

Preparation of Polyurethane/Hectorite, Polyurethane/Montmorillonite, and Polyurethane/Laponite Nanocomposites without Organic Modifiers

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Received 29 November 2008; accepted 2 October 2009

DOI 10.1002/app.31532

Published online 10 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyurethane (PU) nanocomposites were prepared from hectorite (HEC) and laponite without adding any organic modifier. PU-montmorillonite nanocomposites were prepared for comparison. The structure of the composites were investigated by transmission electron microscopy, X-ray diffraction spectroscopy, and Fourier transform infrared spectroscopy. Thermal gravimetric analysis and dynamic mechanic analysis were used for

determination of the thermal and viscoelastic behaviors, respectively. Tensile tests were conducted for characterization of the mechanical properties. The results showed a 113.5% increase in the tensile strength of PU containing 7 wt % HEC compared to that of neat PU. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 832–837, 2010

Key words: clay; nanocomposite; polyurethane

INTRODUCTION

Polyurethanes (PUs) are unique materials with various applications such as biomedical, coating, adhesive, and composite applications.^{1–4} They have a copolymer structure with isocyanates as the hard domain and the polyol as the soft domain.⁵

The properties of PU can be adjusted by two main methods. The first method is the chemical route: formulating the PU with different isocyanate/polyol ratios and using different amounts of chain extender. The second method is the materials route: altering the properties of the PU with different reinforcing phases.⁵ Talc, mica, and glass fiber are commonly used fillers in the preparation of PU composites at the micro scale with increase in tensile strength of the composite material sacrificing the elongation at break and discoloring the polymer.⁶ In recent years, materials reinforced with nano size materials have been prepared, enabling strength increase without a reduction in elasticity, and enabling improved optical, thermal, and barrier proper-

ties. Within this context, clays are an important family of nano fillers.⁷

The clays used in the preparation of polymer nanocomposites are generally of the smectite-type, which have a well-ordered crystalline structure.⁸ Montmorillonite (MMT) is the most important member of smectite-type clays and is widely used in PU-clay nanocomposites.^{9–15} Although hectorite (HEC) is well-known clay for composite preparation, it is not used for PU nanocomposites. In literature, the mechanical properties of some polymers, such as polyethylene and starch, were improved by using HEC.^{8,16,17}

In this work, PU-HEC nanocomposites were prepared, which has never before been reported in literature. Laponite (LAP), which is a synthetic clay, has similar structure with natural HEC. PU-LAP nanocomposites were prepared for comparison. Furthermore, PU-MMT nanocomposites were prepared to compare with the PU-HEC and PU-LAP nanocomposites.

EXPERIMENTAL

Materials

Aromatic PU was commercially obtained from Flokser Group (Turkey) in the form of PU-dimethyl formamide (DMF) solution (35 wt % solid). The

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TABLE I
Chemical Analysis of HEC and MMT

Sample	Ignition loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Li ₂ O
MMT	11.15	61.7	16.45	1.72	0.09	2.1	6.08	0.17	0.34	–
HEC	21.5	50.57	0.8	0.09	0.02	14.49	11.7	0.1	0.1	0.45

molecular weight of PU was 30,000 Dalton. It was synthesized by reacting methyl-diphenyl-diisocyanate (MDI) and polyester polyol and it was further chain extended with 1,4-butane diol.

The natural clay, HEC, was taken from the region of Eskisehir of Turkey. The natural clay, MMT, was taken from Bigadic, Balıkesir region of Turkey. They were analyzed both by chemically and by mineralogically (Table I). The purities of HEC and MMT were determined to be 90 and 95% pure, respectively. The cation exchange capacity was determined to be 95 meq/100 g for HEC and 53 meq/100 g for MMT. The calcite content of HEC and MMT was found to be 5 and 3%, respectively. Both HEC and MMT were used without purification. The Laponite RD (LAP) was obtained from Southern Clay.

