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Radiation Grafting of N-Isopropylacrylamide Onto Polypropylene Films by Preirradiation Method

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The modification of polypropylene films (PP) was performed by radiation-induced graft polymerization of thermosensitive poly(N-isopropylacrylamide) (PNIPAAm). Graft polymerization was obtained by pre-irradiation method with doses from 10 to 200 kGy, at different monomer concentration, temperature, reaction time and dose rate; by using gamma rays from Co-60 source at room temperature. Grafting was confirmed by infrared (FTIR-ATR), and the structure of the grafted films was investigated by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS); low critical solution temperature (LCST) of the films was measured by water absorption and water contact angle.

Keywords: gamma-ray; LCST; N-isopropylacrylamide; radiation-grafting

INTRODUCTION

Poly(N-isopropylacrylamide) (PNIPAAm) has become, perhaps the most popular member of a class of polymers that possess inverse solubility upon heating, a property contrary to the behavior of most polymers in organic solvents under atmospheric pressure near room temperature. Its macromolecular transition from a hydrophilic to a hydrophobic structure occurs rather abruptly at what is known as the lower critical solution temperature (LCST) [1,2]. Experimentally, this lies between

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30 and 35°C, the exact temperature being a function of the detailed microstructure of the macromolecule [3]. Early research focused on this transition as a theoretical curiosity; however, more recently this speciality polymer has been applied in very diverse uses as the potential to apply this transition as a switching device has been recognized [4].

PNIPAAm has been used in many forms including single chains, macroscopic gels, microgels, latexes, thin films, membranes, coatings, and fibers. Moreover, a wide range of disciplines have examined PNIPAAm, encompassing chemistry, physics, rheology, biology, and photography. As a result, many papers fail to cite previous work on PNIPAAm from ignorance or narrowed focus; the literature has thus also been plagued by redundancy [5,6].

Hydrophilic N-isopropylacrylamide (NIPAAm) monomer is a good material that has the easy stripped off function due to its thermosensitive critical property. PNIPAAm exhibits a LCST and remarkable hydration-dehydration changes in response to relatively small changes in temperature [7].

As the radiation, such as γ-ray or UV photografting, provides a sterilization effect and no initiator is required for copolymerization, no environmental pollution and biological toxic substances are generated. The grafting of various vinyl monomers onto thermoplastic rubber, ultrahigh molecular weight polyethylene and nonwoven fabric of polypropylene by γ-ray irradiation or UV treatment method had been reported in some studies [8,9].

EXPERIMENTAL

The polypropylene (PP) film used was a commercial product (PEMEX, Mexico) with molecular weight of 39,000 (M_n) and 179,000 (M_w), density of 0.902, crystallinity of 88%, and thickness of 60 μm. The films was washed with methanol for 24 h and dried in vacuum. They were cut into pieces of 1×2.5 cm and their weights were recorded exactly, N-isopropylacrylamide (NIPAAm) supplied by Aldrich Co, USA was recrystallized from hexane/toluene 50/50 vol. solution before use.

A ^{60}Co Gamma-Beam 651-PT, with activity of 25,000 Curies, was used for irradiation of PP films in air at a dose rate of 0.29 and 3.4 kGy h^{-1}, and radiation doses from 10 to 200 kGy. The irradiated films were placed in glass ampoules which contained acetone solutions with different molar concentration of the monomer (1, 2 and 3 mol·L^{-1}). The ampoules were degassed by repeated freeze-thaw cycles, sealed and placed in a water bath at a temperature from 40°C to 60°C for 5 to 30 h. The grafted films were washed with water for 24 h to extract the residual monomer and any NIPAAm homopolymer that had

formed. The grafting yield (Y_g) was calculated by the equation: $Y_g(\%) = 100[(W_g - W_0)/W_0]$, where W_g and W_0 are the weights of the grafted and initial films, respectively.

