สำนักงานกองทุนสนับสนุนการวิจัย
THE THAILAND RESEARCH FUND

รายงานวิจัยฉบับสมบูรณ์

โครงการ 'Preparation of Poly (vinyl chloride) / Clay Nanocomposites'

โดย ดร. อรุณี ทับเที่ยง และคณะ

31 สิงหาคม 2543

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

กิตติกรรมประกาศ

คณะผู้วิจัยขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัยที่ให้การทุนสนับสนุนงานวิจัยนี้

Abstract

Project Code: PDF/19/2541

Project Title: 'Preparation of Poly(vinyl chloride) / Clay Nanocomposites'

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Project Period: 2 years 2 months

Objectives: 1. To prepare a carrier resin, poly(methyl methacrylate) (PMMA) with a fine dispersion at the molecular level of the clay for use as reinforcing additives in PVC.

2. To control the stabilisation of the clay dispersion in the PMMA / clay hybrids through the use of functional co-monomers.

Methodology: 1. Preparation of the PMMA / clay hybrids through free radical solution polymerisation and direct melt intercalation of PMMA and characterisation of these hybrids

2. Characterisation of the PVC / clay composites prepared through incorporation of the PMMA / clay hybrids into the PVC during compounding.

3. Stabilisation of the clay dispersion in the PMMA/clay hybrids through the use of functional co-monomers.

Results: X-ray diffraction patterns of the PMMA / clay composites showed that the clay particles were greatly expanded, i.e. exfoliated, in the reaction products. The exfoliated structure created during polymerisation was unstable under the processing conditions and consequently reordered into a more stable form. The final interlayer spacings were determined by the orientation and lengths of the pre-intercalated alkylammonium ions. These effects were also found to control the interlayer spacings within the clay aggregates in the PMMA / clay composites prepared through direct melt intercalation of PMMA. However, a finer degree of dispersive mixing of the clay in the polymerisation system was inferred. The chain branching in the polymerisation system was the principal reason for the differences in the thermomechanical behaviour of the two composites. These samples were compounded into PVC formulations. In comparison with the unmodified clay, the PMMA / clay hybrids conferred pronounced increases in dimensional stability to the products at very low clay contents, as indicated by enhanced tensile modulus at 25°C and flexural modulus at elevated temperatures. This effect was thought to be related to the enhanced clay dispersion in the hybrid containing formulations and to the branching of the PMMA.

The functional monomers, namely glycidyl methacrylate (GMA) and maleic anhydride (MA), were copolymerised with MMA in the hybrids in an attempt to stabilise the clay dispersion during melt processing. It was found that the presence of GMA could limit the reaggreagation of the clay. The highly reactive oxirane groups of the GMA led to the formation of a gelled structure during polymerisation. It was found that MA contents of 10 wt% in the copolymer could limit the reaggreagation of the clay. When prepared in the presence of clay, the relaxation characteristics of the latter copolymer were altered, probably due to the reaction of succinic anhydride groups with the amine that was bound to the organophylic clay. The product of this reaction was heterogeneous resulting in the formation of copolymer fractions with different glass-rubber transition temperatures.

Keywords: PVC, nanocomposite, PMMA/clay hybrid

บทคัดย่อ

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Project Title: การเตรียมนาโนคอมพอสิตของพอลิไวนิลคลอไรด์กับดิน

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ระยะเวลาที่ทำวิจัย 2 ปี 2 เดือน

วัตถุประสงค์ 1. เตรียม carrier resin คือ พอลิเมธิลเมธาไครเลต (พีเอ็มเอ็มเอ) ที่มีการกระจายตัวของชั้นดินดีมากระดับโมเลกุล ใช้เป็นสารเสริมแรงที่เติมในพอลิไวนิลคลอไรด์ (พีวีซี)

2. ควบคุมเสถียรภาพของการกระจายตัวของดิน ในไฮบริดระหว่างพีเอ็มเอ็มเอกับดิน

ขอบเขตการวิจัย 1. เตรียมไฮบริดระหว่างพีเอ็มเอ็มเอกับดินโดย free radical solution polymerisation และ การแทรกตัวของพีเอ็มเอ็มเอหลอมเข้าไปในชั้นของดินโดยตรง

2. ศึกษา คอมพอสิตของพีวีซีกับดินที่เตรียมจากการผสม ไฮบริดระหว่างพีเอ็มเอ็มเอกับดิน เข้ากับพีวีซีในขณะที่หลอม

3. ทำให้เกิดเสถียรภาพของการกระจายตัวของชั้นดินในไฮบริดระหว่างพีเอ็มเอ็มเอกับดินโดยใช้ โมโนเมอร์ที่มีหมู่ฟังค์ชัน ร่วมด้วย

ผลจากการวิจัย X-ray diffraction patterns ของคอมพอสิตของพีเอ็มเอ็มเอกับดินที่ได้จากการสังเคราะห์ แสดงให้เห็นว่า ชั้นของดินอยู่ห่างกันมาก นั่นคือ exfoliated โครงสร้างที่ได้มาขณะสังเคราะห์สารนี้ไม่เสถียร ภายใต้ขบวนการผสมและขึ้นรูป ทำให้เกิดการเรียงตัวกลับคืนสู่สภาวะที่มีเสถียรภาพสูงกว่า ระยะห่างระหว่างชั้นดินหาได้จากการจัดเรียงตัวและความยาวของอัลคิลแอมโมเนียมอิออนที่แทรกอยู่ในชั้นดิน ผลนี้ก็ควบคุมระยะห่างระหว่างชั้นดิน ของคอมพอสิตของพีเอ็มเอ็มเอกับดินที่ได้จาก การแทรกตัวของพีเอ็มเอ็มเอหลอมเข้าไปในชั้นของดินโดยตรงด้วย พบว่า "ไฮบริดที่เตรียมจากการสังเคราะห์จะมีการกระจายตัวของชั้นดินดีกว่า การมีสาขาของสายโซ่โมเลกุลของพอลิเมอร์ที่ได้จากการสังเคราะห์เป็นผลสำคัญที่ทำให้เกิดความแตกต่าง thermomechanical behaviour ของคอมพอสิตสองชนิดนี้ เมื่อรวมไฮบริดนี้กับพีวีซี พบว่าผลิตภัณฑ์ที่มีดินผสมน้อยมาก มีโมดูลัสที่ 25°C และ flexural modulus ที่อุณหภูมิสูงขึ้นมีค่าเพิ่มขึ้น เมื่อเทียบกับพีวีซีที่ผสมกับดินที่ไม่ปรับสภาพผิว ผลนี้ควรเป็นผลที่เกี่ยวข้องกับการกระจายตัวของชั้นดินที่ดีขึ้น และ พีเอ็มเอ็มเอที่มีสายโซ่สาขา การใช้โมโนเมอร์ที่มีหมู่ฟังค์ชันได้แก่ไกลซีดิลเมธาไครเลต (จีเอ็มเอ) และ มาลีอิกแอนไฮดราย (เอ็มเอ) สังเคราะห์พอลิเมอร์ร่วมกับ พีเอ็มเอ็มเอ เพื่อให้เกิดเสถียรภาพของการกระจายตัวของชั้นดินในขณะที่พอลิเมอร์หลอม พบว่า จีเอ็มเอ ช่วยลดการกลับคืนการเรียงตัวของชั้นดิน กลุ่ม oxirane ในจีเอ็มเอ ไวต่อปฏิกิริยามาก ทำให้เกิดโครงสร้างที่เป็นร่างแหขึ้น ในกรณีที่มี เอ็มเอ ผสมอยู่ 10%โดยน้ำหนักพบว่าช่วยลดการกลับคืนการเรียงตัวของชั้นดิน relaxation characteristics ของโคพอลิเมอร์ตัวหลังที่เตรียมขณะที่มีดินอยู่ด้วยจะแตกต่างไป อาจเนื่องมาจากปฏิกิริยาระหว่าง กลุ่ม succinic anhydride กับ เอมีนที่ติดอยู่ที่ผิวของดินที่ปรับสภาพ ผลิตภัณฑ์ของปฏิกิริยานี้เป็นเนื้อผสม ทำให้ มีส่วนของโคพอลิเมอร์ที่มี glass-rubber transition temperatures แตกต่างไป

Keywords: PVC, nanocomposite, PMMA/clay hybrid

The work has centre upon the development of methods for the preparation of dispersions of clay primary particles in a carrier resin, and the study of the relationship between preparation method and structure. The effects of the polymer / clay interactions upon the properties of the polymer / clay nanocomposites, and the effects of modifying the interactions with functional monomers have been carried out. The efficacy of using the carrier resin / clay dispersion in a blend with PVC to enhance thermal properties has been investigated.

