Structure Development in Flexible Polyurethane Foam-Layered Silicate Nanocomposites

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Summary: Polyurethane foam nanocomposites were formed via *in-situ* copolymerisations, in which polyether polyol/water-montmorillonite mixtures were reacted with toluene diisocyanate. The unmodified Na^+- montmorillonite (MMT) was swollen in polyol/water using an ultrasound technique resulting in intercalated layers with increased basal spacings of 2.3 ± 0.1 nm. Measurements of quasi-adiabatic temperature rise showed higher reaction rates as MMT loading increased from 0 to 10 wt.-%. Forced-adiabatic FTIR spectroscopy was used to determine the kinetics of both the copolymerisation and of the microphase separation between poly(ether-urethane) soft segments and polyurea hard segments. The apparent microphase-separation transition time decreased from 70 ± 3 to 42 ± 2 s upon addition of $\leq$10 wt.-% MMT, but at reaction times $>$100 s there was significant retardation of the development of hydrogen bonding in the urea groups of the hard-segment phase.

Keywords: clay; foams; FT-IR; nanocomposites; phase separation; polyurethanes

Introduction

Polymer-layered silicate nanocomposites (PLSN) have attracted considerable scientific and commercial interest over the past decade.[1–4] The main driver for this is the potential for significant enhancement in mechanical properties,[1–4] combined with reductions in permeability[5] and flammability,[6] resulting from the incorporation of only a few weight percent (wt.-%) of a nanoscale lamellar filler into a polymer. The polymer nanocomposites studied here are based on montmorillonite (MMT), which displays a hierarchical morphology.[7] Montmorillonite typically exists as particles of $\geq$10 μm in size, comprising aggregated primary particles, or tactoids. These tactoids have a layered structure consisting of thin ($\approx$1 nm) negatively-charged silicate-lamellae separated by charge-balancing cations in the interlayer (or gallery) spacings. Thus, delamination of a tactoid may produce a number of thinner silicate-lamellae stacks, but may also release individual silicate lamellae – a process commonly termed exfoliation. These exfoliated silicate lamellae exhibit both high surface area (700–800 m^2 g^{-1}) and large aspect ratios (often $\geq$100) which, when combined with their high tensile modulus ($\geq$178 GPa), result in significant enhancements in properties.[1–6]

Typically, organo-modified MMT (OMMT), produced via ion-exchange reactions with cationic surfactants,[1–4] is used to form PLSN in order to increase the degree of exfoliation. The aim of this modification is to encourage monomers or polymer chains to diffuse (intercalate) into the interlayer spacings, swelling the layered structure to form intercalated lamellae stacks. Thus, the two most common techniques of initiating exfoliation involve either subsequent polymerisation of intercalated monomers, or the application of high stresses to polymer-intercalated lamellae stacks during melt compounding.[1–4] As an alternative to ion exchange, unmodified MMT readily forms exfoliated slurries

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in water and these have been incorporated into hydrophilic polymers to form PLSN.[8,9]

In this study, 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 PLSN. There have been a number of studies on PLSN based on solid PU matrices,[3,4,10–17] but relatively few on cellular PU-PLSN.[18–20] In addition, no studies on the kinetics of structure-development during the formation of PU-PLSN have so far been reported. The present paper presents preliminary results from studies aimed at understanding the effects of nanoclay fillers on both the kinetics of copolymerisation and microphase separation during the formation of a cellular PU / MMT PLSN.

Experimental Part

Materials

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 co-generation 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. The MMT was characterised using wide-angle X-ray diffraction (WAXD). WAXD was performed in reflection mode using a Philips X'pert PRO MPD. Using an incident X-ray wavelength of 0.1542 nm, WAXD data were obtained between a range of scattering angle (2θ) of $1° \leq 2\theta \leq 30°$ with a step size of 0.05° and a scan rate of $0.3°$ min^{-1}.

Intercalation of MMT in Polyol/water Mixtures

The required amounts of MMT, polyol, water, silicone surfactant and amine catalyst were weighed and mixed in a sealable glass container. The mixture was then subjected to 50–60 Hz ultrasound waves (Precision Ultrasonic Cleaning, Ultrawave) for 2 hours at 60 °C. The extent of intercalation was characterised using WAXD, performed in reflection mode over a range of scattering angle (2θ) of $1° \leq 2\theta \leq 10°$ using a Philips X'pert PRO MPD.