For determining equilibrium water absorbency, the samples were immersed into distilled water for different times; the swelling of the samples was calculated by the equation:

Swelling (%) $= [(W - W_0)/W_0] \times 100$, where W and W_0 are weights of the swelling and initial films respectively. The lower critical solution temperature of the grafted films was determined by measuring the equilibrium swelling ratio of the samples immersed in water at various temperatures between 20°C and 50°C.

FTIR-ATR (attenuated total reflection) spectra were taken using a Perkin-Elmer Paragon 500 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The observation of surface of the films was made using an atomic force microscope (AFM); Model Autoprobe-CP, Park Scientific Instruments, division of Veeco Instruments GmbH, Unterschleis-sheim, (Germany), with 10 μm scanner (contact mode) and an autocalibration by Scanner Master. Measurements were performed on a Kratos AxisUltra XPS using a monochromatic AlKa (300 W) X-ray source, an electron flood gun for charge neutralization and hemispherical analyzer with multichanel photomultiplier detector. Differential scanning calorimetry was performed using a DSC 2010 calorimeter (TA Instruments, New Castle, DE). Thermo gravimetric analysis measured with model Q50 (TA Instruments, New Castle, DE). The contact angle of water droplets was measured using a Ramé-Hart model 1100 goniometer. The temperature-dependence of films wettability was examined by measuring the contact angle at a controlled temperature within a custom-built environmental chamber.

RESULTS AND DISCUSSIONS

Figure 1 shows increase in the grafting value with increase in temperature; in this article 60°C can be consider as an optimal temperature which ensure an efficient thermal decomposition of oxidative products, formed by the PP irradiation in air, to active centers of the grafting process. Graft polymerization is proportional with reaction time and reaction temperature, NIPAAm-g-PP films present higher yields of grafting at 30 h at those two temperatures (50 and 60°C). All copolymer films presented good mechanical properties independent of reaction time or temperature, they did not result in any visible change in their transparency and mechanical durability as compared with the starting ones.

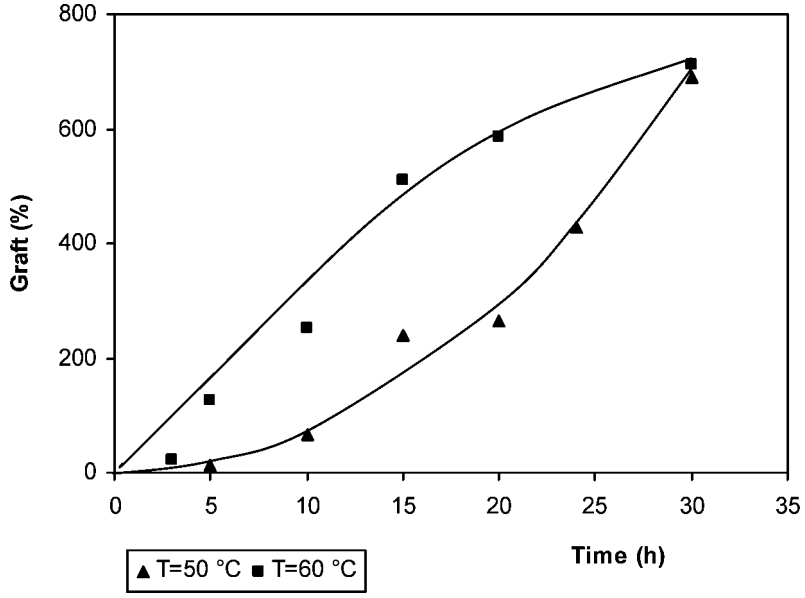


FIGURE 1 Grafting yield of NIPAAm onto PP films as a function of reaction time, at different temperatures; monomer concentration 2 molar, pre-irradiation dose 100 kGy and dose rate 4.2 kGy/h.

Figure 2 shows the effect of monomer concentration on the grafting as a function of preirradiation dose, at reaction time of 24 h, reaction temperature 60°C and dose rate of 4.2 kGy/h. Grafting yield increase with monomer concentration up to 3 mol·L^{-1}, higher concentration of NIPAAm favours "the gel effect," this effect results from a slowing the termination step owing to the lack of mobility of the growing chains, increasing the yield of grafting. In this work, 3 mol·L^{-1} was optimal monomer concentration, because of the saturation of NIPAAm in acetone.

