microdrop, a small PMMA film is mounted on the fibre and heated at 200 °C. For epoxy resin, a drop of the mixture DER 331 and Ancamine 1784 (1:1) was deposited on the fibre and allowed to cure at room temperature for 48 h. Drops with a relation microdrop diameter/fibre diameter of 3 were evaluated using a microtensometer MINIMAT with a 50 g load cell.

Results and discussion

The grafting parameters determine the compatibility degree between the cellulose fibres and a polymeric matrix and the physicochemical properties of the fibre. It has been reported that this parameters are influenced by the type and concentration of the initiator, the monomer to be grafted and the reaction conditions [19, 20]. Figures 1 and 2 show the effect of the initiator concentration on the grafting parameter for MMA and BA grafted onto rayon fibre, respectively. For MMA grafting (Fig. 1) the total monomer conversion and the add-on increase with the CAN concentration up to 6 mmol/l and then they reach a constant value of 80 and 43%, respectively. This behaviour of grafting parameters can be attributed to a high flux of free radicals, which increases by increasing initiator concentration and enhances the possibility of initiating reactive sites on the rayon fibre where the MMA can be grafted. However, when the initiator concentration becomes too large (in this case larger than 6 mmol/L) the homopolymerization of the relatively water-soluble MMA becomes important as a consequence of the high

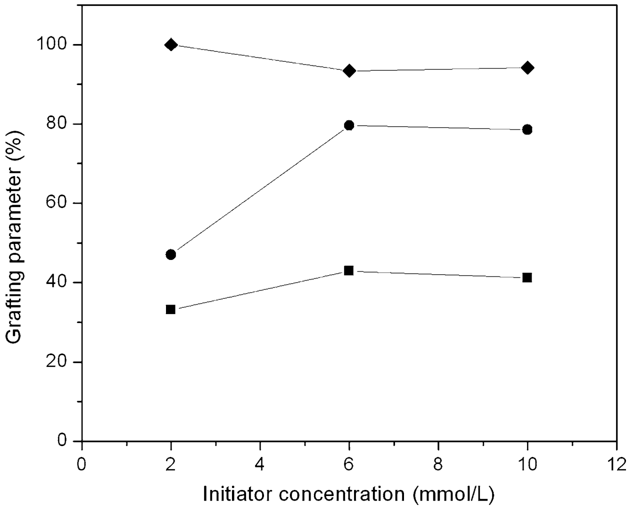

Fig. 1 Grafting parameters as a function of initiator concentration for the grafting polymerization of 1:1 MMA/rayon fibre ratio: (●) Conversion, (■) add-on, (◆) grafting efficiency

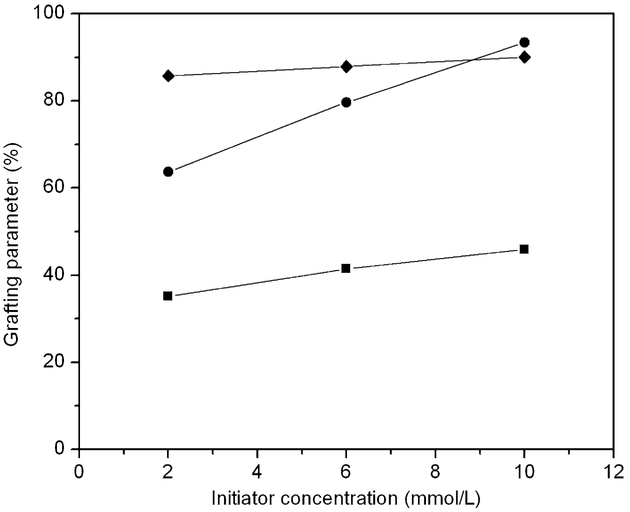

Fig. 2 Grafting parameters as a function of initiator concentration for the grafting polymerization of 1:1 BA/rayon fibre ratio: (●) Conversion, (■) add-on, (◆) grafting efficiency