Composite preparation

All the PU composites were prepared by using the solvent casting method. The DMF-clay dispersion was prepared in an ultrasonic bath at room temperature for 15 min. The PU-DMF solution (35 wt %) was added to this DMF-clay solution. The final solution had 76.6 wt % of DMF. The stirring time for the PU-clay-DMF solution was 4.5 h. An automatic solvent casting machine and an adjustable solvent casting knife were used to obtain wet nanocomposite films of 1000 micrometers. The final PU-clay nanocomposites were obtained by evaporating the solvent and the final dry film thickness was 100 micrometers.

The nanocomposites were designated using the abbreviation PU a b , where a indicated the type of the clay used, and b indicated the clay percentage in the composite.

Characterization of nanocomposites

PANalytical X'pert Pro X-ray was used at 1°/min with a [1/2] slit. Transmission electron microscopy (TEM) was operated at 200 kV and images were obtained by Gatan Model 694 Slow Scan CCD Camera system. Measurements on images were performed by the Gatan Digital Micrograph software. The contact angle was measured with KSV Cam200 goniometer. Fourier transform infrared spectroscopy (FTIR) analysis was carried out on a Perkin Elmer1 spectrometer by using the ATR mode. Shimadzu

AGS-J measurement device was used to conduct tensile testing of neat PU and the nanocomposite films (100 × 10 × 0.1 mm). The speed for the tensile testing was 20 mm/min. The viscoelastic properties of the polymer films (40 × 10 × 0.1 mm) were determined by a Perkin-Elmer Diamond dynamic mechanical analysis machine operating in tensile mode. The relaxation spectrum was scanned from –100 to 100°C with a frequency of 1 Hz and a heating rate of 3°C/min. The thermal gravimetric analysis (TGA) studies were carried out using an Perkin-Elmer Diamond TG/DTA, by heating from room temperature to 1200°C, under nitrogen atmosphere at a heating rate of 100°C/min.

RESULTS AND DISCUSSION

Composite characterization

Polyurethane-hectorite (PU-HEC) nanocomposites were prepared with clay contents of 1–15 wt % Polyurethane-laponite (PU-LAP) nanocomposites could not be prepared above 5 wt % because of agglomeration of LAP in the polyurethane-DMF solution. As a comparison of the nanocomposite properties, polyurethane-montmorillonite (PU-MMT) nanocomposites were prepared with clay contents of 3, 5, and 7 wt % of MMT. X-ray results showing the good exfoliation of the nanocomposites of PU-HEC and PU-MMT were given in our previous study.¹⁸ The X-ray patterns of PU-LAP are given in Figure 1. As the characteristic peak of the clay disappeared, it was concluded that a good dispersion of the clays in PU

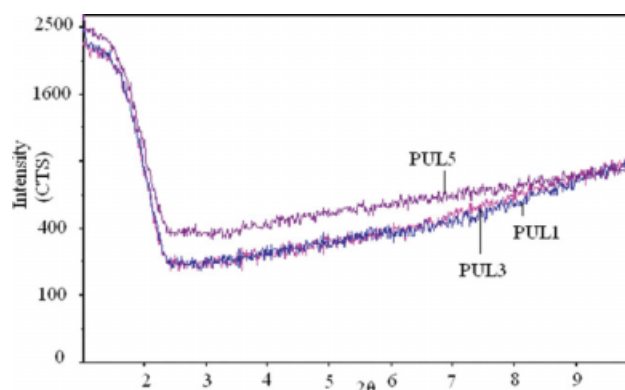


Figure 1 The X-ray patterns of PU-laponite nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