In *part I*, poly(methyl methacrylate) / clay composites were synthesised through free radical solution polymerisation of methyl methacrylate in the presence of clay, that was pre-intercalated with dodecylammonium or hexadecyltrimethylammonium ions. Neither the diffraction peak from the (001) plane nor the *00l* reflections for the (001) plane were observed during X-ray characterisation, showing that the clay particles were greatly expanded, i.e. exfoliated, in the reaction products, due to the presence of large quantities of polymer between the clay layers. Syntheses carried out with high clay loadings resulted in reductions in the weight and number average molecular weights and increases in the polydispersities of the polymers, caused by chain transfer to active sites upon the surface of the clay. It was found that heat and shear, during subsequent processing of the reaction products, resulted in reordering of the microstructure through narrowing of the clay galleries with the partial exclusion of the polymer. The final interlayer spacings were determined by the orientation and lengths of the pre-intercalated alkylammonium ions. It was concluded that the exfoliated structure created during polymerisation was unstable under the processing conditions and consequently reordered into a more stable form.

Part II is concerned the influence of preparation method upon the structure and relaxation characteristics of poly(methyl methacrylate) / clay composites. Poly(methyl methacrylate) (PMMA) / clay composites were prepared using two methods: through solution polymerisation of methyl methacrylate in the presence of alkylammonium-modified clay and through direct melt intercalation of PMMA. Both composites were fluxed in an internal mixer to give comparable melt processing histories. In the reaction product of the polymerisation method, the clay layers were separated to a distance greater than 80 Å; after melt processing, the layers were partially re-aggregated. The length and orientation of the alkylammonium ions principally controlled the interlayer spacings within these aggregates. A finer degree of dispersive mixing of the clay in the polymerisation system was observed. The presence of modified clay in the polymerisation system led to branching, reduction of average molecular weight, increase in polydispersity, and to a bimodal molecular weight distribution of the PMMA. The glass-rubber transitions were observed around 120°C in the polymerisation system in comparison with 105°C for the melt intercalation materials and the PMMA resin. Moreover, PMMA extracted from the polymerisation composites had similarly elevated glass transition temperatures. The chain branching in the polymerisation system was the principal reason for the differences in the thermomechanical behaviour of the two composites.

In *part III*, poly(methyl methacrylate) (PMMA) / clay composites were prepared through solution polymerisation of methyl methacrylate in the presence of dodecylammonium-modified clay. These samples were compounded into poly(vinyl chloride) (PVC) formulations. In comparison with the unmodified clay, the PMMA / clay hybrids conferred pronounced increases in dimensional stability to the products at very low clay contents, as indicated by enhanced tensile modulus at 25°C and flexural modulus at elevated temperatures. This effect was thought to be related to the enhanced clay dispersion in the hybrid containing formulations and to the branching of the PMMA. Even distributive mixing of the clay aggregates in the PVC matrix was found from TEM micrographs; the fine mixing was related to the miscibility of PMMA with the PVC, as inferred from a single glass transition intermediate between that of the pure PMMA and the base PVC compound. The enhanced moduli in the hybrid systems were obtained at the expense of some of the compound toughness. The hydrodynamic effects of the enhanced clay dispersion were the probable cause of both effects.

Part IV and V are the studies in an attempt to stabilise the clay dispersion during melt processing. In *part IV* polymer / clay hybrids were prepared through the copolymerisation of methyl methacrylate and glycidyl methacrylate (GMA). The latter was included as a functional monomer in an attempt to stabilise the clay dispersion during melt processing. It was found that the presence of GMA could limit the reaggreagation of the clay. The highly reactive oxirane groups of the GMA led to the formation of a gelled structure during polymerisation.

Part V describes the use of maleic anhydride as a comonomer to stabilise the clay dispersion. Polymer / clay hybrids were prepared through the copolymerisation of methyl methacrylate and maleic anhydride. The latter was included as a functional monomer in an attempt to stabilise the clay dispersion

during melt processing. It was found that maleic anhydride contents of 10 wt% in the copolymer could limit the reaggreagation of the clay. When prepared in the presence of clay, the relaxation characteristics of the copolymer were altered, probably due to the reaction of succinic anhydride groups with the amine that was bound to the organophylic clay. The product of this reaction was heterogeneous resulting in the formation of copolymer fractions with different glass-rubber transition temperatures.

Out put from the PROJECT
International journal

1. Tabtiang, A., Lumlong, S., and Venables, R. A., *'The influence of preparation method upon the thermomechanical characteristics of poly(methyl methacrylate) / clay composites'*, ***Eur. Polym. J.***, **36**(12), pp. 2559-2568 (2000)
2. Tabtiang, A., Lumlong, S., and Venables, R. A., *'The effects of shear and thermal history upon the microstructure of solution polymerised poly(methyl methacrylate) / clay composites'*, ***Polym.-Plast. Technol. Eng.***, **39**(2), pp. 293-303 (2000)
3. Tabtiang, A. and Venables, R. A., *'The stabilisation of the clay dispersion in poly(methyl methacrylate) / clay hybrids through the use of functional co-monomers'*, in preparation.

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Part I

The effects of shear and thermal history upon the microstructure of solution polymerised poly (methyl methacrylate) / clay composites

Abstract

Poly(methyl methacrylate) / clay composites were synthesised through free radical solution polymerisation of methyl methacrylate in the presence of clay, that was pre-intercalated with dodecylammonium or hexadecyltrimethylammonium ions. Neither the diffraction peak from the (001) plane nor the *00l* reflections for the (001) plane were observed during X-ray characterisation, showing that the clay particles were greatly expanded, i.e. exfoliated, in the reaction products, due to the presence of large quantities of polymer between the clay layers. Syntheses carried out with high clay loadings resulted in reductions in the weight and number average molecular weights and increases in the polydispersities of the polymers, caused by chain transfer to active sites upon the surface of the clay. It was found that heat and shear, during subsequent processing of the reaction products, resulted in reordering of the microstructure through narrowing of the clay galleries with the partial exclusion of the polymer. The final interlayer spacings were determined by the orientation and lengths of the pre-intercalated alkylammonium ions. It was concluded that the exfoliated structure created during polymerisation was unstable under the processing conditions and consequently reordered into a more stable form.

INTRODUCTION

Polymer / clay composites with fine dispersions of reinforcing particles may be prepared by using the swelling properties of smectite clays [1], whereby a polar molecule intercalates the clay layers and consequently increases the interlayer spacing. This process may be carried out in several steps, the essential features of which are: 1) exchange of the clay's sodium ions with alkylammonium ions to partially expand the clay galleries and to reduce the hydrophylicity of the clay's surface, yielding a modified clay; 2) swelling of the modified clay with monomer and 3) polymerisation of the monomer. An example of this type of system is the polyimide / clay hybrid described by Yano *et al.* [2], where a film containing montmorillonite clay was synthesised from a dimethylacetamide solution of poly (amic acid) and a dimethylacetamide dispersion of montmorillonite, intercalated with an ammonium salt of dodecylamine. The final product showed improved barrier properties to the permeation of vapours, in comparison with the unmodified polyimide. Other systems have shown improved mechanical properties at elevated temperature [3].

Whilst poly(vinyl chloride) (PVC) is a low cost material with versatile properties, its performance is limited in some applications where elevated temperatures are experienced, due to its low softening temperature. Properties may be improved, however, by blending the PVC with engineering resins that possess high glass transition temperatures (T_g). These resins have been referred to as HT-additives [4]. Examples include those based upon PMMA, styrene-maleic anhydride copolymer and brominated polycarbonate. The HT-additive should be miscible or partially miscible with the PVC to maintain optical clarity. Owing to the outstanding heat distortion temperature properties of polymer / clay hybrids [3], a hybrid may perform suitably as a HT-additive for PVC. Thus, in this work, an additive of this type was prepared through solution polymerisation of methyl methacrylate in the presence of modified-clays, for use in rigid PVC formulations. PMMA was chosen due to its known compatibility with PVC [5] and inherently high T_g. The PMMA is intended to act as a carrier polymer to bring the dispersed clay layers into the PVC matrix. The objectives of the work described herein were to establish the initial structure of the additive and, since it will experience heat and hydrodynamic stresses during processing, to determine the processing effects upon the final structure.

