Macromolecules
ADDITIONS AND CORRECTIONS

The Role of Nanoparticle Layer Separation in the Finite Deformation Response of Layered Polyurethane−Clay Nanocomposites [*Macromolecules* **2009**, *42*, 6588]. Amit K. Kaushik, Paul Podsiadlo, Ming Qin, Charles M. Shaw, Anthony M. Waas, Nicholas A. Kotov, and Ellen M. Arruda*

There is an error in the reported value of montmorillonite (MTM) specific gravity in second paragraph of Materials subsection leading to errors in its volume fraction in polyurethane−montmorillonite (PU−MTM) nanocomposites in Table 1, consequently changing the PU−MTM nanocomposite nomenclature in Tables 1−4 and MTM volume fraction in PU−MTM nanocomposites in Figures 1 and 3−6, in paragraphs 9−11 of the Results and Discussion, and in the first two paragraphs of the Conclusions and Future Work subsection. In summary, the changes in MTM specific gravity and the MTM volume fractions in PU−MTM nanocomposites reported in the text and the table nomenclature are as follows:

- specific gravity of MTM changes from 1.98 g/cm^3 to 2.86 g/cm^3
- 7 vol % (PU−MTM7) changes to 5 vol % (PU−MTM5)
- 10 vol % (PU−MTM10) changes to 7 vol % (PU−MTM7)
- 12 vol % (PU-MTM12) changes to 9 vol % (PU−MTM9)
- 16 vol % (PU-MTM16) changes to 12 vol % (PU−MTM12)
- 26 vol % (PU-MTM26) changes to 20 vol % (PU−MTM20)

The corrected Tables, Figures, and text are given below.

Page 6590.

Page 6592.

Page 6593.

Page 6593.

Page 6590.

Page 6592.

Page 6593.

Page 6594.

Page 6594.

Table 1. PU−MTM Nanocomposite Nomenclature

sample name	MTM loading (wt %)	MTM loading (vol %)
PU−MTM5	13	5
PU−MTM7	18	7
PU−MTM9	21	9
PU−MTM12	27	12
PU−MTM20	41	20

Table 2. Thickness of 300-Bilayer PU−MTM Nanocomposites and Average Bilayer Thickness as a Function of Average Volume Fraction of MTM Nanoparticles

sample name	film thickness (μm)	av bilayer thickness, t_b (nm)
PU−MTM5	16.1 ± 1.2	53
PU−MTM7	8.7 ± 0.7	31
PU−MTM9	6.8 ± 0.7	24
PU−MTM12	5.1 ± 0.3	17
PU−MTM20	3.2 ± 0.1	11

Table 3. Summary of the Mechanical Properties of Pure PU and PU−MTM Nanocomposites

sample name	modulus (GPa)	yield strength (MPa)	modulus ratio (E_{nc}/E_{pu})
PU	0.025 ± 0.005	2.0 ± 0.1	1
PU−MTM5	0.45 ± 0.05	21.1 ± 0.3	18
PU−MTM7	0.74 ± 0.10	25.2 ± 0.4	30
PU−MTM9	1.0 ± 0.20	27.3 ± 0.4	40
PU−MTM12	1.65 ± 0.15	28.5 ± 0.7	66
PU−MTM20	3.6 ± 0.2		144

Table 4. Summary of the Mechanical Properties of Pure PU and PU−MTM Nanocomposites

sample name	ultimate tensile strength (MPa)	ultimate strain
PU	13.2 ± 0.9	4.1 ± 0.10
PU−MTM5	41.2 ± 3.8	3.16 ± 0.10
PU−MTM7	39.5 ± 3.0	1.56 ± 0.08
PU−MTM9	41.0 ± 2.7	1.11 ± 0.09
PU−MTM12	37.4 ± 2.9	0.15 ± 0.14
PU−MTM20	34.2 ± 9.3	0.008 ± 0.003

Page 6589. Corrected paragraph in Materials section:

Na$^+$−montmorillonite (MTM) (Cloisite Na$^+$) clay with a specific gravity of 2.86 g/cm^3 was purchased from Southern Clay Products (Gonzales, TX). The as-received MTM nanoparticles were disk-like elements of thin silicate layers, 1 nm thick and ranging in diameter from 100 to 1000 nm, the average diameter being 110 nm as described by the manufacturer. A 0.5 wt % dispersion of MTM nanoparticles was used for the preparation of nanocomposites. 5 g of the as-received MTM clay was dissolved in 1 L of 18 MΩ cm^{-1}, pH = 5.6 deionized water under vigorous stirring for 1 week. This resulted in the exfoliation of clay into silicate layers due to the solvation of Na$^+$ cations holding them together.[29] After 1 week, the nondispersible fraction was allowed to precipitate and the supernatant was collected.