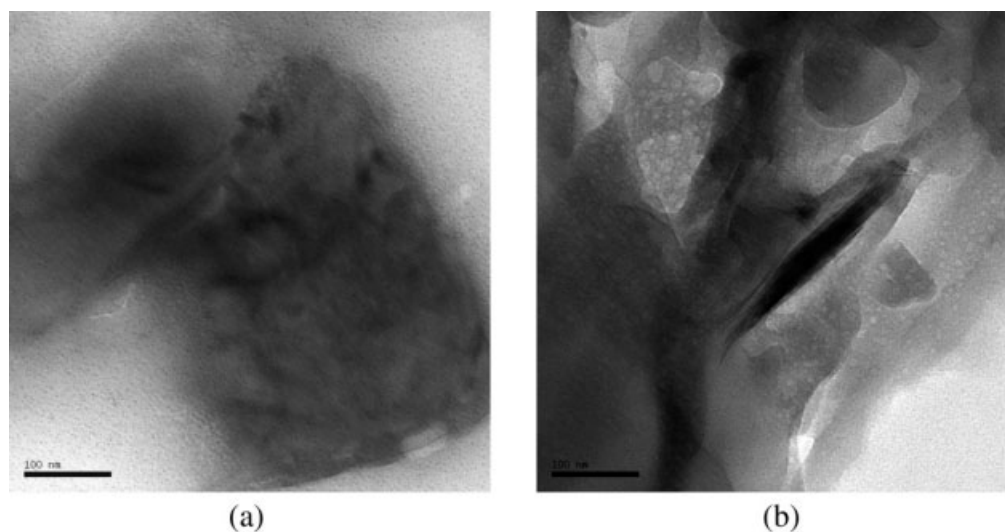


Figure 2 (a) TEM image of PUH1, (b) TEM image of PUH10.

matrix was achieved. The X-ray result was also confirmed by TEM studies. In Figure 2(a), the TEM micrograph showed that a good exfoliated structure was obtained for the PU-HEC composite containing 1 wt % of HEC. The TEM images of the composites containing 10 wt % of HEC are given in Figure 2(b). Even though the exfoliated structure was not obtained, the intercalated structure was observed for the PUH10 composite.

The FTIR spectra of the PU and PUH10 nanocomposites are shown in Figure 3(a). One of the peaks at 959.97 cm^{-1} disappeared in the PU structure after 1 and 3 wt % HEC addition. Takeichi and Guo¹⁹ stated that there is C—O out of plane deformation at this wavelength. Wu et al.²⁰ stated that there is O—H out of plane stretch around the same wavelength. This led the researchers to think that there was a C—O—H deformation that showed excellent interaction of the OH groups of the clays. On the other hand, the peak at around 960 cm^{-1} did not disappear for the MMT-clay nanocomposites [Fig. 3(b)]. This was attributed to the weaker interaction of the MMT with PU. The FTIR spectra of the PU-LAP were also measured [Fig. 3(c)]. The loss of the 959.97 cm^{-1} peak was observed for the LAP nanocomposites as well. This was attributed to the good interaction of the clay and the PU. With 7, 10, or 15 wt % HEC addition, the peaks belonging to the clay appeared at be close to 998.30 cm^{-1} .

One of the major important reasons for achieving successful nanocomposites was the easy swelling of the clays in DMF solvent, so the clay could be easily dispersed in the PU matrix. The second reason for achieving good nanocomposite structures was the hydrophilicity of the PU. Because of the incompatibility between the hydrophilic clays and hydrophobic polyolefins, it is not easy to prepare nanocompo-

sites.²¹ For this reason, organophilic clays are required for the thermoplastic polyolefins. However, the PU used in this study was hydrophilic. Its contact angle was measured as to be 63.7° . Thus, the nanocomposite could be successfully prepared from the unmodified HEC and LAP.

Mechanical properties

Mechanical properties of the composites prepared in this study are given in Figure 4. The tensile strength of the HEC-based PU composites was significantly increased by increasing the clay content up to about 7 wt % clay, and the tensile strength increased 113.48% by the addition of 7 wt % HEC. In literature, similar results were obtained.^{10,22} The researchers observed a peak value among the clay nanocomposites. The increase in the mechanical properties was attributed to the individual HEC platelets dispersed into the PU matrix.^{8,14} The hydrogen bonding occurred mainly between the PU and the HEC because of the hydrophilicity of both the HEC and the PU. Above a certain level of clay loading, as the polymer integrity was lost, the tensile strength was decreased. When the PU-MMT, PU-LAP, and PU-HEC results were compared, the HEC was the most effective type of clay for increasing the strength of polymer in this study.