Preparation of Polyurethane Foam Nanocomposites

Table 1 contains 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). Each formulation was based on 200g of polyol. 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)

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

Component[a]	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

[a] Parts by weight.

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 before being poured into a mould (a standard laboratory-scale cardboard box, 310 × 150 × 150 mm) to allow *in-situ* polymerisation to form the PU foam nanocomposite.

Adiabatic Temperature Rise (ATR)

ATR measurements were carried out over 1200 s using two thermocouples (Omega Eng. Inc.) positioned at the midpoint of the mould. Temperatures were recorded as a function of time and at a frequency of 1 Hz via a Macintosh® PC equipped with Strawberry Tree ACM-12-8 data acquisition hardware and a Workbench™ V3.1 software package. The reaction exotherm generated during foam formation produced temperature-time (ATR) profiles that were then corrected for small heat losses using the following equation:[21]

$$T_{t,corr} = T_t + \frac{U}{\rho C_p} \int_0^t (T_t - T_{amb})dt$$

where C_p and ρ are the specific heat capacity and density of the PU, respectively, T is the temperature, t is the reaction time and U is the heat transfer coefficient per unit volume.

Forced-adiabatic Fourier Transform-Infrared (FTIR) Spectroscopy

The technique used was attenuated total reflectance (a.t.r.) FTIR spectroscopy. For each foam formulation, the ATR heating profile was calibrated before being applied to the FTIR reaction cell containing a ZnSe crystal. The cell was placed between the infrared generator and the receiver in a FTIR spectrometer (Impact 410, Thermo Nicolet). A 1 cm^3 sample of the liquid reaction mixture was poured onto the crystal surface, and the infrared data were collected at a resolution of 4 cm^{-1}, co-adding 4 scans per spectrum: the total time per spectrum was 2.2 seconds. The temperature of the FTIR reaction cell was recorded as a function of time at a frequency of 1 Hz via two type-J single-wire thermocouple wires, positioned adjacent to the ZnSe crystal in the cell. The FTIR data were corrected for baseline and ATR geometry effects and analysed using Omnic© software (Nicolet Instrument Corp.) to give FTIR absorbance versus time profiles.

Results and Discussion

Characterisation of Clays and Clay/Water/Polyol Mixtures

Figure 1 shows a typical WAXD profile between $1^\circ \leq 2\theta \leq 10^\circ$ for PGW. The (001)-reflection is seen to occur at $2\theta = 7.2^\circ$, giving a d_{001}-spacing of 1.24 nm and an interlayer spacing (calculated as d-spacing minus the silicate lamella thickness of 0.94 nm) of 0.30 nm, which corresponds to a residual monolayer of water.[22] MMT added to the polyol/water mixture becomes hydrated and swells. The WAXD profiles for the clay mixtures in Figure 1 show that intercalation/exfoliation of the MMT by the polyol/water (P/W) mixture has occurred during ultrasound treatment. The polyol/water-MMT mixture (P/W/MMT-1) shows weak scattering around $2\theta \approx 4^\circ$ and 6°, features that are more clearly defined in the polyol/water-MMT mixture (P/W/MMT-2) indicating that the extent of intercalation and order increases with MMT content. The initial, poorly-defined peaks ($2\theta \approx 4^\circ$) for the P/W/MMT-1 and P/W/MMT-2 mixtures correspond to d_{001} values of 2.3 ± 0.1 nm for the basal spacings in the nanoclay compared to 0.9 nm for that in the pure MMT sample. Water swells MMT by forming molecular layers in the galleries, with each layer of water increasing the basal spacing by approximately 0.28 nm.[22] Thus, the intercalation of two and four molecular layers of water in the MMT would generate WAXD peaks at $2\theta \approx 5.9^\circ$ and 4.3°, respectively, which corresponds well with the WAXD profiles of the clays mixtures. In addition to the intercalation of water it is possible for exfoliation of silicate lamellae to occur, which would reduce the scattering intensity in the system. It is also possible for the