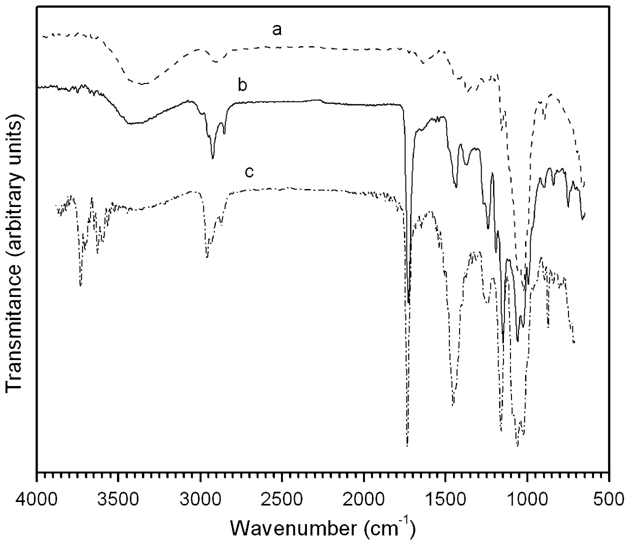

Fig. 3 ATR FTIR spectra of rayon fibre: (a) ungrafted rayon, (b) PMMA grafted rayon, (c) PBA grafted rayon

concentration of Ce(IV) ions in the aqueous phase. These reactions, of course, should decrease grafting reactions as show in Fig. 1. On the other hand, the constant values of the monomer conversion at higher CAN concentrations can be attributed to the cellulosic radicals already generated that are rapidly oxidized by ceric ions resulting in a minor monomer polymerization [21]. A different behaviour is obtained when BA is grafted onto rayon fibre (Fig. 2). In this case, the grafting parameter and monomer conversion increases with the initiator concentration and higher values of the grafting parameter for BA compared to MMA were obtained. This behaviour can be attributed to the lower solubility of BA in water (medium used in the reaction) in comparison to MMA. The rayon fibre swells with water and in the case of MMA, part of the dissolved monomer can be diffused into the fibre, diminishing the amount of monomer available for reaction. On the other hand, BA monomer is dispersed through the aqueous phase due their low solubility in water and it is more available to react with the cellulosic radicals formed on the fibre surface or initiating the homopolymerization in the aqueous medium. Then, an increase of radical flux results in high values of monomer conversion.

The grafted of polymer (PBA or PMMA) onto the rayon fibre surface was confirmed by ATR FTIR spectra, as show in Fig. 3. A wide band at 3,650–3,000 cm^{-1}, which is characteristic of the hydroxyl groups of anhydroglucose unit, is detected in the grafted and ungrafted rayon spectra. Also, a band at 2,950–2,920 cm^{-1} which corresponds to stretching of methyl and methylene C–H bonds and a broad band at 1,150–1,000 cm^{-1} region which corresponds to the overlapping of the C–C and C–O bands are observed. The spectra of the grafted fibres (rayon-g-PMMA or rayon-g-PBA) show in addition to the characteristic peaks of the cellulose, a strong sharp band at 1,730 cm^{-1} which corresponds to the stretching of the carbonyl group of the grafted PMMA or PBA. Also shows a peak at 1,450 and 1,150 cm^{-1} due the flexion of C–H of the alquene mono-substituted and asymmetric stretching of C–O–C, respectively.

Figure 4 show the TGA and the differential TGA (DTGA) curves of PBA-grafted, PMMA-grafted and ungrafted rayon fibre. It can be observed that the rayon

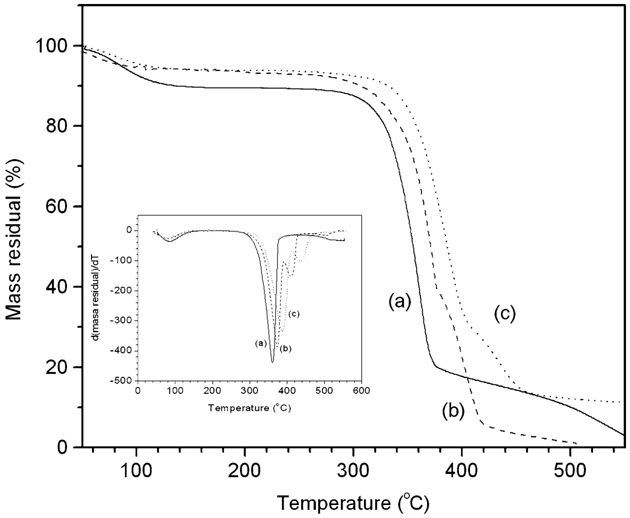

Fig. 4 TGA decomposition thermograms: (a) ungrafted, (b) rayon-g-PMMA and (c) rayon-g-PBA