Viscoelastic and thermal properties

The dynamic mechanical analysis results for HEC, LAP, and MMT-based PUs are demonstrated in Figure 5. Except for the addition of 15 wt % HEC, the modulus in the rubbery region increased for HEC-based composites compared to that of pristine PU [Fig. 5(a)]. The same trend is also reported in

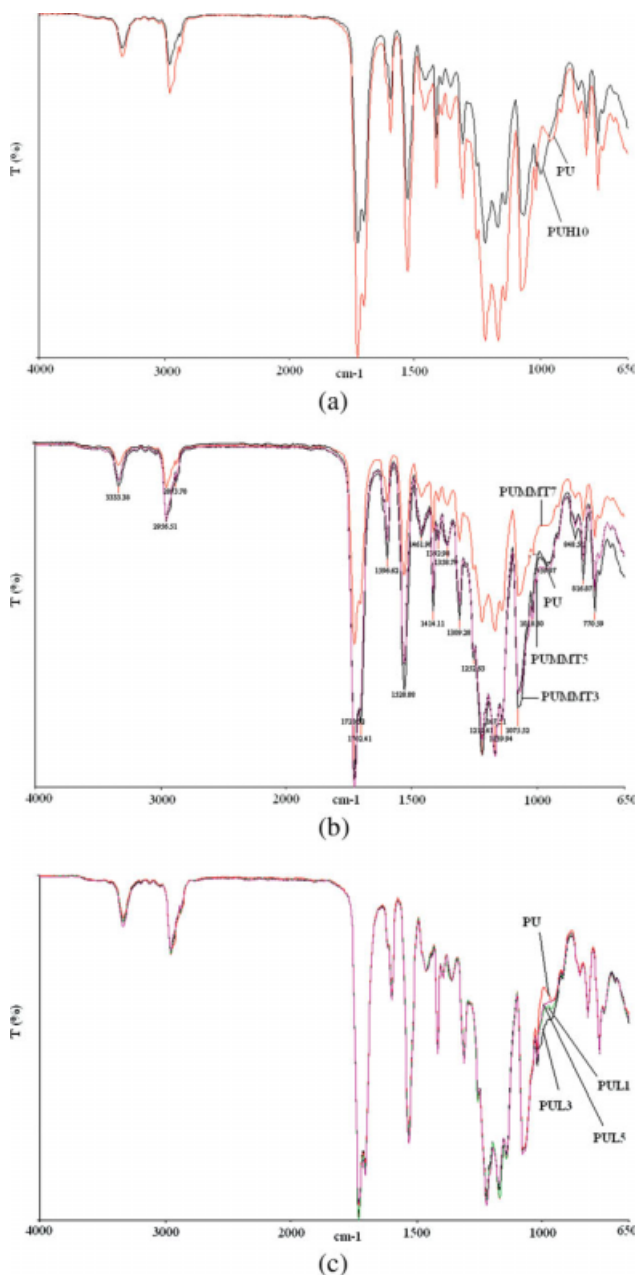


Figure 3 (a) The FTIR spectra of PU and PU-HEC nanocomposite, (b) The FTIR spectra of PU and PU-MMT nanocomposites, and (c) The FTIR spectra of PU and PU-LAP nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

literature.⁶ The highest value was obtained for PU with 7 wt % HEC. This result confirmed the results of the tensile tests. The high amount of HEC (15 wt %) caused the modulus to decrease. Tan delta peaks did not shift significantly for the HEC-based composites [Fig. 5(b)]. This shows that the nanocomposites did not alter the T_g of the neat PU. The height of the tan delta peak gives important information on the flexibility of the polymer. When the polymer loses its flexibility and becomes more rigid, the chains lose their elasticity and this is reflected in

the tan delta peaks as a decrease in the height of the peak. The height of the tan delta peak for all nanocomposites prepared from HEC decreased. The peak height of the high-strength compositions (5 and 7 wt % HEC content) decreased significantly.