Figure 3 showed higher rate of grafting of the NIPAAm onto PP films at dose rate of 0.29 kGy/h as compared with 3.4 kGy/h, but low dose rate favours the oxygen diffusion and produce more oxidation products as the peroxides and hidroperoxides, with the increase of number of radical to initiate the grafting process, but also increase the degradation of the PP; then, after a radiation dose of 50 kGy, the PP films have poor mechanical properties because of excessive degradation; therefore 3.4 kGy/h can be considered the more appropriate dose rate for these systems.

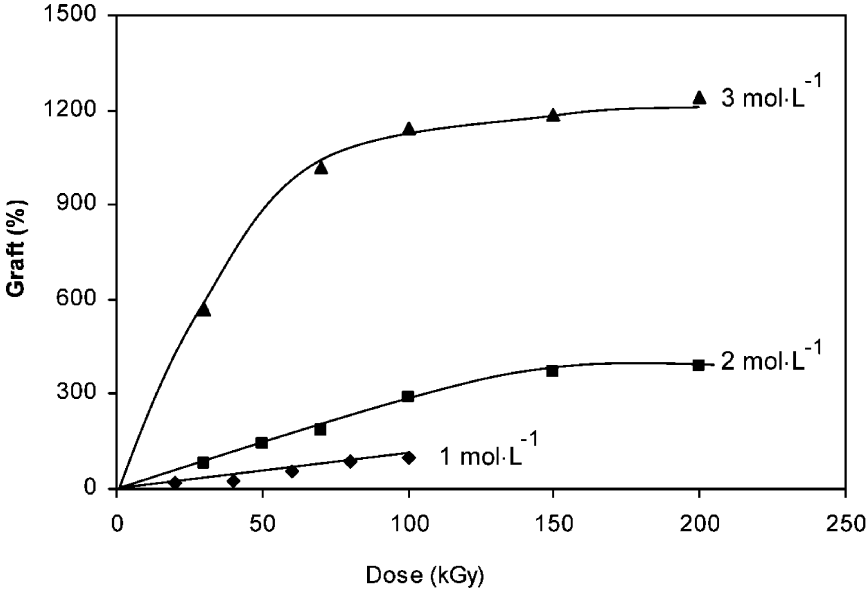


FIGURE 2 Grafting yield of NIPAAm onto PP films as a function of pre-irradiation dose, at different monomer concentrations (1, 2 and 3 molar); dose rate of 4.2 kGy/h, reaction time 24 h, and reaction temperature 60°C.

Two different methods were used to study LCST; by films swelling (gravimetrically), and by determination of surface properties (Figure 4a and 4b); using the variations in the contact angle of a water droplet at temperatures ranging from 22°C to 45°C, LCST were found at 33°C (98% graft) and 32°C (1250% graft). Typical swelling profiles of NIPAAm-g-PP films immerged in water at room temperature, followed by gravimetrically determination are plotted in Figure 5a and 5b (previous swelling measurement found limited swelling in 2 h); LCST determined by this last method for graft contents of 550%, 1020%, and 1150% was observed at 32.5°C, and not depended of grafting, in all cases the same results were obtained.

The membrane surface morphology before and after grafting were analysed by AFM. Figure 6a, 6b and 6c show AFM topographies of the PP films, and the films grafted with NIPAAm 23 and 251%. The surface of PP films contains a smoth surface with average roughness of 17.5 Å, when the surface has 23% graft a small disperse lumps with size of a few micrometers appeared on the surface, at higher grafting