EXPERIMENTAL

Materials

The inhibitor was extracted from methyl methacrylate (MMA) (Fluka) with $NaOH_{(aq)}$, then washed with distilled water and subsequently dried over anhydrous Na_2SO_4. Bentonite clay, containing a minimum of 90% montmorillonite was from Colloid Environmental Technologies Co., Ltd. Dodecylamine was from Fluka, hexadecyltrimethylammonium chloride from Merck and 2,2'-azo-bis (isobutyric-nitrile) (AIBN) initiator was supplied by TPI Co., Ltd., Thailand.

Synthesis of modified-clay

Clay (20 g) was dispersed in distilled water (600 mL) at 80°C. To this was added a solution of dodecylamine or hexadecyltrimethylammonium chloride (0.05 mol) and concentrated hydrochloric acid (4.8 mL) in distilled water (100 mL). Heating and stirring was continued for one hour, whilst maintaining the temperature at 80°C. The suspension was then filtered and the solid residue washed with hot distilled water until no chloride was left, as determined by using the silver nitrate test. The product was dried at 60°C for several days in a fan oven, then milled in a ball mill and subsequently dried at 60°C under vacuum for 24h, yielding the dodecylammonium-clay (DDA-clay) and hexadecyltrimethylammonium-clay (HDA-clay).

Composite preparation

AIBN (0.1 g) was dissolved in the extracted MMA (10 g), followed by the addition of the modified clay (1, 2, 5 or 10 g) and distilled hexane (40 ml). For the highest clay contents, 100 ml of hexane was needed to disperse the clay. The reaction flask was suspended in a thermostated water bath at 68°C for 5 h, with a condenser fitted. The powdered product was recovered from the reaction mixture by evaporation of the solvent, followed by drying under vacuum at 60°C. Portions of the products were either melt-fluxed in a Haake Rheocord 90 at 180°C for 5 min, with a rotor speed of 50 rpm, to give the samples a melt processing history, or statically annealed in a fan oven for 30 min at 175°C. All melt-fluxed samples were compression moulded at 180°C to form plaques for characterisation.

Characterisation

Wide angle X-ray diffraction measurements (WAXD) were carried out using a JEOL JDX-3530. The source was operated at 30 kV and 30 mA; all but the Cu K_α X-rays were filtered from the beam. The scanning speed, step angle and count time were 1.2 °2θ/minute, 0.04 °2θ and 2 seconds, respectively. For the scan range 1 to 10 °2θ, the divergence slit, receiving slit and scattering slit were 0.5°, 0.1 mm and 0.5°, respectively, whilst for the range 3 to 40 °2θ these values were 1°, 0.2 mm and 1°, respectively. Infrared data were collected using a Perkin Elmer FT2000 and diffuse reflectance (DRIFT) accessory. Gel permeation chromatography (GPC) was carried out upon polymer extracted from the composites with tetrahydrofuran at room temperature, using a Waters 150-CV Plus. Thermogravimetric analyses (TGA) were carried out using a Perkin Elmer TGA7.

RESULTS AND DISCUSSION

Characterisation of modified clay

Figure 1 shows DRIFT spectra of the unmodified clay and DDA-clay. The presence of protonated dodecylamine in the clay galleries is shown by the N-H stretching of the NH_3^+ group in the region 3260 to 3181 cm^{-1} and the CH stretching peaks in the range of 2925 to 2852 cm^{-1}. The O-H stretching bands at 3400 to 3200 cm^{-1} and the HOH bending peak at 1641 cm^{-1}, of adsorbed interlayer water [6] found in the original clay, were absent in the modified sample, due to the reduced hydrophylicity of the internal surfaces of the clay. The average quantity of intercalated dodecylammonium ions, from four replicated TGA analyses upon the modified clay, was 17.7 wt%. The X-ray diffraction patterns of the unmodified and modified clays are displayed in Figure 2. The d-spacing of the (001) plane, d_{001}, in the original clay was 12.9 Å, whilst that of the DDA-clay was 17.9 Å. The gallery spacing, that is the distance between the internal surfaces of neighbouring clay layers, is calculated from the difference between d_{001} and the van der Waal's thickness of the clay layer. This thickness is estimated at 9.6 Å [7]. For the DDA-clay, the gallery spacing was 17.9 - 9.6 = 8.3 Å. This

gallery spacing is too small to accommodate the dodecylammonium ions standing perpendicular to the surface of the clay, since the total length of the extended ion is around 20 Å [7].

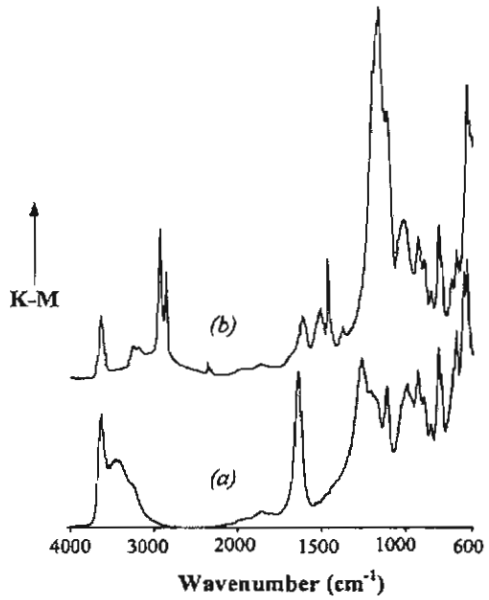

Figure 1. DRIFT spectra of (a) unmodified clay and (b) DDA-clay.

The more probable orientation is that one molecule lies parallel to each of the internal surfaces of the clay, in a bilayer orientation [8]. Similar results were obtained for HDA-clay.

Characterisation of polymerisation products

In the X-ray traces of the reaction products from solution polymerisation, containing DDA-clay, neither peaks from the montmorillonite's (001) plane nor the *00l* reflections for the (001) plane were seen in the range 1 to 10 °2θ.

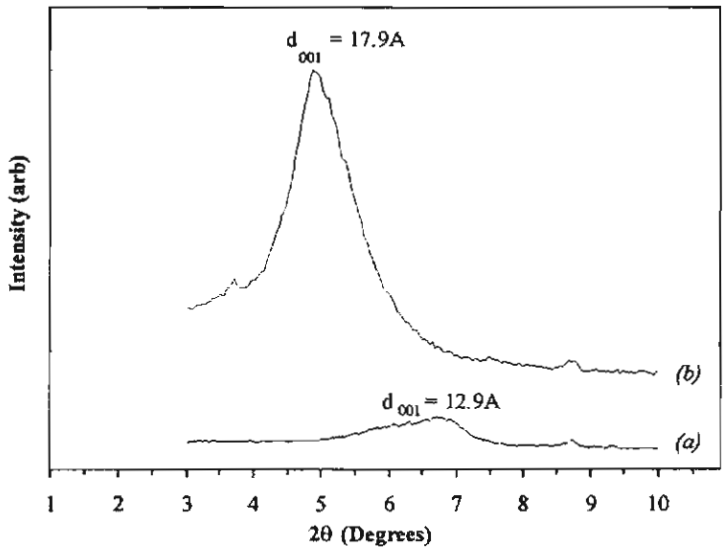

Figure 2. X-ray diffraction traces of (a) unmodified clay and (b) DDA-clay.

The absence of the (001) diffraction peak shows that during polymerisation d_{001} increased to a distance greater than that measurable with the minimum scan angle of the powder diffractometer, i.e. greater than around 88Å. This may be considered an exfoliated arrangement of the clay layers [9]. In the X-ray trace for the PMMA without clay, an increase in intensity at low angles was observed that

was caused by the primary beam contribution to the signal. For the clay containing samples, the onset of a very broad scattering signal, from the (001) plane, associated with the clay sheets at distant irregular spacings was superimposed upon the primary beam signal. The original structure of the modified clay is largely destroyed, however.