fibre presents a lost of mass of 10% at 100°C due the absorbed water. The principal lost of mass (70%) occurred between 320 °C and 390 °C. The maximum in decomposition is obtained at 360 °C as show in figure 4. It has been reported that the thermal decomposition of cellulose includes two processes [25]. One consists on the reduction in chain length due to bond scission with the generation of free radicals, dehydration, formation of carboxyl and carbonyl groups and char formation. The other process includes the depolymerization of cellulose by scission of the glucosidic units and the formation of levoglucosan. Both processes occur simultaneously. The TGA curves of grafted rayon fibre (PMMA or PBA) shows a minor lost of moisture (5% lost mass at 120 °C); the thermal decomposition started at higher temperatures than ungrafted rayon and they present two temperature ranges of decompositions. This can be seeing better in the DTGA curves (inset in Fig. 4) of the grafted rayon fibres. In these curves, the first peak caused by cellulose degradation is shifted to 372 °C for PMMA grafted rayon and 388 °C for PBA grafted rayon. The second peak, represent the degradation of PMMA or PBA. These patterns indicate a better stability of grafted rayon fibre in comparison to ungrafted one. The better stability shown by the grafted rayon fibre can be attributed to the polymer formed on the surface. When the fibre is heated, the PMMA or PBA on the surface act as isolative material delaying the start of cellulose degradation [12], as can be seen by the shift of the cellulose decomposition peak in the DTGA curves (inset in Fig. 4).

Figure 5 depicts the X-ray diffraction spectra for the grafted and ungrafted rayon fibre. Fibres from regenerated cellulose have a semi-crystalline structure and, therefore, are composed of crystallites together with more o less disordered (“amorphous”) regions [22]. It can be observed that the X-ray spectra of ungrafted rayon show small peaks at 11–17° (2θ) and an intense peak in the region of 18–24° (2θ). These peaks can be attributed to the different crystalline structures presented in the rayon fibre. Then, peaks characteristic of cellulose I (2θ = 15.5°, 16.5° and 22.8°) and cellulose II (2θ = 12.7°, 20° and 22.8°) can be observed in the diffraction pattern of the ungrafted rayon fibre. The grafted of PMMA onto rayon lead to changes in the X-ray spectra. An increment in the amorphous zone is observed and the peak in the region of 18–24° (2θ) looks as doublet. These changes indicate a modification of the crystalline structure of the grafted rayon due the presence of PMMA at the inner structure of the fibre. On the other hand, the X-ray spectrum of the PBA-grafted rayon is similar to the ungrafted rayon, indicating that the grafted PBA does not modify the crystalline structure of the rayon fibre. This behavior can be attributed that the grafted BA mainly occurs on the fibre surface.

Figure 6 shows the effect of the grafted polymer onto the mechanical properties of rayon fibre. It can be observed that the grafted rayons show a reduction in the modulus and tensile strength independently of the kind monomer (MMA or BA) used. Then, a drop of 15% on the modulus is observed with the grafted fibre and a drop of 12 % and 45 % are observed for the tensile strength of PBA grafted rayon and PMMA grafted rayon, respectively. Those results are similar to the ones obtained by other authors, who have reported a reduction of mechanical properties of the grafted