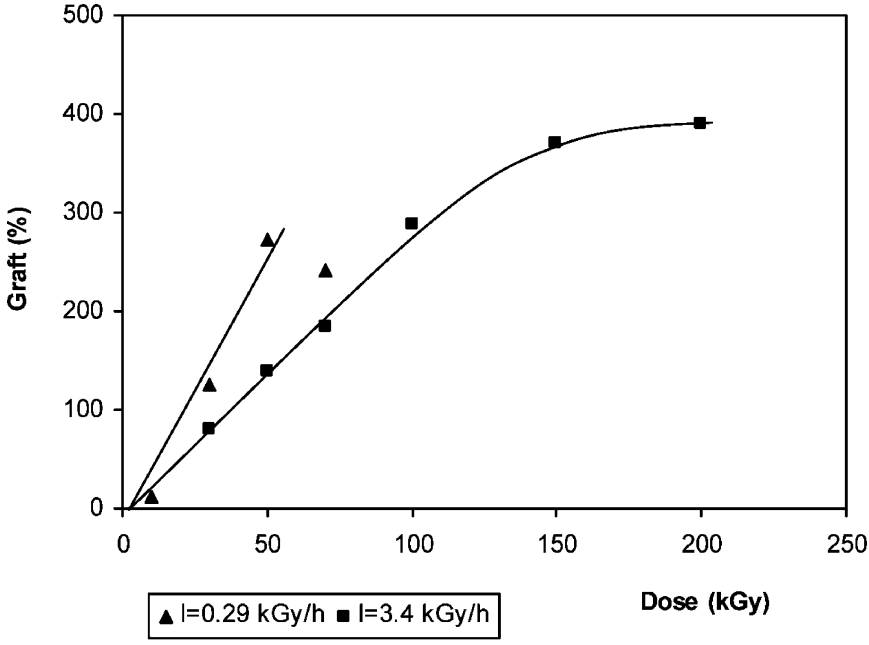


FIGURE 3 Grafting yield of NIPAAm onto PP films as a function of pre-irradiation dose; monomer concentration 2 molar, reaction time 24 h, and reaction temperature 60°C.

percentage of 251%, the surface is cover with the monomer (according XPS measurement), but the texture changes significantly with many conglomerated lumps in the surface.

The membrane surface composition after grafting was analyzed by XPS. Figure 7 shows the $C1_s$ peak of the PP membrane and the binding energy for a carbon bonded with electron attractive groups, as the amide group forming NIPAAm at about 280–285 eV; and the $N1_s$ peak and $O1_s$ of the grafted NIPAAm, with a N/C atomic ratios on the surface film of 0.21 measured for the film with 98% graft, indicating that the surface was covered by the graft polymer, according of the theoretical values for the NIPAAm monomer (0.17) [10].

Figure 8 shows PP film CH_2, CH_3 of PP (2914 and 2950 cm^{-1}); NIPAAm C=O (1655 cm^{-1}), N–H (3268 cm^{-1}) and CH_3 (2970 cm^{-1}); copolymer of NIPAAm-g-PP C=O (1640 cm^{-1}), CH_2 (2917 and 1453 cm^{-1}), CH_3 (1373 cm^{-1}) and N–H (1538 cm^{-1}); this characterization confirmed grafting of NIPAAm onto PP films, amide and carbonyl groups were found in modified PP.

