Structure Development in Flexible Polyurethane Foam Nanocomposites

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ABSTRACT

Polyurethane (PU) foam–layered silicate nanocomposites were formed via reaction of polyol/water/sodium montmorillonite (Na-MMT) mixtures with toluene diisocyanate (TDI). The kinetics of both the PU copolymerisation and the microphase separation between poly(ether-urethane) soft segments and polyurea hard segments were determined using forced-adiabatic, attenuated total reflectance FTIR spectroscopy. Real-time chemo-rheological measurements under forced-adiabatic conditions were used to give modulus development and changes in normal force during the formation of reacting foams. Increasing silicate content accelerates polymerisation and decreases the time for microphase separation between soft and hard segments within PU foam nanocomposites.

Keywords: polyurethane, foam, nanocomposites, formation, structure

1 INTRODUCTION

Polymer-layered silicate nanocomposites provide the potential for materials with significantly enhanced mechanical properties combined with reductions in permeability and flammability, resulting from the incorporation of only a few weight percent of nanoscale lamellar filler into a polymer [1-4]. Reduced flammability [5] is particularly important in materials applications that require the use of flexible polyurethane foams.

The reactive processing of flexible water-blown polyurethane foam, from liquid monomers and oligomers, involves a complex combination of chemical and physical events. From room temperature and in less than five minutes, a liquid mixture of relatively low molar mass components is transformed into a segmented block copoly(urethane-urea) with a supramolecular architecture in the form of a cellular solid. Such structure development is determined by the relative kinetics of polymerisation and phase separation [6].

The polymer nanocomposites used in the present studies are based on montmorillonite (MMT), which displays a hierarchical morphology [7]. Montmorillonite typically exists as particles of ≥10 μm in size, comprising aggregated primary particles, or tactoids. These tactoids comprise a layered structure of thin (≈ 1 nm) negatively charged silicate-lamellae separated by charge-balancing cations in the interlayer (or gallery) spacings. The presence of intercalated MMT during PU foam formation is expected to significantly affect structure development that, in turn, determines the final morphological structures and properties of the resulting foam nanocomposites.

In the present studies, MMT intercalated with water is incorporated into a polyurethane (PU) bulk copolymerisation, in which the intercalated water is utilised as a chemical blowing agent during the formation of a flexible PU foam nanocomposite. Emphasis has been placed on real-time measurements such as FTIR spectroscopy and chemo-rheology carried out under forced-adiabatic temperature conditions identical to those created during typical foam manufacture.

This paper presents preliminary results from studies that establish the sequence of chemical and physical events and the role that the kinetics of polymerisation and micro-phase separation play in the development of morphology and structure in flexible polyurethane foam/clay nanocomposites.

2 EXPERIMENTAL

2.1 PU Foam Formulations and Processing

The polyurethane foams were formed via the reaction of toluene diisocyanate (TDI) with a mixture of a polyether polyol and de-ionised water acting as a chemical blowing agent. Thus, the simultaneous reactions of TDI with the polyether polyol and water leads to the formation of a segmented multiblock copoly(urethane-urea), which is blown into a foam by the cogeneration of carbon dioxide gas evolved from the water-isocyanate reaction. The polyol used was Alcupol F-4811 (Repsol Quimica), a triol of $M_n \approx 3{,}500$ g mol^{-1} comprising predominantly polyoxypropylene repeat units with a few mol % of polyoxyethylene units distributed randomly throughout the chain structure. The polyol/water mixture also contained an amine catalyst, N,N-dimethylethanolamine (ATOFINA), an organo-tin catalyst, dibutyltin dilaurate (Sigma-Aldrich) and a silicon surfactant, Tegostab B4900 (Goldschmidt). The TDI used was Voranate T80 (Dow Chemicals), an 80:20 isomeric blend of toluene 2,4- and 2,6-diisocyanate. The unmodified MMT used, PGW (Nanocor), is a high-purity grade.