Page 6590. Corrected Paragraphs in Results and Discussion section:

PU−MTM nanocomposites demonstrated an increase in the stiffness, yield strength, and ultimate tensile strength when compared with pure PU (Figure 4A, Figure 4B, Table 3, and Table 4). With only 5 vol % of MTM nanoparticles, there was a 10.5-fold increase in the yield strength and an 18-fold increase in the stiffness of the PU−MTM nanocomposite compared to pure PU. The ultimate (nominal) tensile strength increased by a factor of 3.1. The stiffness

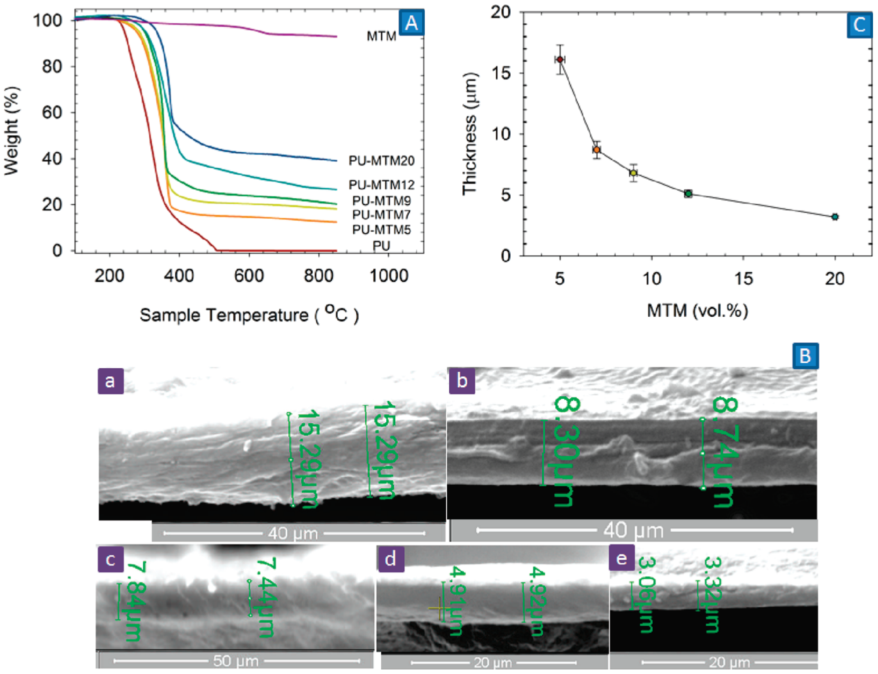

Figure 1. (A) Thermogravimetric analysis for PU, a series of PU−MTM nanocomposites, and MTM clay. (B) Typical SEM images showing cross sections of (a) 5, (b) 7, (c) 10, (d) 12, and (e) 20 vol % 300-bilayer PU−MTM nanocomposite. (C) Thickness of 300-bilayer PU−MTM nanocomposites as a function of volume fractions of MTM nanoparticles. Error bars indicate the uncertainty in thicknesses and volume fractions.