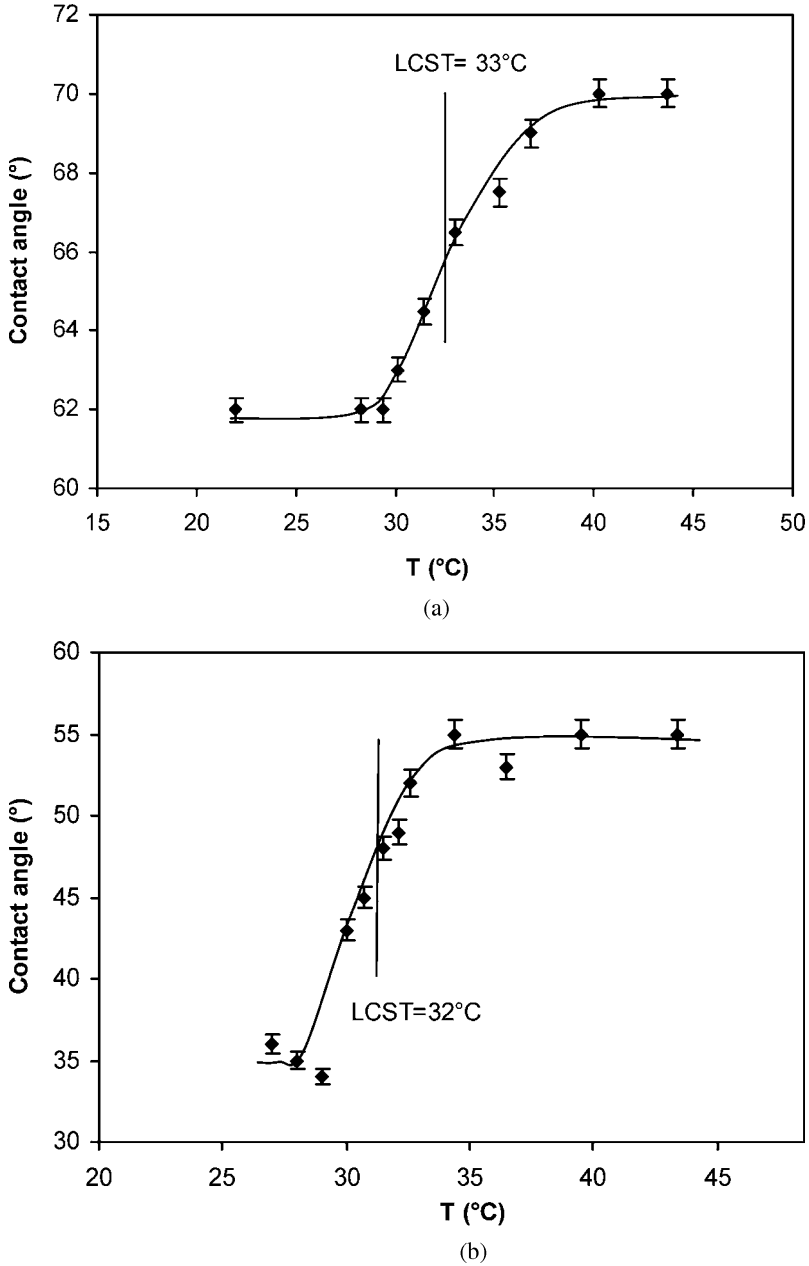
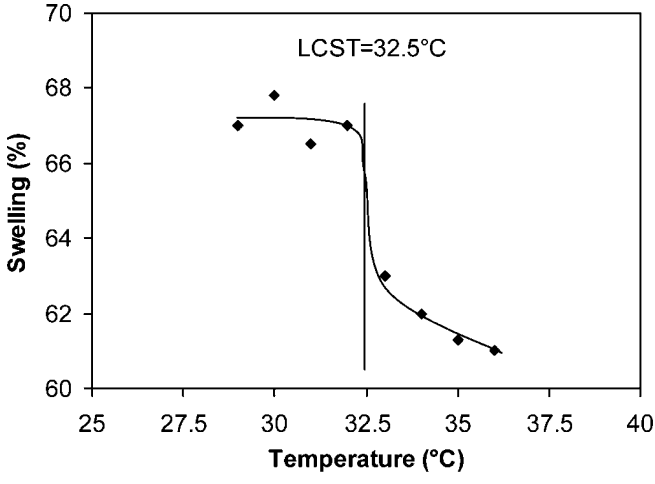
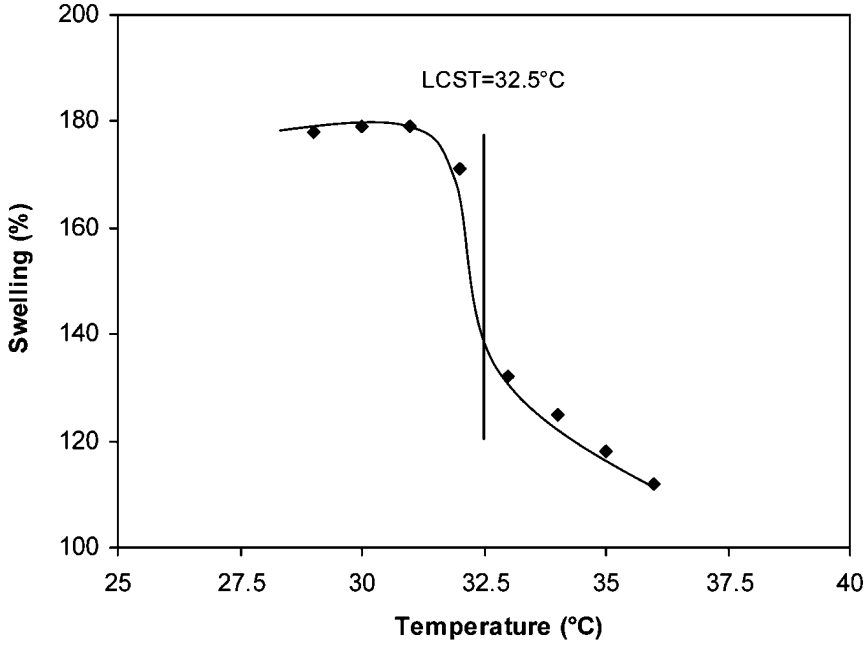