The dispersion force, dipole-dipole interaction and hydrogen bonding contributions to the solubility parameter [10] of MMA are around 15.7, 8.2 and 6.7 $(MPa)^{1/2}$, respectively, compared to the corresponding values of 16.7, 0.0 and 0.0 $(MPa)^{1/2}$ for hexane, and hence the MMA monomer will tend to displace the hexane from the clay galleries, due to its more favourable specific interactions with the surface of the clay, causing the clay to swell. The gain in freedom of the dodecylammonium ions and hexane molecules as the interlayer spaces enlarge counterbalance the loss in entropy of the monomer. As the polymer precipitates from solution, it is trapped in the interlayer, thereby fixing the distant separation of the clay sheets. The quantity of clay present during polymerisation did not affect the extent of clay delamination.

GPC data showed that DDA-clay contents up to 7 vol% significantly affected neither molecular weight nor polydispersity. Clay contents of 15 vol% or more caused reductions in molecular weight and increased polydispersity. When the ratio of clay to monomer is high, chain transfer to the clay due to interactions with Brönsted sites upon the clay's surface, may become significant, with consequent alterations to the molecular weight parameters. This may be related to the larger quantities of solvent that were required during synthesis in the presence of high clay contents, resulting in more dilute reaction conditions. Chain transfer to the solvent itself may not be the predominant mechanism, however, since n-hexane cannot form sufficiently stable radical intermediates [11].

The effects of shear and thermal history

X-ray traces of the melt-processed polymerisation products, containing DDA-clay, are shown in Figure 3. It is apparent that the (001) diffraction, followed by two less intense signals with regular displacement along the °2θ axis, is present. The less intense signals are the *00l* reflections for the (001) plane; the corresponding d-spacing is around 29 Å. Thus, at least some of the clay layers change from the expanded arrangement that is created during solution polymerisation to a closer packed configuration after melt processing. Moreover, the resultant d_{001} changes little with increasing clay content.

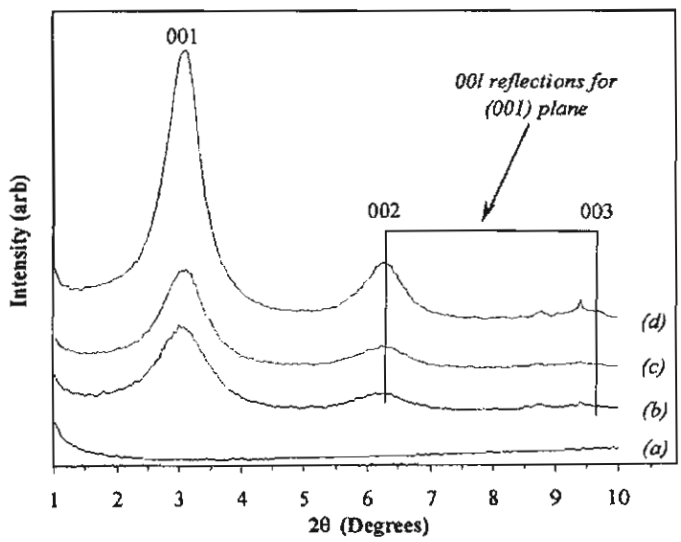

Figure 3. X-ray diffraction traces of (a) PMMA without clay and the melt-processed DDA-clay composites containing (b) 10; (c) 20, and (d) 50 phr of clay.

To assess the effect of heat alone without the concurrent application of pressure and stress, the powdered reaction products were statically annealed. The presence of the *00l* reflections for the (001) plane implied that some thermally induced reordering of the clay layers occurs upon static annealing. The peaks were less intense than in the melt-fluxed samples, showing that the extent of reordering was lower. This difference may simply be kinetic in origin, whereby the mechanical work

during mixing greatly accelerates the system towards the thermodynamic equilibrium position. The structural changes may also be influenced by the melt elasticity contribution to the free energy of the system, however. This is analogous to the situation in partially miscible blends where the temperatures of phase dissolution or separation are altered under shear; both enhanced and reduced miscibility has been observed [12]. The absence of the (100) peak, at °2θ = 19.5, in the melt processed sample shows that during compression moulding, the silicate sheets move under pressure to lie parallel to the mould surface. In the powdered reaction products, the clay is randomly oriented, and hence the (100) plane is detected.

At the processing temperature, the specific interactions between the PMMA and the clay surface become weakened by the increased thermal motion of the molecules. The clay particles rearrange to a more thermodynamically stable state. This occurs through the expulsion of some of the PMMA chains from between the silicate sheets, allowing the layers to approach one another more closely. The driving force may be the gain in entropy of the polymer chains as they are freed from their confinement. The d_{001} values in the melt processed DDA-clay composites were typically around 29 Å, giving an interlayer spacing of 19.4 Å. The length of the extended dodecylammonium ion is estimated to be 20.2 Å [7], that is, its length is approximately the same as the gallery spacing. This suggests that the gallery ions adopt a near perpendicular orientation to the clay sheets in the presence of the PMMA melt, and span the gallery from one clay layer to the next, thereby partially controlling the interlayer distance. This phenomenon was investigated further by using HDA-clay, containing the longer alkylammonium ion, to prepare the composites. The X-ray data for these materials show that the polymerisation products (Figure 4a) similarly contained greatly expanded clay, inferred from the absence of the (001) peak and the *00l* reflections from the (001) plane. The statically annealed and melt processed HDA-clay composites (Figure 4b and 4c, respectively) both show series of *00l* reflections, which correspond to a d_{001} of 38.8 Å and gallery spacing of 29.2 Å. The extended chain length of the hexadecyltrimethylammonium ion is around 29 Å, and hence, it is reasonable to infer that the aliphatic chains of the ion are oriented perpendicular to the surface of the clay and therefore control the gallery spacing. This indicates that the same reordering of the dispersed clay layers occurs for both of the modified clays.

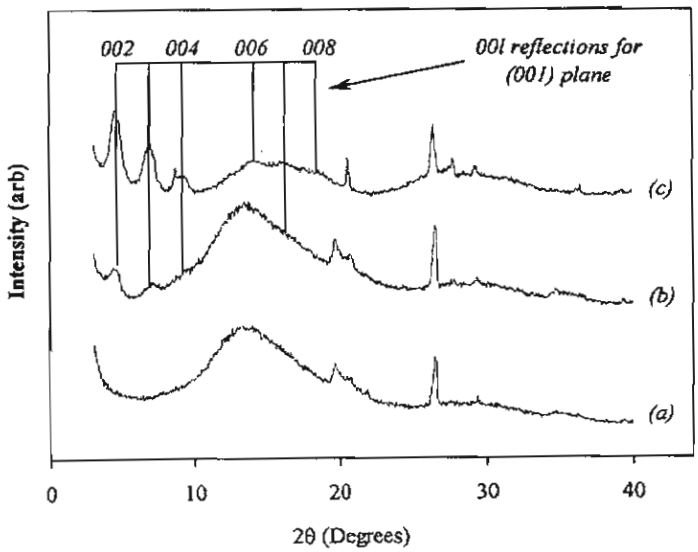

Figure 4. X-ray diffraction traces of HDA-clay composites: (a) powder reaction product; (b) reaction product after static annealing and (c) the reaction product after melt processing.

The d_{001} in the melt-processed composites can be explained qualitatively through consideration of the thermodynamic forces that drive the system [13,14]. The gallery spacing is restricted through the loss in entropy due to the confinement of the polymer and by any unfavourable pairways interactions between the clay surface, polymer, and alkylammonium ions. It is driven to expand through the gain in entropy of the alkylammonium chains and the exothermic interactions between the clay and PMMA. Upon melt fluxing, the distance between the clay layers reduces, as the PMMA chains move out from between the clay layers to gain entropy, until the

distance that is equal to the length of the extended alkylammonium ions is reached. At this point, the contraction is arrested, because further narrowing of the galleries would result in the unfavourable loss in entropy of the alkylammonium ions. The final gallery spacing is therefore approximately the same as the length of the alkylammonium ions. The heat of polymer / clay interaction under these conditions is sufficient to overcome the loss in entropy of the remaining confined polymer. Hence, some of the PMMA remains in the galleries, causing the alkylammonium ions to maintain their perpendicular orientation.