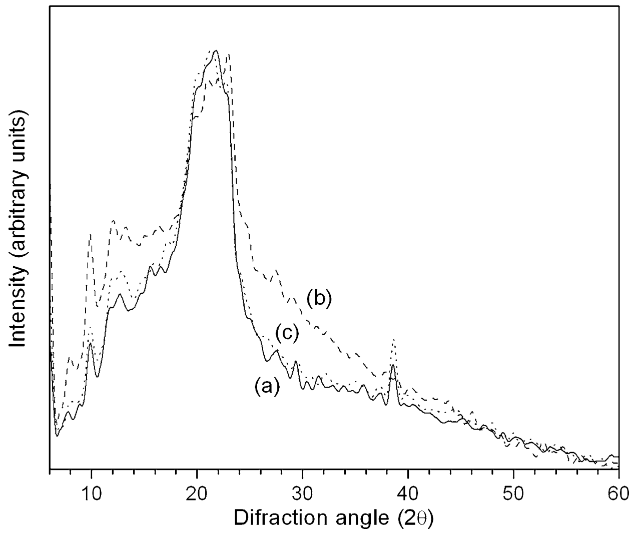

Fig. 5 Wide-angle X-ray diffractogram: (a) ungrafted, (b) rayon-g-PMMA and (c) rayon-g-PMMA

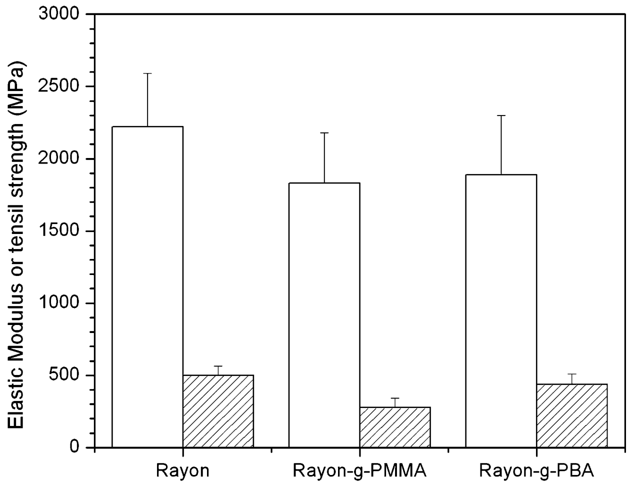

Fig. 6 Mechanical properties of grafted and ungrafted rayon fibre: (Unfilled) elastic modulus and (filled) tensile strength

rayon fibres due the grafted polymer and this effects are most notorious at higher add-on values [23, 24]. The changes in the morphology of the rayon fibre due to the grafted polymer change the mechanical properties. On the other hand, the higher tensile strength of grafted PBA rayon fibre in comparison to PMMA grafted rayon fibre can be attributed to the lower changes of the inner morphology of the grafted PBA rayon fibre, as shown by the X-ray spectra.

In composites, a good interfacial bond between the fibre and matrix can improve their mechanical properties. Interfacial shear strength (ISS) is a parameter to measure bonding between fibre and matrix. This value is dependent on fibre surface treatments. In this work a micro bond test was used for characterizing the single fibre-matrix interface to evaluate the changes in fibre's surface due the grafting acrylic monomer on the surface of rayon fibre. Figure 7 shows the effect of the kind of grafted polymer onto the rayon fibre on the ISS when PMMA or epoxy is used as matrix. The ISS of PMMA grafted rayon is higher to the ISS of the ungrafted rayon fibre when PMMA is used as matrix. The poor compatibility between the PBA and PMMA results in a lower ISS value when PBA grafted rayon is used as fibre and PMMA as matrix. The ISS for PMMA or PBA grafted rayon is lower than the ISS for ungrafted rayon when an epoxy resin is used as matrix. This behavior can be attributed to a better ''wetting'' of the ungrafted rayon in comparison with the grafted one. Then, the exposed OH groups of cellulose can react with the epoxy resin and make a good interface and improve compatibility. On the other hand, the polymer grafted onto the fibre surface limits the accessibility of the epoxy to the cellulose chain and reduces the interaction between them. The lower ISS value of PBA grafted rayon confirms this assumption. As mentioned before, the PBA is grafted mainly on the fibre surface.