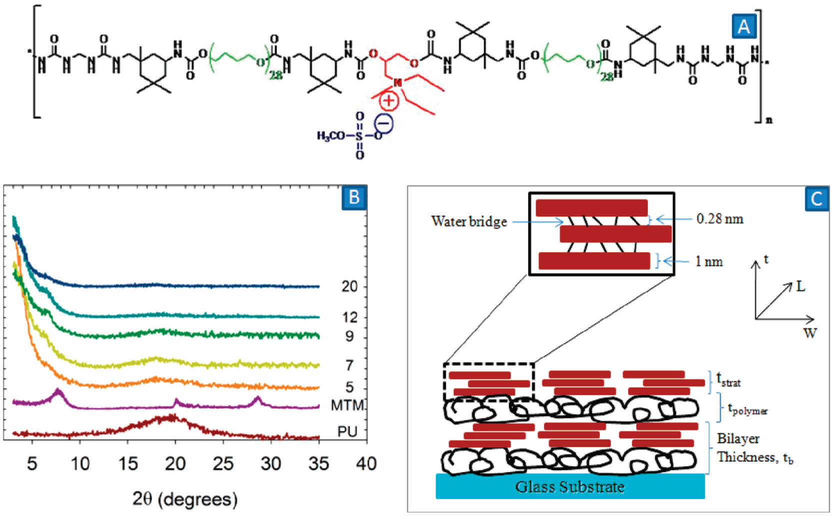

Figure 3. (A) Chemical structure of cationic PU copolymer. The cationic functional group of the polymer is highlighted in red, the counterion in blue, the soft segment in green, and the hard segment in black. (B) Wide-angle X-ray diffraction patterns of PU, MTM clay, and PUMTM nanocomposites. Numbers indicate average volume fractions of MTM nanoparticles. (C) Schematic nanostructure of the PU−MTM nanocomposite.

and yield strength continued to increase with an increase in the volume fraction of MTM nanoparticles. With 9 vol % MTM nanoparticles, the yield strength and stiffness increased 14 and 40 times, respectively, over pure PU. This enhancement in mechanical properties, viz., stiffness, yield strength, and ultimate strength, is attributed to the strong MTM nanoparticles alignment parallel to the direction of applied load that allowed a substantial fraction of the load to be transferred to the stiffer, stronger MTM nanoparticles. The ultimate strain-to-failure, however, decreased with increased volume fraction of MTM nanoparticles.

PU−MTM nanocomposites with less than 12 vol % MTM nanoparticles failed in tension with a pronounced yielding of the polymer phase. At 12 vol %, some of the specimens fractured with no yielding while a few specimens failed after yielding (cf. Figure 4C). This is also evident from a large standard deviation on the strain-to-failure value for only this nanocomposite in Table 4.

The large variation in strain-to-failure indicates a transition at this volume fraction from ductile to brittle behavior. Further increase in the volume fraction of MTM nanoparticles resulted in a brittle nanocomposite. The 20 vol % MTM nanocomposite had a strain-to-failure of 0.008 and