In the case of MMT addition, the storage modulus of the composite at 3 wt % clay addition was lower than the PU at all the temperatures [Fig. 5(c)]. For 5 wt % MMT content, the storage modulus was slightly higher than that of the 3 wt % MMT addition, but it was still lower than that of the pristine polymer. For the composite containing 7 wt % MMT, the storage modulus was slightly higher than the neat PU for lower temperatures, but for higher temperatures, the modulus values were lower than the pristine polymer. When compared with the PU-HEC nanocomposites, PU-MMT nanocomposites were inferior in terms of the mechanical and viscoelastic properties, as shown from the tan delta curves [Fig. 5(d)]. However, the T_g for the polymer and the nanocomposite was almost the same. This indicated that the clay does not affect the T_g of the polymer. A similar result was observed by Korley et al.²³ The height of the tan delta curves for the composites containing 3 wt % and 5 wt % clay increased [Fig. 5(d)] compared to that of pristine PU. This showed that the nanocomposites became more elastic, which was reflected as a decrease in the elastic modulus. The nanocomposite with 7 wt % MMT gave lower tan delta curves, which were consistent with the modulus values.

The same modulus value was determined for the pristine polymer and the composite prepared with 1 wt % LAP in the glassy region [Fig. 5(e)]. On the other hand, all composites prepared with LAP showed a higher modulus than PU in the rubbery region. The height of the tan delta peak for the LAP-based composites was lower than that of pristine polymer [Fig. 5(f)]. The reason for this behavior is explained above for the HEC-based PUs.

The PU group was not thermally stable, and it started to degrade thermally around 300°C (Fig. 6). The 50% weight loss was around 420°C. The same trend was observed in literature.²⁴ The clay addition

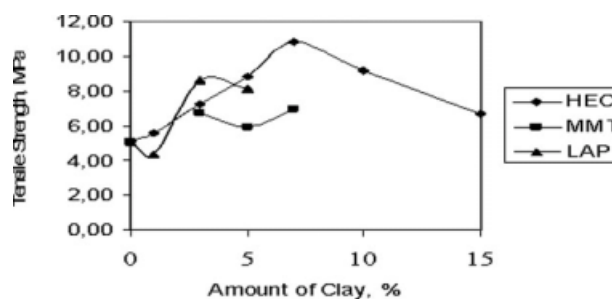


Figure 4 The mechanical properties of PU and PU nanocomposites.