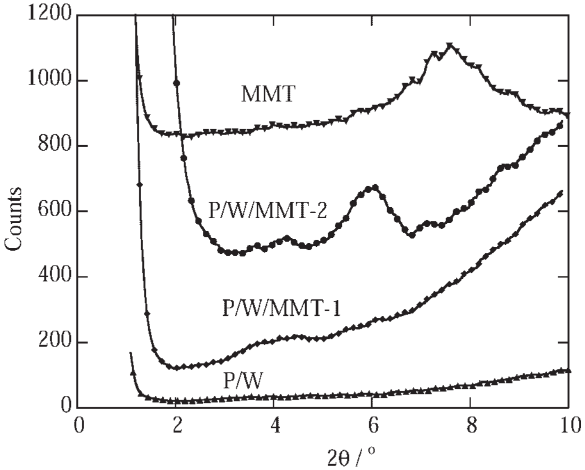

Figure 1.
WAXD patterns of the polyol/water mixture (P/W), MMT and polyol/water-MMT mixtures (P/W/MMT-1 and P/W/MMT-2). P/W/MMT-1 and P/W/MMT-2 mixtures contain 7.65 and 14.9 wt.-% MMT, respectively, giving 5 and 10% wt.-% MMT in the final PU foams.

polyol to intercalate the swollen MMT, which would tend to increase the interlayer spacing still further, although there is little evidence to suggest that this occurs to a significant extent.

Processing Behaviour

The formation of flexible PU foams involves a complex combination of chemical and physical events that occur within minutes, as a liquid mixture of relatively low molar mass reactants polymerises to form a solid, but cellular, supramolecular material with a phase-separated morphology. Table 2 shows data derived from observations made during the formation of PU foams. 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 (commonly known as the "cream-time") was 18 s, which fell to only 5s upon addition of MMT indicating a significant increase in the initial rate of CO_2 generation. In addition, the time available for the foam PLSN to rise height before cell opening occurs reduced significantly, indicating that phase separation occurs more rapidly upon addition of MMT. However, the values of the maximum rise height increased upon addition of MMT, indicating an increased rate of CO_2 generation prior to cell opening.

Adiabatic Temperature Rise

The rapid reactions occurring during PU foam formation and their associated exotherms, together with the self-insulating nature of the developing foam, result in quasi-adiabatic temperature conditions. Copolymerisation kinetics control both the temperature-time profile and the conversion of functional groups. Thus, plots of temperature versus time (ATR profiles) yield information on overall reaction kinetics during foam formation as well as providing the profiles essential for

Table 2.
Processing behaviour of the unfilled foam (F0) and the PLSN foams (F5 and F10).

System	Cream time/s	Cell opening 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

subsequent forced-adiabatic FTIR studies. The ATR profile of the unfilled foam (F0), corrected for heat loss, is shown in Figure 2. The chemical reactions proceed rapidly during foaming hence the temperature profile also shows a rapid rise to reach approximately 150 °C during the first 150s, after which the temperature typically rises by only another 10–20 °C over the following 600 s. Figure 2 also contains comparative ATR profiles for the PLSN foams (F5 and F10). In the initial stage ($t < 150$ s) there is a significant increase in the rate of reaction with increasing MMT content, due possibly to a surface catalytic effect associated with the high-surface area of the MMT. Kim et al. [23] in a DSC study of PU elastomers based on TDI and a polyoxypropylene triol, also reported increased rates of reaction upon addition of an OMMT. At longer reaction times ($t > 150$ s) the differences in the rates of reaction are reduced with the profile for the foam (F5) in Figure 2 exhibiting only slightly higher temperatures than those observed for the unfilled foam (F0) and the PLSN foam (F10). As the overall heat rise in these systems is dominated by the reaction between TDI and water (with a molar ratio of reactive groups, water:polyol ≈6.4), these significant increases in heat generation with MMT content indicate that the water within the swollen, intercalated MMT is readily accessible to the TDI.

Forced-Adiabatic FTIR Spectroscopy

The kinetics data for both copolymerisation and microphase separation, determined from forced-adiabatic FTIR spectra, are shown in Figure 3–6. Figure 3 shows the reaction of isocyanate determined from the normalised decay in the intensities of the isocyanate absorption band at 2270 cm^{-1} with time, used to monitor conversions of TDI functional groups during the formation of copoly(urethane-urea) foams. These data show significant increases in the rate of reaction of isocyanate groups as MMT content is increased, in agreement with the ATR data. 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, in particular, relative absorbances for soluble urea (~1711 cm^{-1}) and hydrogen-bonded bidendate urea (~1639 cm^{-1}).[24] Figure 4 shows the evolution of soluble and hydrogen-bonded ureas for the unfilled foam (F0). Soluble urea is formed initially and, up to approximately 50 s, its concentration increases