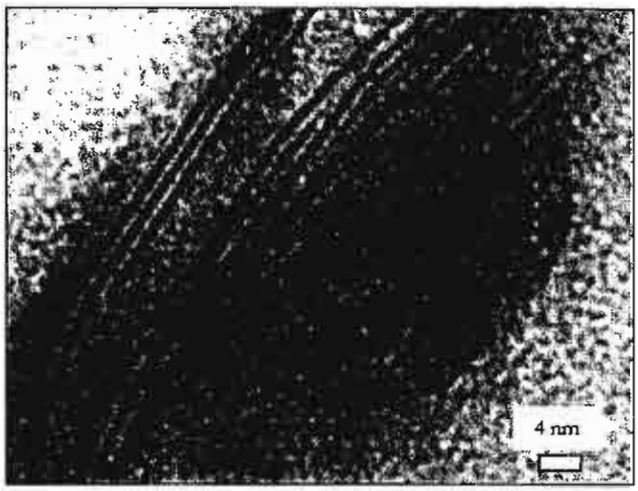

Figure 5. TEM photomicrograph of DDA-clay aggregates in a melt processed sample.

In the TEM photomicrograph of a melt processed DDA-clay composite, shown in figure 5, it can be seen that the silicate sheets are present in aggregates of 3 to 5 primary layers; the distances between these aggregates are around 85Å. Moreover, in the top region of the image, an isolated sheet can be seen. The X-ray analysis described above responds to the structure within the aggregates, showing that the interlayer distance within the aggregates is small and is typically 19.4Å. These observations show that the clay layers are still partially delaminated after melt processing.

CONCLUSIONS

- Solution polymerisation of MMA in hexane, in the presence of DDA-clay and HDA-clay, produces PMMA / clay composites containing silicate sheets that are exfoliated to a separation beyond the detection limit of the X-ray analysis.

- Free radical polymerisations in the presence of high clay loadings result in reductions in the weight and number average molecular weights and increases in the polydispersity of PMMA.

- The exfoliated structure is unstable under processing conditions and consequently reordering of the clay particles, through narrowing of the clay galleries with the exclusion of some of the polymer, takes place. The final clay structure is partially delaminated and comprises small aggregates of sheets, separated by distances of around 85Å. The interlayer spacing within the aggregates is considerably smaller and is controlled by the orientation and length of the extended pre-intercalated alkylammonium ions.

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Part II

The influence of preparation method upon the structure and relaxation characteristics of poly (methyl methacrylate) / clay composites

Abstract

Poly(methyl methacrylate) (PMMA) / clay composites were prepared using two methods: through solution polymerisation of methyl methacrylate in the presence of alkylammonium-modified clay and through direct melt intercalation of PMMA. Both composites were fluxed in an internal mixer to give comparable melt processing histories. In the reaction product of the polymerisation method, the clay layers were separated to a distance greater than 80 Å; after melt processing, the layers were partially re-aggregated. The length and orientation of the alkylammonium ions principally controlled the interlayer spacings within these aggregates. A finer degree of dispersive mixing of the clay in the polymerisation system was observed. The presence of modified clay in the polymerisation system led to branching, reduction of average molecular weight, increase in polydispersity, and to a bimodal molecular weight distribution of the PMMA. The glass-rubber transitions were observed around 120°C in the polymerisation system in comparison with 105°C for the melt intercalation materials and the PMMA resin. Moreover, PMMA extracted from the polymerisation composites had similarly elevated glass transition temperatures. The chain branching in the polymerisation system was the principal reason for the differences in the thermomechanical behaviour of the two composites.

Introduction

Polymer / clay composites have been prepared through *in-situ* polymerisation of monomers within the galleries of modified-clays [1] and through intercalation from solution [2]. It has been reported that several of these composites exhibited improved mechanical [3] and barrier properties [4], in comparison with the matrix polymer. Vaia *et al.* [5] presented a method for the melt intercalation of polymer chains. The process involves mixing a modified layered silicate with the polymer and heating to above the glass transition temperature and melting point, where appropriate, of the polymer. The materials that have been prepared through melt intercalation include polystyrene [6] and polypropylene [7] composites.

In a previous report by the authors [8], the preparation of poly(methyl methacrylate) (PMMA) / clay composites, through solution polymerisation of methyl methacrylate (MMA) in the presence of dodecylammonium and hexadecyltrimethylammonium modified montmorillonite clay, was described. X-ray diffraction showed that the clay layers were separated by a distance greater than 80 Å in the powdered reaction products, as there were no reflections from the (001) plane of montmorillonite in the range 1 to 10 °2θ. This resulted from the large expansion of the clay aggregates during polymerisation. Re-aggregation of the clay particles during subsequent melt processing was observed, however. After melt processing, the interlayer spacings in the clay aggregates were approximately the same as the lengths of the extended pre-intercalated alkylammonium ions, i.e. around 20 Å for dodecylammonium-clay and 29 Å for the hexadecyltrimethylammonium-clay. From this observation, it was suggested that the alkylammonium ions were fully extended and stood perpendicular to the internal clay surfaces, thereby controlling the interlayer spacings, with the PMMA chains occupying the remainder of the interlayer volume. Thus, the clay layers changed from the expanded arrangement created during solution polymerisation to a closer packed configuration during melt processing.

In the work described herein, PMMA / clay composites were prepared through direct melt intercalation during melt mixing. The microstructures and relaxation characteristics of these samples were compared with those in the solution-polymerised composites. Of particular interest were the thermomechanical properties and how they were affected by the composite preparation methods, the objective being to find the most suitable method of preparing PMMA / composites that gives enhanced modulus at elevated temperatures.

Experimental

Materials

The hydroquinone inhibitor was extracted from methyl methacrylate (MMA) monomer, from Fluka, with aqueous sodium hydroxide, then washed with distilled water, and dried over anhydrous sodium sulphate. Bentonite clay, containing a minimum of 90% montmorillonite, was from Colloid Environmental Technologies Co., Ltd. Dodecylamine was from Fluka and 2,2'-azo-bis(isobutyric-nitrile) (AIBN) initiator was supplied by TPI Co., Ltd., Thailand.

Modification of clay

The clay (20g), possessing a d-spacing of the (001) plane, d_{001}, of 12.9 Å, was dispersed in distilled water (600 mL) at 80°C. A solution of dodecylamine or hexadecyltrimethylammonium chloride (0.05 mol) and conc. hydrochloric acid (4.8 mL) in distilled water (100 mL) was added; heating and stirring was continued for one hour. The suspension was filtered and the solid residue washed with hot distilled water until no chloride was left, as determined by using the silver nitrate test. The product was dried at 60°C for several days in a fan oven, then milled in a ball mill and subsequently dried at 60°C under vacuum for 24 hr, yielding the dodecylammonium-modified clay or hexadecyltrimethylammonium-clay; d_{001} of these clays were 17.9 Å and 19.7 Å, respectively.

Solution polymerisation

AIBN (0.1 g) was dissolved in the extracted MMA (10 g), followed by the addition of the modified clay (1, 2, 5, or 10 g) and distilled hexane (40 ml). For the highest clay contents, 100 ml of hexane was needed to disperse the clay. The reaction flask was suspended in a thermostated water bath at 68°C for 5 h, with a condenser fitted. The solid, powdered product was recovered from the reaction mixture by evaporation of the solvent, followed by drying under vacuum at 60°C.

Melt processing

Melt intercalated composites were prepared by melt mixing PMMA resin with the modified clay (10, 20, and 50 phr) in a Haake Rheocord 90 at 180°C for 10 min, with a rotor speed of 50 rpm. This procedure was repeated with the unmodified clay, for comparison. The products from the solution polymerisations were also melt fluxed to provide a processing history. All samples were compression moulded at 180°C to form plaques for characterisation.