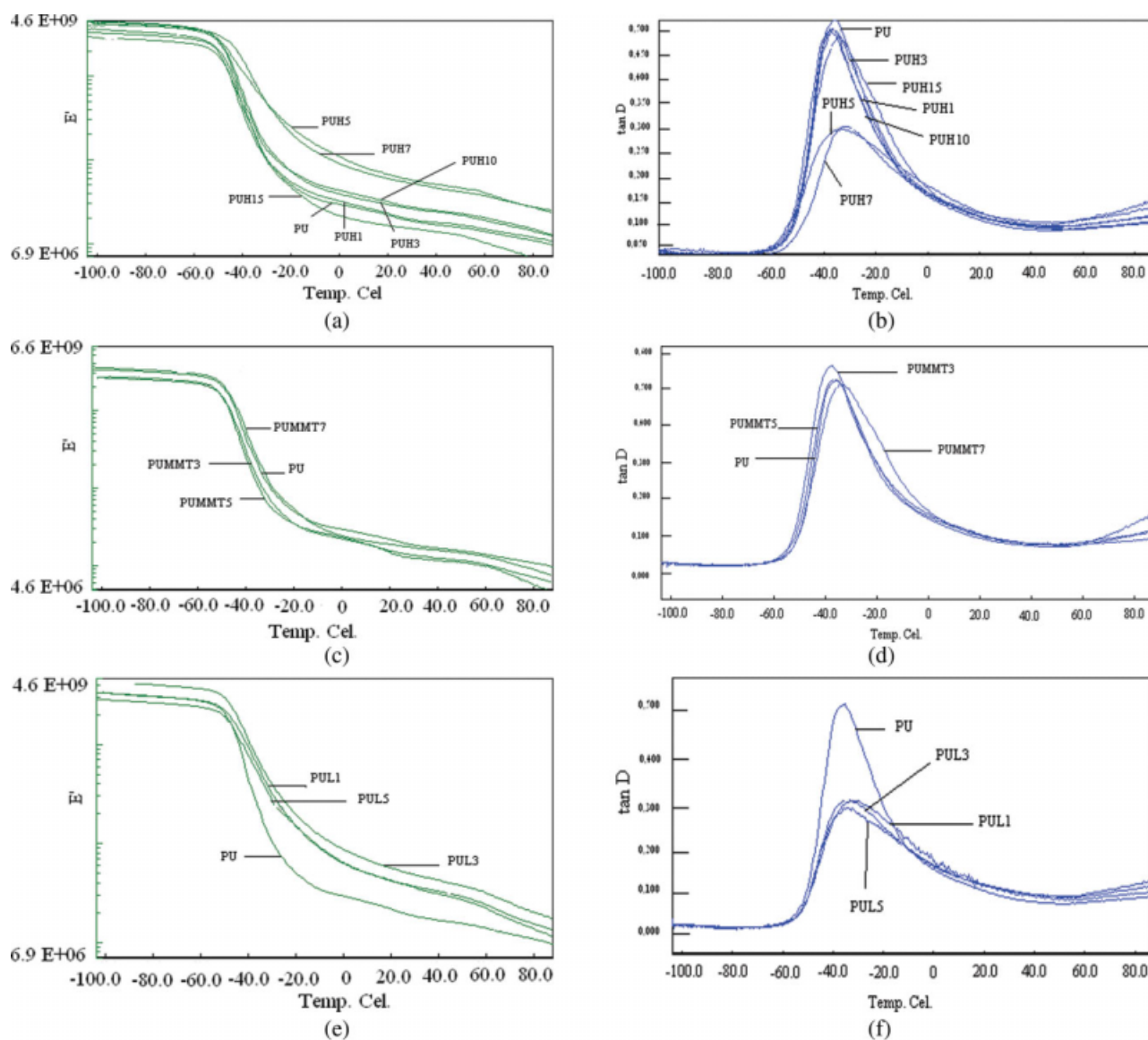


Figure 5 (a) The storage modulus (MPa) versus temp ($^{\circ}\text{C}$) of PU and PU-HEC nanocomposites, (b) the tan delta versus temp ($^{\circ}\text{C}$) of PU and PU-HEC (PUH) nanocomposites, (c) the storage modulus (MPa) versus temp ($^{\circ}\text{C}$) of PU and PU-MMT nanocomposites, (d) the tan delta versus temp ($^{\circ}\text{C}$) of PU and PU-MMT nanocomposites, (e) the storage modulus (MPa) versus temp ($^{\circ}\text{C}$) of PU and PU-LAP (PUL) nanocomposites, and (f) the tan delta versus ($^{\circ}\text{C}$) of PU and PU-LAP nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

did not cause a significant increase in the thermal stability of the composites.

CONCLUSIONS

In this study, PU nanocomposites were prepared with the HEC, MMT, and LAP clays. As the PU and the clays were hydrophilic and the clays could easily swell in the organic solvent used, the exfoliated structure could be obtained with organically unmodified clays. The significant improvements in the mechanical properties were obtained with nanocomposite structure. The best result was obtained

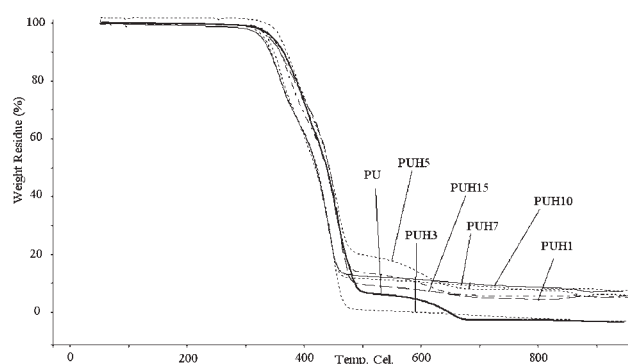


Figure 6 TGA analysis of PU and PU-HEC nanocomposites.

for the composite prepared with 7 wt % HEC. A 113.5% increase in the tensile strength occurred in PU containing 7 wt % hectorite, however, the material elasticity dramatically decreased. It was not possible to prepare LAP nanocomposite above 5 wt % by the method used in this study because of agglomeration of LAP.

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