Component (pbw)	F0	F5	F10
Polyol	100.00	100.00	100.00
Montmorillonite	-	8.69	18.34
De-ionised water	4.90	4.90	4.90
Tin catalyst	0.14	0.14	0.14
Amine catalyst	0.25	0.25	0.25
Silicone surfactant	1.10	1.10	1.10
TDI	58.65	58.65	58.65

Table 1: Formulations used to form the unfilled foam (F0) and the foam nanocomposites (F5 and F10) with 5 and 10 wt.-% MMT, respectively.

The as-received MMT (dried) and intercalated MMT (after sonication in mixtures comprising polyol, water, silicone surfactant and amine catalyst) were characterised using wide-angle X-ray diffraction (WAXD). Experimental WAXD details have been reported previously [8] and the results showed that the extent of intercalation and ordering in the polyol/water-MMT mixtures increased with MMT content.

The formulations used to form the unfilled PU foam (designated as F0) and the PLSN foams containing 5 and 10 wt.-% MMT (designated as F5 and F10, respectively) are summarised in Table 1. The required amount of intercalated polyol/water-MMT mixture was placed in a 900 ml polypropylene beaker and stirred at 3000 rpm for 10 s using a Multifix 4000 mechanical agitator. Tin catalyst (10 wt.-% solution in polyol) was added and the mixture stirred for another 10 s. Finally, the TDI was added and the reactant mixture was stirred for a further 10 s and then poured into a mould (a standard laboratory-scale cardboard box, 310 x 150 x 150 mm) to allow *in-situ* polymerisation to form the PU foam nanocomposite.

System	Cream time / s	Rise time / s	Rise height / mm
F0	18±1	110±10	160±10
F5	5±1	30±1	180±10
F10	5±1	32±2	200±10

Table 2: Processing behaviour of the unfilled (F0) and nanocomposite foams (F5 and F10).

Observations made during the processing of PU foams are shown in Table 2. For the unfilled foam system (F0), the time required for the bubbles within the reaction mixture to grow to a size where the mixture becomes opaque (a phenomenon commonly known as the "cream-time") was 18 s, which fell to only 5 s upon addition of MMT indicating a significant increase in the rate of CO_2 generation. Additionally, the time required to achieve maximum rise height before cell opening reduced significantly, indicating that phase separation occurs more rapidly on addition of MMT. However, the values of maximum rise height increased upon addition of MMT, indicating an increased rate of CO_2 generation prior to cell opening.

2.2 Real-time Analytical Techniques

As copolymerisation proceeds, the core of the rising polyurethane foam becomes self-insulated by the surrounding polymerising mixture creating, in effect, a quasi-adiabatic temperature environment. The adiabatic temperature rise (ATR) profile was measured for each unfilled and MMT nanocomposite foam. After correction for small heat losses, each ATR profile was used to calibrate apparatus in the time-resolved techniques, FTIR spectroscopy and chemo-rheometry, to obtain forced-adiabatic kinetics and rheological data for the respective formulation. Experimental details of the ATR and FTIR spectroscopy techniques have been reported previously [8].

New rheological apparatus including parallel-plates with integral heating elements was developed for use on a Rheometrics 800 rheometer to measure real-time chemo-rheological changes during the formation of foams reacting under forced-adiabatic conditions. Typically, using a plastic syringe, a 5 cm^3 sample of a polyol/water mixture was injected into the gap between the 50 mm diameter plates. A 5 % strain deformation at 1 Hz was employed for all formulations in conjunction with a 2.5 mm gap and a 75 mm cup. Temperature control of the heated plates and rheological data acquisition were initiated simultaneously with the addition of isocyanate to the polyol-water froth (i.e. time, $t = 0$). Rheological data (shear moduli, G', G") were recorded at a frequency of 0.2 Hz over a period of 1000 seconds. The normal force (exerted by the expanding foam on the upper plate) was recorded once every second throughout the duration of the experiment.

2 RESULTS AND DISCUSSION

Comparative heat-loss corrected ATR profiles are shown in Figure 1(a) for unfilled PU foam F0 and foams F05 and F10 containing 5 and 10 % w/w of MMT. In the initial stages ($t < 100$ s) there is a significant increase in the rate of reaction with increasing MMT content due possibly to some surface catalytic effects associated with the high-surface area MMT. At longer times ($t > 100$ s) and after microphase separation has occurred, the rates of reaction decrease dramatically with the F05 foam showing slightly more reaction than observed for the F0 and F10 foams.