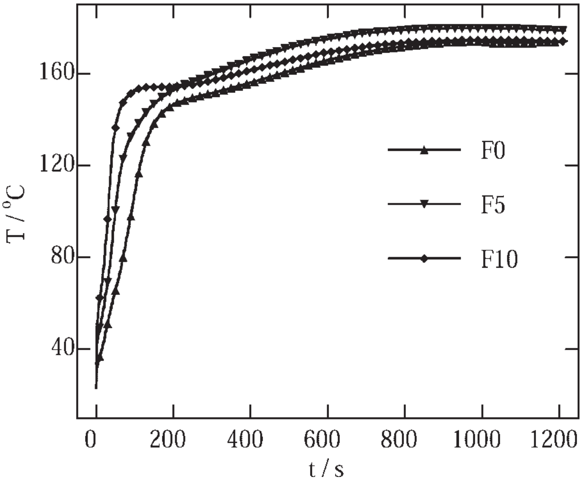

Figure 2.
Adiabatic Temperature Rise (ATR) profiles of the unfilled PU foam (F0) and the PLSN foams (F5 and F10).

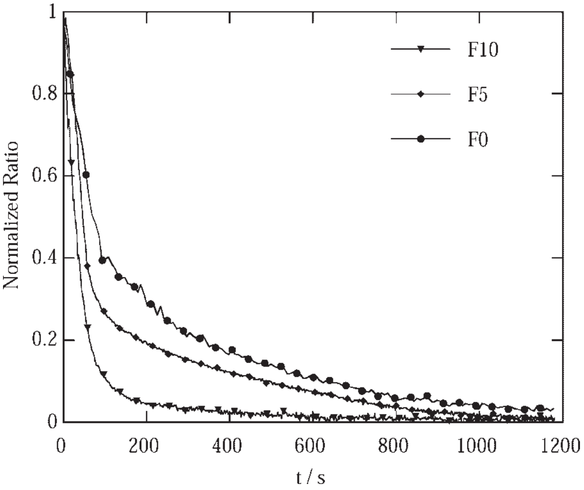

Figure 3.
Normalised reaction kinetics data for the formation of unfilled foam (F0) and PLSN foams (F5 and F10). Data determined from the decay in isocyanate absorbances (2270 cm^{-1}) in forced-adiabatic FTIR spectra.

rapidly and then more steadily during the remainder of foam formation. The amount of hydrogen-bonded urea formed initially is small and shows little increase with time over the first 50 s. At around 50 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 as 70 ± 3 s (mean of three measurements) by the intersection of tangents drawn to the data before and after the rapid rise in the 1639 cm^{-1} absorbance.

Figure 5 shows the growth of soluble-urea for all three systems during foam formation. Growth is equivalent for all three systems up to approximately 50 s, after which the profile for the unfilled foam (F0) begins to level off whereas the profiles

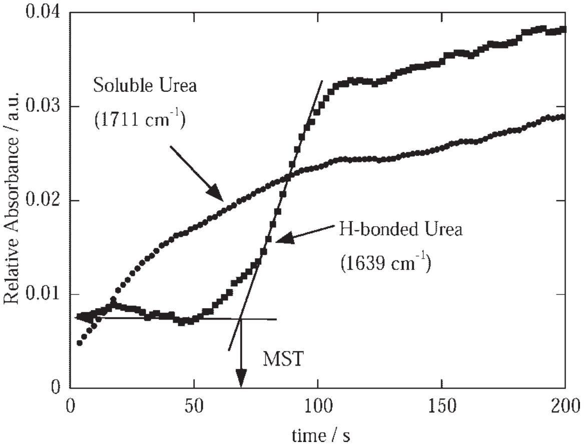

Figure 4.
Phase-separation kinetics data showing the microphase-separation transition (MST) during the formation of unfilled foam (F0). Data determined from the relative absorbances of hydrogen-bonded urea (1639 cm^{-1}) and soluble urea (1711 cm^{-1}) in forced-adiabatic FTIR spectra.