FIGURE 4 (a) Advancing water contact angle on NIPAAm-g-PP films, 98% graft as a function of temperature; (b) Advancing water contact angle on NIPAAm-g-PP, 1250% graft film, as a function of temperature.

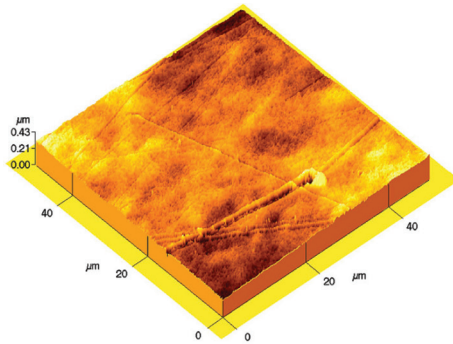


(a)



(b)

FIGURE 5 (a) Temperature dependence of the swelling ratio in water as a function of temperature, for NIPAAm-g-PP, 525% graft film; (b) Temperature dependence of the swelling ratio in water as a function of temperature, for NIPAAm-g-PP, 1150% graft film.



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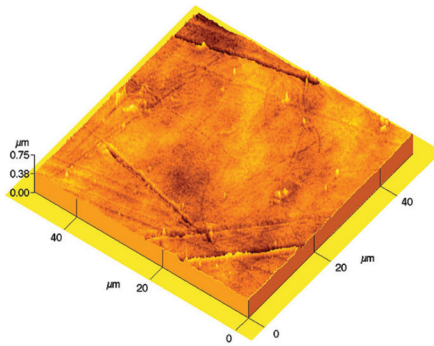

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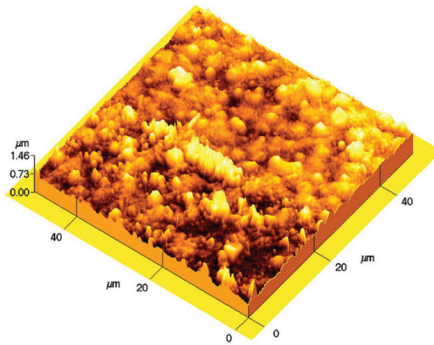

(c)

FIGURE 6 AFM topography of untreated and NIPAAm grafted PP films; PP film alone (a), and with increasing graft content: 25% (b) and 251% (c).