Forced-adiabatic FTIR spectroscopy provided kinetics data for both copolymerisation and microphase separation. The decay in the intensity of the NCO absorption band at 2270 cm^{-1} was used to monitor the conversion of TDI functional groups, and the results confirmed that the rate of polymerisation

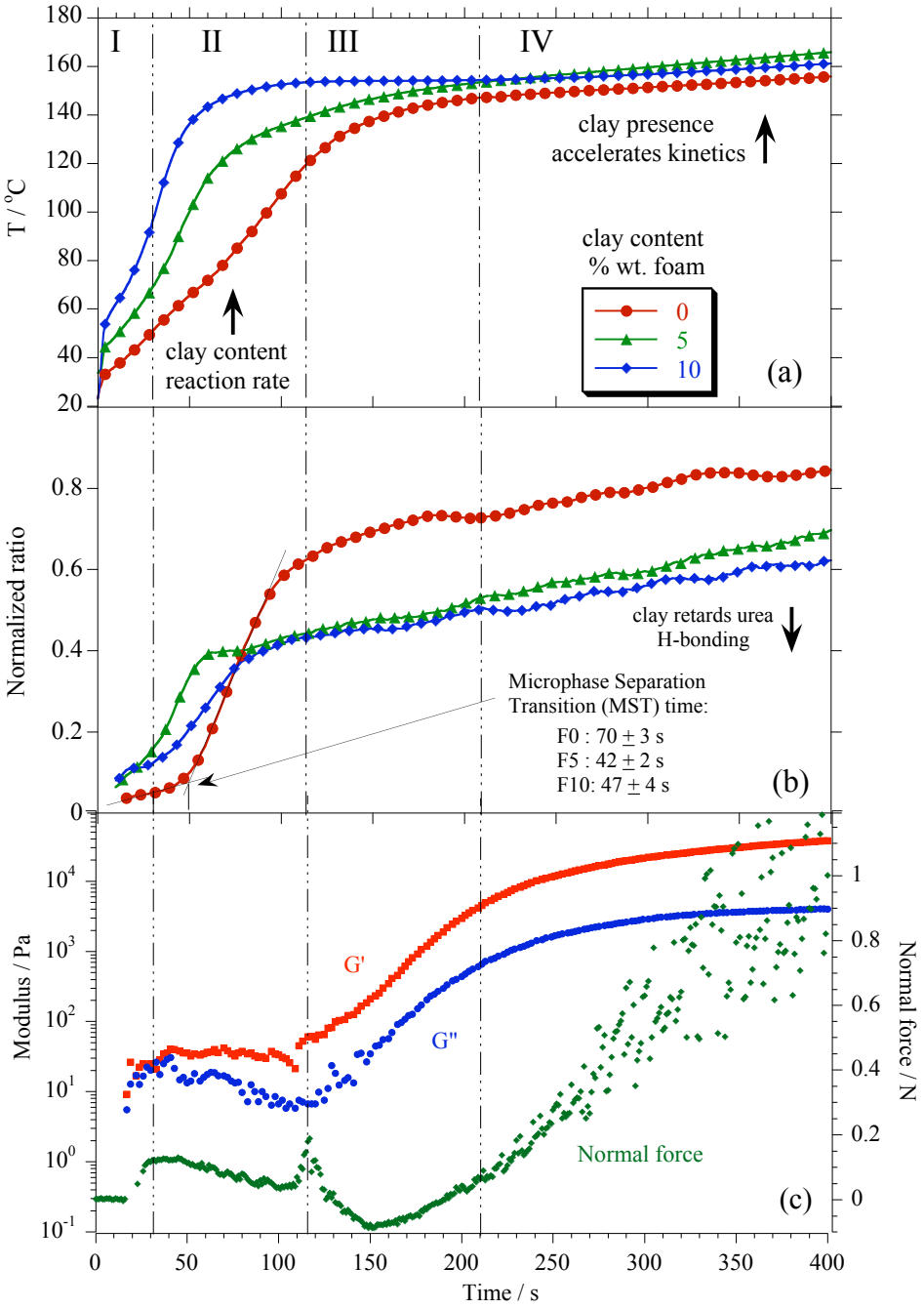

Figure 1. Time-correlated plots showing the four main regions (I-IV) of structure development during the reactive processing of water-blown flexible PU foam nanocomposites.