Characterisation

X-ray diffraction (WAXD) was carried out using a JEOL JDX-3530 diffractometer. The radiation source was operated at 30 kV and 30 mA; all but the Cu K_α X-ray photons were filtered out of the beam. The scanning speed, step angle, and count time were 1.2 °2θ/min, 0.04 °2θ, and 2 sec, respectively. For the scan range 1 to 10 °2θ, the divergence slit, receiving slit, and scattering slit were 0.5°, 0.1 mm, and 0.5°, respectively, whilst for the range 3 to 40 °2θ these values were 1°, 0.2 mm, and 1°, respectively. The precision of the d-spacings calculated from the X-ray data was assessed by measuring the d-spacing associated with a diffraction due to a biotite impurity in the clay at 10.2 °2θ as an internal standard. The mean d-spacing was 8.5 Å, standard deviation 0.08, and coefficient of variation 1 %, based upon nine measurements. Transmission electron microscope (TEM) observations of sections were carried out with a JEOL JEM-100CX instrument. To assess the degree of dispersion of the clay particles in the TEM images, a line intersection method was employed. The frequency of clay aggregate intersections with a line drawn along the micrograph, corresponding with the direction normal to the surfaces of the compression moulded plaque, was determined for each formulation. The results are given in the form of frequencies, expressed as the number of aggregate intersections with the line per μm. Dynamic mechanical analyses (DMA) were obtained with a Polymer Laboratories DMTA mkII thermal analyser. Glass transition temperature, T_g, was determined from the maximum in the tan δ versus temperature scan. PMMA was extracted from the compounds with tetrahydrofuran using a Soxhlet apparatus; the polymer was recovered through precipitation with methanol followed by drying. Differential scanning calorimetry (DSC) data were obtained with a Perkin Elmer DSC7 instrument. Samples were heated at 10°C/min to 180°C, cooled at 10°C/min to 50°C and finally heated at 10°C/min to 180°C. The data discussed herein were taken from the second heating phase of the cycle. T_g was determined from the mid-point of the step transition in the heat capacity versus temperature thermogram. Several replicate thermal analyses were carried out for each sample; the data reported are the mean values. ^1H and ^{13}C nuclear magnetic resonance

(NMR) spectra were collected using a Bruker 300 MHz spectrometer employing $CDCl_3$ as the solvent. Gel permeation chromatography (GPC) was carried out using a Waters 150-CV Plus instrument at room temperature with tetrahydrofuran as the solvent and PMMA calibration standards.

Results and discussion

Clay expansion during composite preparation

Figure 1 displays representative X-ray diffraction traces for (a) samples prepared through melt-intercalation, (b) polymerisation compounds after melt processing, and (c) reaction products from polymerisation before melt processing, each containing 20 phr of dodecylammonium-clay; (d) is PMMA without clay. The abscissa are given in d-spacings calculated from the Bragg equation:

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \qquad [1]$$

where n = 1, λ = 1.542 Å, and angle, θ. The X-ray traces for the unmodified clay filled PMMA were little different from the original unmodified clay, since the unmodified clay particles are simply incorporated into the polymer matrix in an agglomerated state, with no intercalation of the polymer.

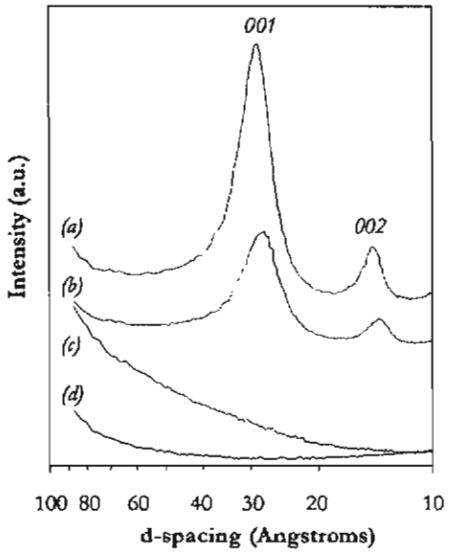


Figure 1. WAXD traces of composites, containing 20 phr of dodecylammonium-clay, prepared through (a) melt-intercalation; (b) polymerisation (after melt processing); (c) polymerisation (powder reaction products before processing), and (d) PMMA synthesised in the absence of clay.

For both the melt processed polymerisation and melt-intercalation composites, series of reflections exhibiting periodicity along the d-axis are present in the diffraction traces. These are the *00l* reflections for the (001) plane and indicate that the clay layers are at least partially arranged into aggregates that comprise regularly spaced layers. The average d_{001} for the melt-intercalation composites was 30.2 Å and changed little with clay content. The corresponding value for the melt processed polymerisation composites was 29.2 Å, and was independent of clay content. The gallery spacing, S_g, is the distance between the internal surfaces of neighbouring clay layers; it is calculated:

$$S_g = d_{001} - t \qquad [2]$$

where t is the van der Waal's thickness of the clay layer, that is 9.6 Å [9]. The gallery spacings are thus 20.6 Å and 19.6 Å for the intercalation and melt processed polymerisation composites, respectively. The length of an extended dodecylammonium ion is estimated to be 20.0 Å [9], and hence it is inferred that the extended ions stand perpendicular to the surface of the clay with the PMMA chains occupying the remaining space.

For the melt-intercalation composites, the preparation process may be described qualitatively through the following reasoning. In the dodecylammonium modified-clay, before composite preparation, the d_{001} was 17.9 Å, giving a corresponding interlayer spacing of 8.3 Å. This result suggests that the ions assume a bilayer arrangement [9], that is with one ion lying parallel to each of the internal surfaces of the clay. During melt mixing the PMMA chains intercalate the clay interlayers, with the alkyl chains of the ions turning through 90° to become oriented perpendicular to the clay surface, thereby providing room to accommodate the PMMA. The favourable interactions between PMMA and the surface of the silicate sheets, and the gain in entropy of the alkyl chains as the interlayer spaces expand, permits the unfavourable loss in entropy of the polymer, due to its confinement between the silicate sheets, to be overcome [10,11]. Consequently, intercalation of the PMMA chains takes place during melt mixing. Further polymer intercalation does not occur, however, because once the alkyl chains are fully extended, no further entropy can be gained by the alkylammonium ions with continued layer expansion and therefore there is no driving force to overcome the associated loss in entropy as extra polymer is confined in the galleries. This hypothesis was tested by melt intercalating PMMA into the galleries of a clay sample that had been modified with an ion possessing a different length from the dodecylammonium ions, namely hexadecyltrimethylammonium ions. The d_{001} of the composite was 39.7 Å, and hence the gallery spacing was 30.1 Å. The estimated extended chain length of the hexadecyltrimethylammonium ion is 29.0 Å, and therefore it is reasonable to conclude that the extended ions assume a perpendicular orientation to the inner surfaces of the clay, thereby playing a major role in determining the interlayer spacing. The gallery spacings for all formulations are plotted versus clay content in figure 2.

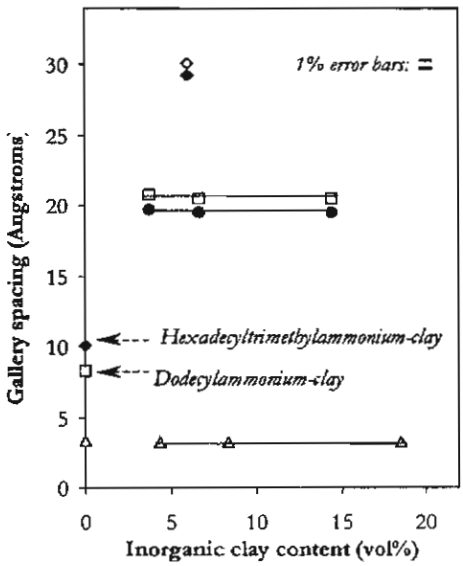


Figure 2. Gallery spacings for all composites as a function of clay content: (Δ) PMMA / unmodified clay composites; (●) polymerisation composites containing dodecylammonium-clay; (□) melt intercalation composites containing dodecylammonium-clay; (♦) polymerisation composites containing hexadecyltrimethylammonium-clay, and (◊) melt intercalation composites containing hexadecyltrimethylammonium-clay.

It can be seen that the melt-intercalation samples have slightly higher spacings than the melt processed polymerisation materials. This result is obtained for every concentration of clay, suggesting that the difference is reproducible, and hence significant relative to the estimated 1% error of the measurements. The origin may lie in the microstructure differences of the polymers, as discussed in the following section.

Polymer microstructure

For both the polymerisation and melt-intercalation composites, all the PMMA could be extracted with tetrahydrofuran in a Soxhlet apparatus. Thus, in each composite the polymer interacts with the clay through physical bonds that can be displaced through the formation of tetrahydrofuran-clay specific interactions. Each extracted polymer was characterised through GPC and NMR spectroscopy. The GPC

data for the polymerisation system are displayed in figure 3; the melt intercalation polymer was unchanged from the original resin.