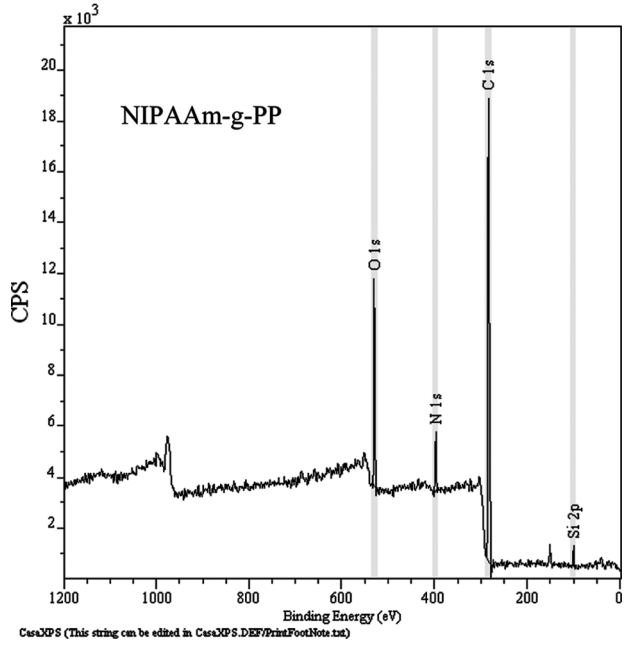

FIGURE 7 XPS spectra of NIPAAm-g-PP, 98% graft film.

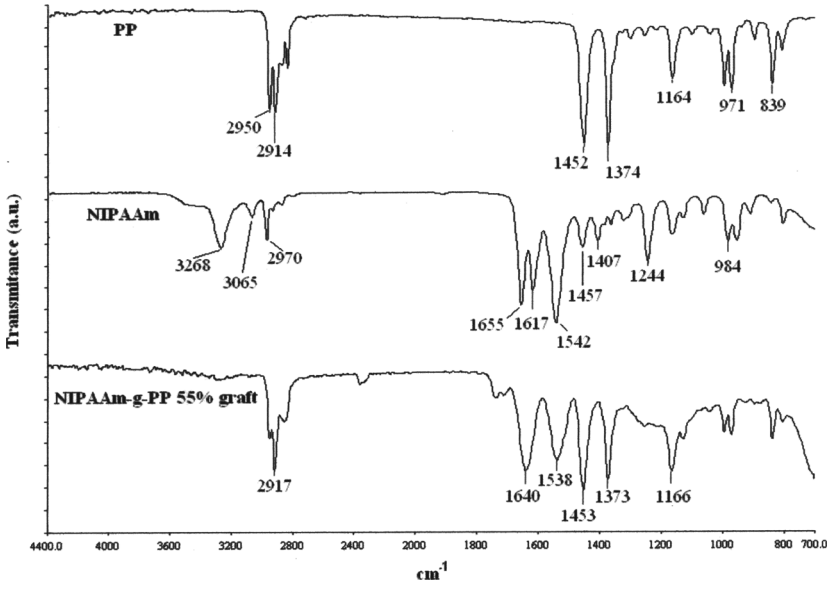

FIGURE 8 FTIR-ATR spectra of the starting and modified: PP film, NIPAAm and NIPAAm-g-PP 55% graft film.

Thermal behavior of films were characterized by thermogravimetric analysis in argon atmosphere, results indicated decomposition at 460°C for PP and 425°C for grafted films; they presented high thermal stability. Differential scanning calorimetry in second heating indicated melting point (m.p.) 156°C and 150°C for PP film and NIPAAm-g-PP (1150% graft) respectively.

CONCLUSIONS

The grafting of NIPAAm onto PP films by gamma preirradiation method was obtained from 10 to 1250% yield, at different preirradiation dose, dose rate, monomer concentration and reaction temperature, and the optimum condition of grafting were founded at 50°C, molar concentration of monomer of 3 mol L^{-1}, dose rate of 3.4 kGy/h and radiation dose of 100 kGy. NIPAAm-g-PP characterized by FTIR-ATR confirmed presence of a new copolymer with presence of amide and carbonyl in copolymer films; XPS confirmed by FTIR-ATR information, thermal analysis showed good thermal properties; swelling and water contact angle measured confirm LCST at 32.5°C ± 0.5°C in all grafting percentage, near of the value for NIPAAm hydrogels, but with better mechanical properties.

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