(I) Bubble nucleation and expansion. (II) Development of a packed bubble network. (III) Microphase separation. (IV) Final structure development.

(a) Polymerisation kinetics (ATR profiles). (b) Phase-separation kinetics (FTIR, hydrogen-bonded urea, 1639 cm^{-1}). (c) Elastic and loss shear moduli (G', G"), and normal force profiles (chemo-rheometry).

throughout the formation of the foams increases with increased MMT content. The kinetics of microphase separation between poly(ether-urethane) soft segments and polyurea hard segments were obtained from the carbonyl regions of the mid-infrared spectra that were used to monitor the evolution of soluble urea (~1711 cm^{-1}) and hydrogen-bonded bidendate urea (~1639 cm^{-1}).

The evolution of soluble and hydrogen-bonded ureas for the unfilled foam F0 is shown in Figure 1(b). Soluble urea is formed initially and its concentration increases steadily during foam formation. At around 70 s the concentration of hydrogen-bonded urea increases sharply, and the microphase-separation transition (MST), the point defining the onset of rapid evolution of hydrogen-bonded urea, was determined by the intersection of tangents drawn to the data before and after the sudden increase in the 1639 cm^{-1} absorbance. Such analysis of the derived FTIR data gave MST times of 42±2 s and 47±3 s for F05 and F10 foams, respectively, compared to 68±3 s for the unfilled F0 foam. However, despite the significant reductions in MST times, the presence of MMT in the foams retards the development of hydrogen-bonded urea groups in the hard-segment phases at longer processing times ($t > 100$ s), after the MST.

The forced-adiabatic chemo-rheology data in Figure 1(c) show sudden and rapid increases in both moduli (G' and G") that coincide with the formation of bidentate urea species (as evidenced by FTIR measurements) and result from the formation of physically-bound, polyurea hard-segment domains. The specially-designed parallel plates fitted on the rheometer enable the normal force exerted on the upper plate by the expanding foam to be used as an accurate method of identifying the point at which a phase-separated morphology is developed. The onset of cell opening was determined by a sudden drop in normal force and was observed to occur typically 5-15 seconds after polymer stiffening begins.

Chemo-rheology, in conjunction with FTIR spectroscopy, enables identification of the four main regions of morphological development occurring during foam formation. The regions are summarised as follows.

Region I: Bubble Nucleation and Expansion. The expanding foam between the plates causes the initial rise in normal force, and the formation a bubble network (Marangoni effect) increases the modulus.

Region II: Packed Bubble Network. In the packed bubble network region, G'~50 Pa. Polymerisation increases modulus, whereas simultaneous temperature-induced thinning and increased gas volume fraction decrease modulus. Once the volume fraction of bubbles exceeds 0.85 the modulus is relatively insensitive to further increments in gas content, hence the observed plateau in Region II.

Region III: Microphase Separation. Cell opening suddenly arrests foam expansion after the start of Region III, clearly shown by a rapid drop of normal force. At cell opening, the foam must possess enough dimensional stability to avoid foam collapse. With polymer vitrification and hard-phase segregation, modulus increases, indicating a rapid formation of stronger cell structures.

Region IV: Final Curing. Here, final foam structure is achieved, as modulus slowly increases and normal force rises. Structure development is completed over relatively longer time period, and increases in modulus occur due to covalent cross-linking and hard segment annealing, although skin formation around the foam may make a major contribution.

3 SUMMARY

These unique studies show how the development and use of real-time analytical techniques enable structure development to be monitored continuously during the reactive processing of flexible polyurethane foam nanocomposites. Each technique provides some specific information, but only by correlating the information from **all** of the techniques is the full sequence of chemical, physical and morphological events that occur during the reactive processing of water-blown flexible polyurethane foam completely defined. The excellent correlation of the analytical techniques and their identification with the four main regions (I-IV) of structure development is clearly illustrated in Figure 1.

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