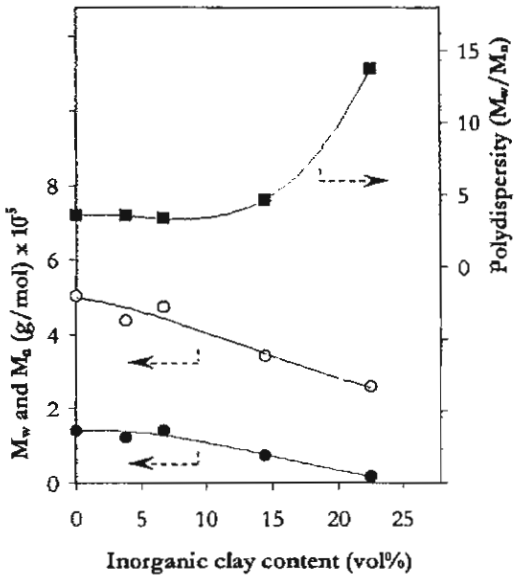


Figure 3. GPC data for PMMA extracted from polymerisation composites: (O) weight average molecular weight, M_w; (●) number average molecular weight, M_n, and (■) polydispersity.

Polymerisation of MMA in the presence of higher loadings of modified clay resulted in the formation of polymers with reduced molecular weight and increased polydispersity, in comparison with PMMA prepared under comparable conditions in the absence of clay. This may be due the interference of active sites upon the clay surface with the free radical polymerisation; chain transfer to Lewis or Brönsted acid sites may take place.

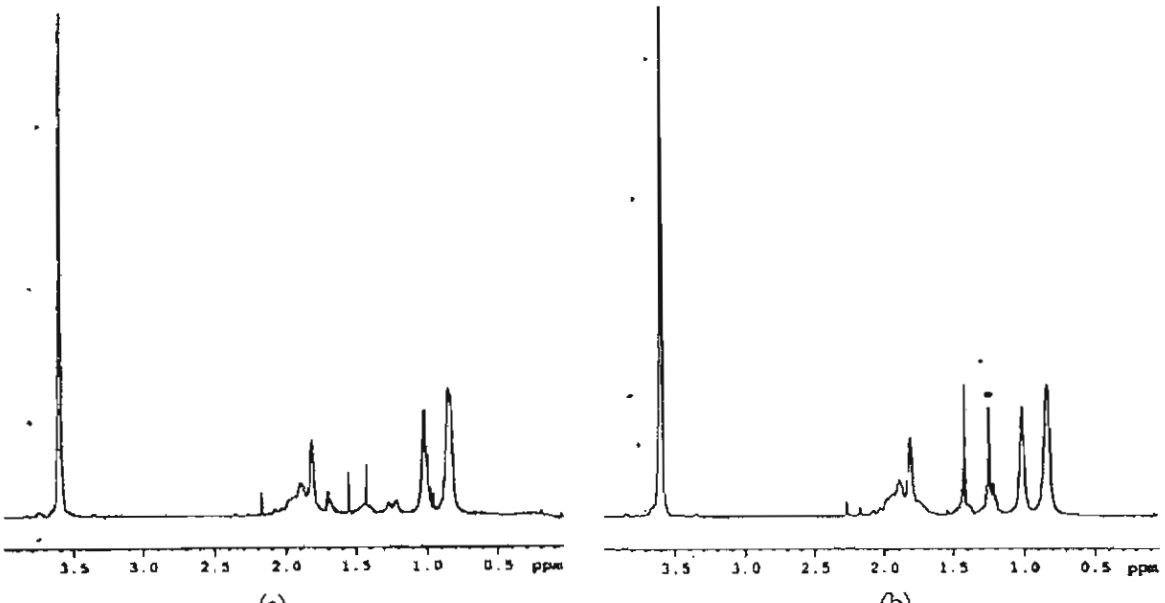
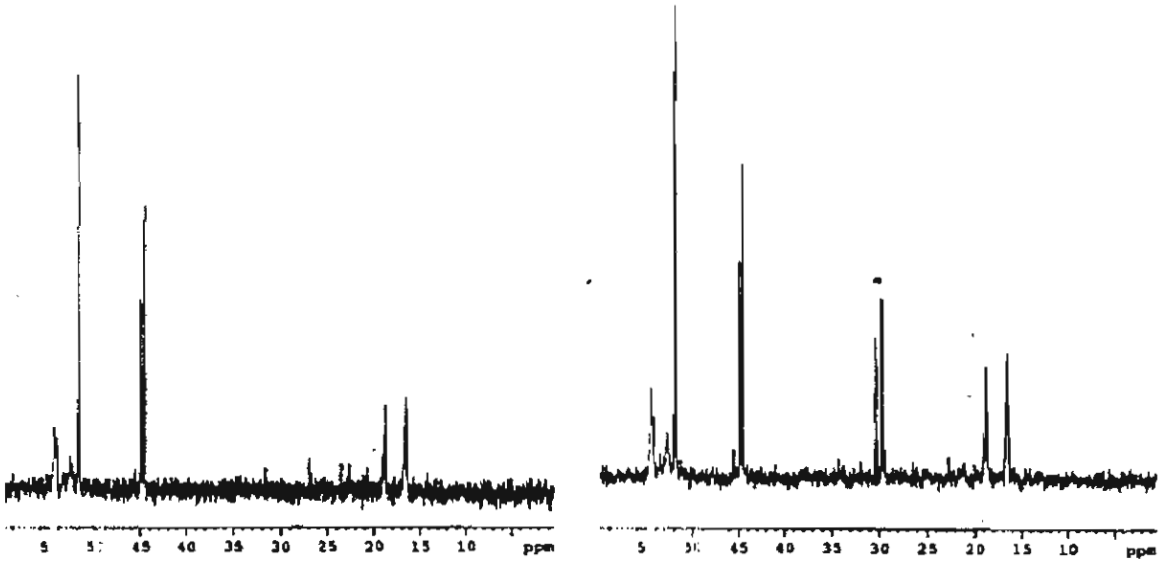


Figure 4. ^{1}H-NMR spectra of (a) PMMA synthesised in the absence of clay and (b) PMMA extracted from a polymerisation composite containing 20 phr of dodecylammonium-clay.

In figure 4 the ^{1}H-NMR spectrum of PMMA synthesised in the presence of modified clay is compared with the spectrum of PMMA prepared in the absence of clay; figure 5 shows the corresponding ^{13}C-NMR spectra. The resonances observed in the ^{1}H-NMR spectrum of PMMA prepared in the absence of clay may be assigned from previous studies [12]: $OC\underline{H}_3$ at δ = 3.60 ppm, $C\underline{H}_2$ in the range δ = 2.50 to 1.30 ppm, $C\underline{H}_3$ at δ = 1.21, 1.02, and 0.85 ppm, from isotactic, heterotactic, and syndiotactic triads,

respectively. PMMA synthesised in the presence of clay has an additional resonance at 1.25 ppm (marked with the symbol '■' in figure 4b); the area of this peak increased with increasing quantity of clay in the reaction vessel. Whilst this peak is in close proximity to the $\underline{CH_3}$ resonance of the isotactic triads, it can be discounted as resulting from an increase in the fraction of isotacticity since the splitting pattern of the $\underline{CH_2}$ protons are not consistent with this result [12]. The ^{13}C-NMR spectrum of PMMA synthesised in the presence of clay has chemical shifts of 29.7 and 30.3 ppm, marked with the symbol '■' in figure 5b, that are not present in the spectrum of PMMA synthesised in the absence of clay.



(a) (b)

Figure 5. ^{13}C-NMR spectra of (a) PMMA synthesised in the absence of clay and (b) PMMA extracted from a polymerisation composite containing 20 phr of dodecylammonium-clay.

The ^{13}C-NMR and ^{1}H-NMR results are consistent with the formation of ≡C-H structures, with the 29.7 and 30.3 ppm resonances being assigned to the tertiary carbon and the 1.25 ppm resonance to the methine proton. These results suggest that the polymer prepared in the presence of clay contains branch points, and hence it is concluded that this is promoted by the active involvement of the clay surface during polymerisation.