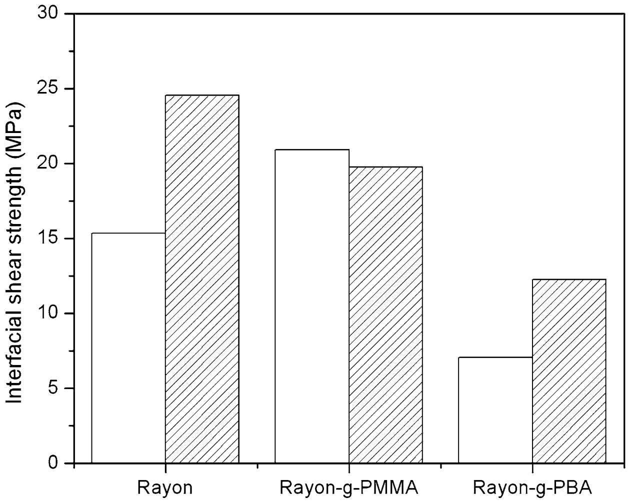

Fig. 7 Interfacial shear strength (ISS) of grafted and ungrafted rayon fibre: (Unfilled) PMMA matrix and (filled) epoxy resin matrix

Conclusions

The grafting of acrylic monomers lead to a change in the physicochemical properties of the rayon fibres. This change depends of the kind of monomer used. Thermal properties are improved with the grafted polymer and mechanical properties are diminished when PMMA or PBA was grafted onto rayon. Good interface rayon fibre-PMMA matrix was obtained when PMMA was grafted onto rayon. Grafted polymer reduces the accessibility of the epoxy resin to the rayon fibre and the grafted fibres have lower ISS in comparison to the ungrafted rayon fibre.

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References

1. Shibata M, Oyamada S, Kobayashi S, Yaginuma D (2004) J Appl Polym Sci 92:3857
2. Rodríguez CA, Medina JA, Reinecke H (2003) J Appl Polym Sci 90:3466
3. Puglia D, TomassuciA, Kenny JM (2003) Polym Adv Technol 14:749
4. Eichhorn SJ, Baillie CA, Zafeiropoulus N, Mwaikambo LY, Ansell MP, Dufresne A, Entwistle KM, Herrera-Franco PJ, Escamilla GC, Groom L, Hughes M, Hill C, Rials TG, Wild PM (2001) J Mat Sci 36:2107
5. Cai X, Riedl B, Ait-Kadi A (2003) Composites Part A 34:1075
6. Zadorecki P, Mitchell AJ (1989) Polym Composites 10:66
7. Maldas D, Kokta BV (1991) Polym Eng Sci 31:1351
8. Raj RG, Kokta BV (1991) Polym Eng Sci 31:1358
9. Woodhams RT, Thomas G, Rodgers DK (1984) Polym Eng Sci 24:1166
10. Gaylord N.G.. Us Patent 3,645,939, 29 February 1972 (To Us Plywood Champion Paper Inc.)
11. Shukla SR, Athalye AR (1995) J Appl Polym Sci 57:983
12. Das RK, Basu D, Banarjee A (1999) J Appl Polym Sci 72:135
13. Canche-Escamilla G, Cauich-Cupul JI, Mendizabal E, Puig JE, Vazquez-Torres H, Herrera Franco PJ (1999) Composites Part A 30:349
14. Paunikalio T, Suvanto M, Pakkanen TT (2004) J Appl Polym Sci 91:2676
15. Goncalves-Costa V, Reis-Nunes RC (1994) Eur Polym J 30:1025
16. Paunikallio T, Kasanen J, Suvanto M, Pakkanen TT (2003) J Appl Polym Sci 87:1895
17. Canche-Escamilla G, Rodriguez-Trujillo G, Herrera-Franco PJ, Mendizabal E, Puig JE (1997) J Appl Polym Sci 66:339
18. Zhandarov S, Mäder E (2005) Composites Sci Technol 65:149

19. Rabby B, Gädda L (1994) In: Graft copolymerization of lignocellulosics fibers, Acs Symposium Series, American Chemical Society
20. Patra CM, Singh BC (1994) J Appl Polym Sci 52:1557
21. Fernandez J, Casinos I, Guzman GM (1990) J Appl Polym Sci 41:2221
22. Müller M, Riekel C, Voung R, Chanzy H (2000) Polymer 41:2627
23. Mc Dowall DJ, Gupta BS, Stannet VT (1987) Polym J 19:643
24. Basu D, Khan AK, Maji TK, Banerjee A (1998) J Appl Polym Sci 69:2585
25. Madorsky SL (1975) Thermal degradation of organic polymers, Krieger R.E. Pub. Co, p 238–261