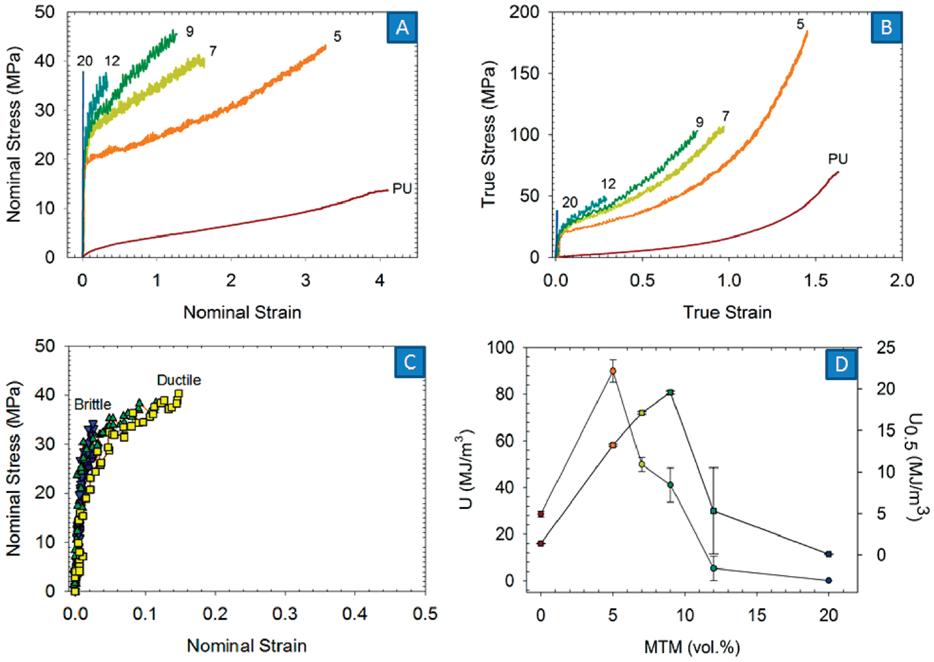

Figure 4. (A) Representative nominal stress−strain constitutive response of PU and PU−MTM nanocomposites. (B) Representative true stress−strain constitutive response of PU and PU−MTM nanocomposites. (C) Representative nominal stress−strain constitutive responses for 12 vol % PU−MTM nanocomposite specimens. (D) Strain energy at failure (shown as circular data points) and at 0.5 strain (shown as square data points) for PU and PU−MTM nanocomposites as a function of average volume fraction of MTM nanoparticles. Numbers shown in (A) and (B) indicate average volume fractions of MTM nanoparticles.

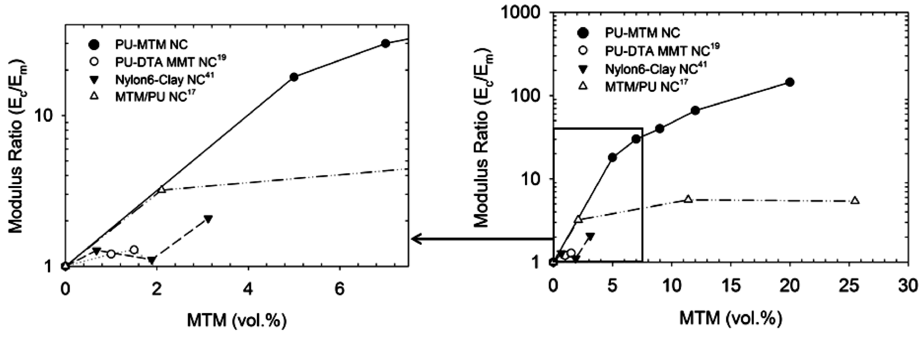

Figure 5. Comparison of enhancement in modulus of PU−MTM nanocomposites with other clay nanocomposites.[17,19,41]

a stiffness increase of more than 2 orders of magnitude over pure PU. Thus, these nanocomposites demonstrated an increasing stiffness (and yield strength) with nanoparticle volume fraction, in contrast to previous various attempts (Figure 5).[11,12,16−19,23,41] The strain energy at failure (area under the true stress−strain curves) increased 3.25-fold with an incorporation of 5 vol % of MTM nanoparticles when compared with PU (Figure 4D). Further increase in the volume fraction of MTM nanoparticles decreased the toughness due to the decrease in the ultimate strain-to-failure. The energy at moderate strains, however, increased with increasing MTM volume fraction until the volume fraction reached the transition point from ductile to brittle. The energy at 0.5 strain, $U_{0.5}$, increased ∼10 times with 9 vol % MTM nanoparticles when compared with pure PU (Figure 4D).

We believe that simultaneous improvement in stiffness, strength, and toughness in these PU−MTM nanocomposites is the result of both a strong interaction between the MTM nanoparticles and the PU and the control of defects such as regions of particle agglomeration and particle occlusions. The presence of MTM nanoparticles in alternate nanolayers modified the bulk PU in close proximity to the nanoparticles to that of a material composed of confined and stiffened PU chains with restricted mobility.[23,42−44] The PU particle size measured by dynamic light scattering suggested that PU chains attained a similar conformation at all MTM loadings.[45] Since the thickness of the PU layer decreased with an increase in MTM loading, the volume of confined PU chains increased with increased volume fractions of MTM nanoparticles or decreased PU layer thicknesses. An increase in the MTM loading or decrease in the polymer layer thickness gradually resulted in a transition of bulk PU into confined PU chains, thus resulting in brittle nanocomposites with enhanced stiffness and reduced ultimate strain-to-failure. This transition occurred at 12 vol %