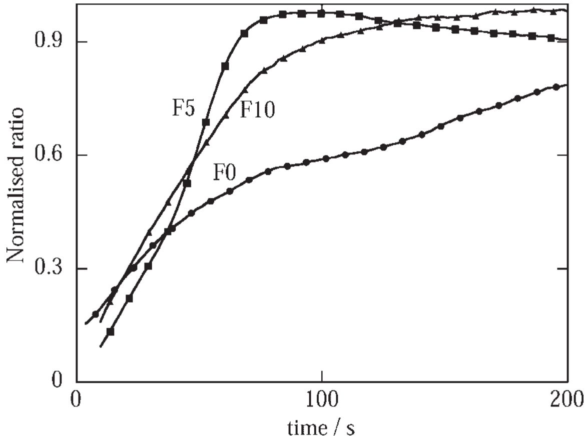

Figure 5.
Comparative plots of normalised soluble urea concentration versus time for unfilled foam (F0) and PLSN foams (F5 and F10). Data determined from forced-adiabatic FTIR spectroscopy.

of the PLSN foams (F5 and F10) continue to show strong growth that only begins to level off after 70–80s. Thus, the addition of clay appears to inhibit the association of the soluble urea, resulting in a reduced conversion to H-bonded urea. Figure 6 shows that the PLSN foams (F5 and F10) exhibit more rapid development of H-bonded urea compared to the unfilled foam (F0) but only up to approximately 80 s, so that after 200 s of reaction the PLSN foams exhibit only 60–65 % of the H-bonded urea concentration formed in the unfilled foam (F0). Microphase separation also occurred more quickly in the PLSN foams, which exhibited MST times of 42 ± 2 s and 47 ± 3 s, respectively, for the F05 and F10 foams compared to 70 ± 3s for the unfilled foam (F0).

Generally, polymers capable of hydrogen bonding when used to form PLSN, tend to exhibit strong interactions with the surfaces of silicate lamellae, with Nylon 6 being the most widely studied example.[4] In the case of segmented multiblock copoly(urethane-urea) and copolyureas,

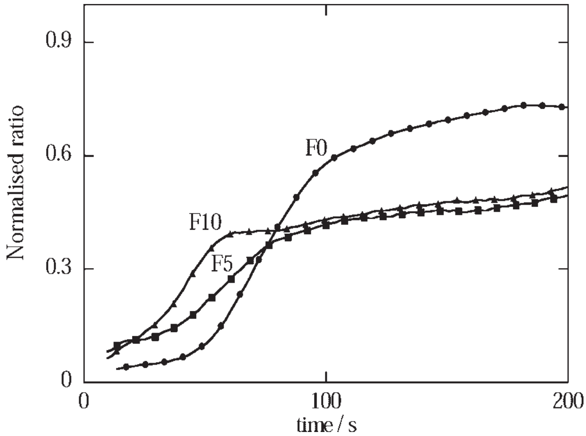

Figure 6.
Comparative plots of normalised hydrogen-bonded urea concentration versus time for unfilled foam (F0) and PLSN foams (F5 and F10). Data determined from forced-adiabatic FTIR spectroscopy.

urea groups are capable of forming strong, bidentate H-bonds and it is therefore not surprising that the incorporation of the high surface-area MMT disrupts the formation of H-bonded hard segments. Similar disruption of H-bonding between hard segments has been reported previously for solid PU systems.[17]

Conclusions

Water-blown polyurethane foam nanocomposites were formed in the presence of MMT at levels of up to 10 wt.-%. The polyol/water mixtures used in foam formulations were shown by WAXD to intercalate the MMT giving increased gallery basal spacings (2.3 ± 0.1 nm), and the extent of intercalation and ordering in the polyol/water-MMT mixtures was shown to increase with MMT content.

ATR measurements and forced-adiabatic FTIR spectroscopy showed that the rates of polymerisation increased with increased MMT content. The changes in soluble and hydrogen-bonded urea group contents in the hard-segment phases were used to determine microphase-separation (MST) times which decreased from 70 ± 3s for the unfilled foam down to 42 ± 3 s for the nanocomposite foam containing 5 wt.-% MMT.

This study has demonstrated clearly that the incorporation of intercalated MMT significantly affects structure development during the reactive processing of polyurethane foams in terms of the observed changes in the kinetics of copolymerisation and microphase separation.

Acknowledgements: The authors gratefully acknowledge a Ph.D. scholarship awarded to NHF from the Asian Development Bank and the Government of the Republic of Indonesia under the TPSDP Scheme. The authors would also like to acknowledge Nanocor Inc. and Caligen Foam Ltd for the provision of materials.

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