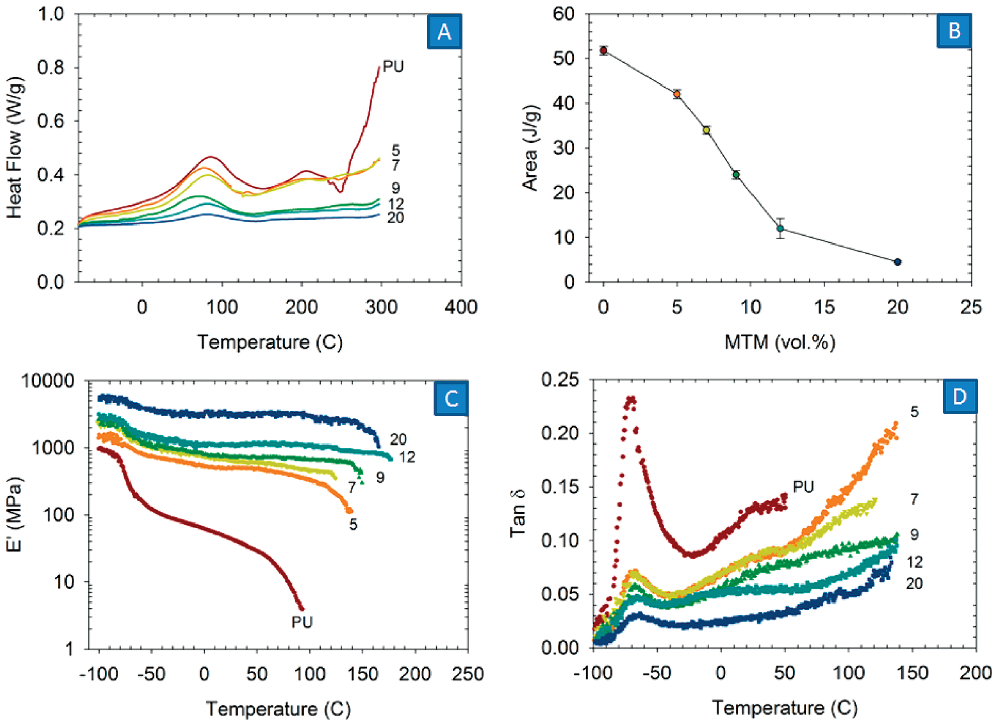

Figure 6. (A) DSC traces of pure PU and PU−MTM nanocomposites. (B) Area under the transition peak for pure PU and PU−MTM nanocomposites normalized by the amount of PU present. (C) Storage modulus as a function of sample temperature for pure PU and PU−MTM nanocomposites. (D) tan δ as a function of sample temperature for pure PU and PU−MTM nanocomposites. Numbers in (A), (C), and (D) indicate average volume fractions of MTM nanoparticles.

MTM nanoparticles corresponding to a polymer layer thickness or MTM nanoparticle separation of ~13 nm (with three silicate sheets in each clay nanolayer). Below this separation, brittle behavior dominated the nanocomposite response. At low levels of MTM nanoparticle loadings, the bulk polymer regions were sufficiently mobile and flexible to plastically deform and provide ductility to the nanocomposite response.

Page 6594. Corrected Paragraphs in Conclusions and Future Work section:

In summary, the role of MTM nanoparticle separation in controlling the finite deformation constitutive response of polymer−clay nanocomposites has been demonstrated. A series of PU−MTM nanocomposites, with alternating PU and MTM nanolayers, were prepared using the LBL manufacturing technique. LBL allowed us to vary the MTM nanoparticle volume fraction by systematically varying the MTM nanoparticle separation while retaining the structural organization at all volume fractions. The PU−MTM nanocomposites demonstrated enhanced mechanical properties at all volume fractions of MTM nanoparticles, e.g., the yield strength and stiffness increased 14 and 40 times, respectively, over pure PU with 9 vol % of MTM nanoparticles. The PU−MTM nanocomposite with 20 vol % MTM nanoparticles demonstrated a stiffness increase of more than 2 orders of magnitude.

A transition from ductile to brittle behavior in deformation response was observed at 12 vol % of MTM nanoparticles. We demonstrated the existence of a critical MTM nanoparticle separation below which brittle behavior dominated the nanocomposite response. Further reduction in MTM nanoparticle separation led to an increased restricted motion of PU chains, resulting in brittle fracture of PU−MTM nanocomposites.

DOI: 10.1021/ma100678b