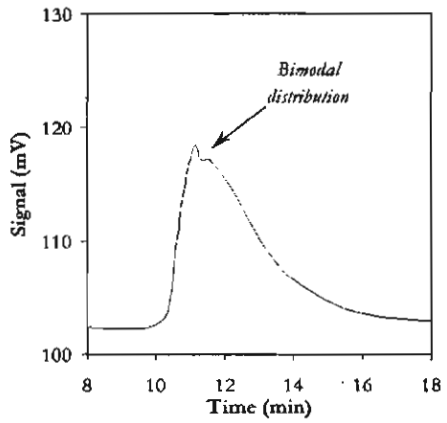


Figure 6. GPC chromatogram of PMMA extracted from the polymerisation composite containing 50 phr of dodecylammonium-clay.

In the GPC chromatograms of PMMA extracted from composites containing 20 phr or more of clay, as exemplified in figure 6, it is evident that there is a bimodal distribution of molecular weights. This may result from the heterogeneous conditions of the polymerisations carried out in the presence of clay. Reactions taking place in close proximity of the clay surface may readily interact with the active sites of the clay leading to the formation of the lower molecular weight and more highly branched polymer. Both

factors lead to reduced coil dimensions, and therefore longer retention times in the GPC column. Polymerisations progressing at some distance from the clay have lower probabilities of being affected, and hence a higher molecular weight fraction may be formed. It is possible that the more highly branched polymer, with lower molecular weight, formed near the clay surfaces locates in the clay galleries. It was noted previously that the clay gallery spacings were always smaller in the polymerisation system than in the intercalation system. The observation may be related to the altered microstructure of the PMMA when prepared in the presence of clay. Branching results in reduced coil dimensions, changes in the conformations of the polymer chains, and to an increase in the number of polymer chain ends in comparison with a linear polymer of the same molecular weight [13]. Thus, the free energy of interaction between the PMMA, alkylammonium ions, and the clay is affected resulting in the modification of the clay aggregate structure.

Clay aggregate dispersion

The appearances of the polymerisation and melt-intercalation composites to the naked eye were similar, in that both were transparent. It may be inferred from the observation that the clay aggregates in these materials are small relative to the wavelengths of visible light, and hence little diffraction occurs. Conversely, the compounds containing unmodified clay were opaque, indicating the presence of large agglomerates that scatter light. The SEM micrographs shown in figure 7 confirm the presence of large agglomerates in the composites prepared with the unmodified clay, in comparison with the finer textures seen for the melt-processed polymerisation and melt-intercalation composites.

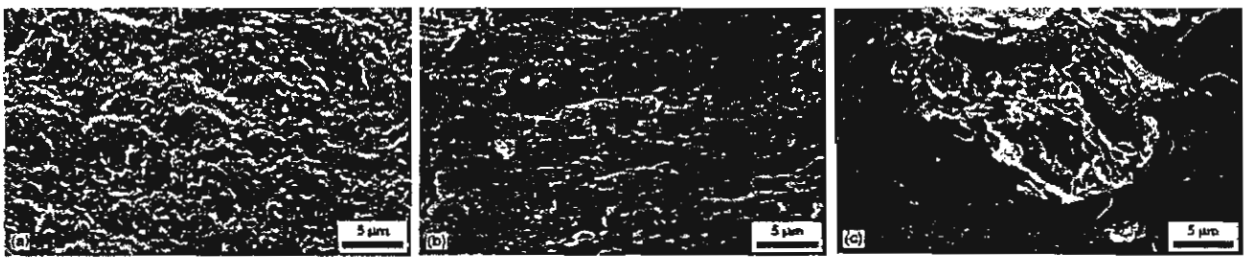


Figure 7. SEM micrographs of fracture surfaces: (a) melt processed polymerisation PMMA / dodecylammonium-clay composite; (b) PMMA / dodecylammonium-clay melt intercalation composite, and (c) unmodified clay filled PMMA; content is 10 phr in each sample.

The alkylammonium ions reduce the attractive forces between the clay layers and enable the polymer or monomer to intercalate into the clay galleries thereby aiding the dispersion of the clay. The average thickness of the clay crystal aggregates perpendicular to the (001) plane, L_c, was calculated using the Scherrer equation:

$$L_c = \frac{k\lambda}{\beta_{001}\cos\theta} \qquad [3]$$

where k = 1 and β_{001} is the width, in radians, at half maximum intensity of the 001 reflection. The average number of layers in each aggregate, N_c, was calculated:

$$N_c = \left(\frac{L_c}{d_{001}}\right) + 1 \qquad [4]$$

L_c and N_c values for the two types of composite are plotted as functions of clay content in figure 8. It is inferred from the data that in the polymerisation system, for the two lowest clay contents, the clay is dispersed into a larger number of aggregates each comprising fewer silicate sheets than in the melt intercalation composites. At the highest clay content, however, the X-ray analysis reveals little difference between the two types of composite. The peak width, β_{001}, may be increased by disorder in the crystals in addition to the influence of finite crystallite size, and hence the calculated L_c may decrease. The TEM measurements plotted in figure 9 show that for a given clay content there is a larger number of clay

aggregates in the polymerisation composites than in the intercalation composite; i.e., the aggregates are smaller in the former material.

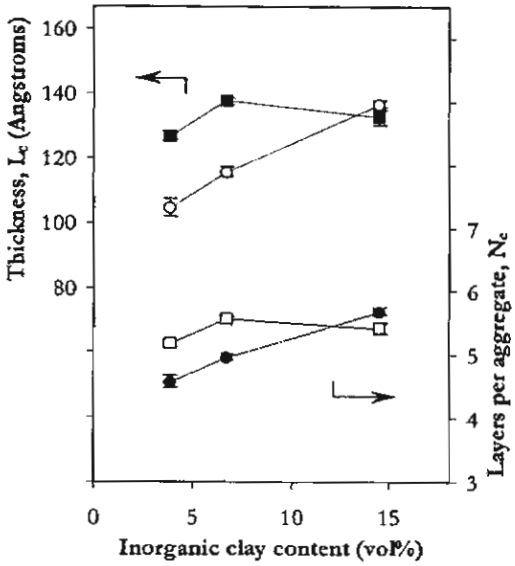


Figure 8. Average crystallite thickness, L_c, in the (O) melt processed polymerisation and (■) melt-intercalation systems containing dodecylammonium-clay; average number of clay layers per aggregate, N_c, versus clay content in the same (●) polymerisation and (□) melt intercalation composites.

This confirms that the increases in β_{001} at least partly reflect reductions in crystallite thickness. Examples of the TEM micrographs from which the data in figure 9 were obtained are displayed in figure 10. The clay layers are oriented in one plane that is with the basal surfaces, and hence the (001) plane, parallel to the platens of the compression press. Moreover, the 100 reflection of the quartz in the clay was not seen in the X-ray diffraction traces of the moulded samples, indicating its perpendicular orientation to the platens.

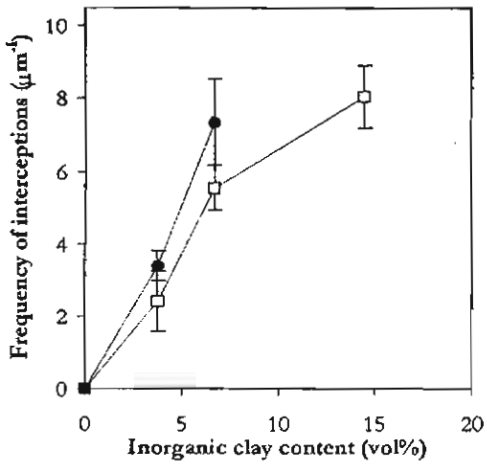


Figure 9. Plot of number of clay aggregate - line intersections per micron for: (□) melt intercalation composites and (●) melt processed polymerisation composites, both containing dodecylammonium-clay.

The TEM micrographs of the composites containing the highest clay content, shown in figure 11, reveal differences in the arrangement of the clay aggregates in the two composites. In the polymerisation composite, the aggregates form an almost continuous pattern, with a large amount of connectivity, overlap, and misalignment within the aggregates, making differentiation of individual aggregates unclear. The line intersection method was uncertain for this micrograph and consequently no data are given in figure 9 for the sample. The melt intercalation composite has more regular and clearly defined aggregates. The differences in the polymerisation and melt-intercalation composite structures originate from the conditions during sample preparation.

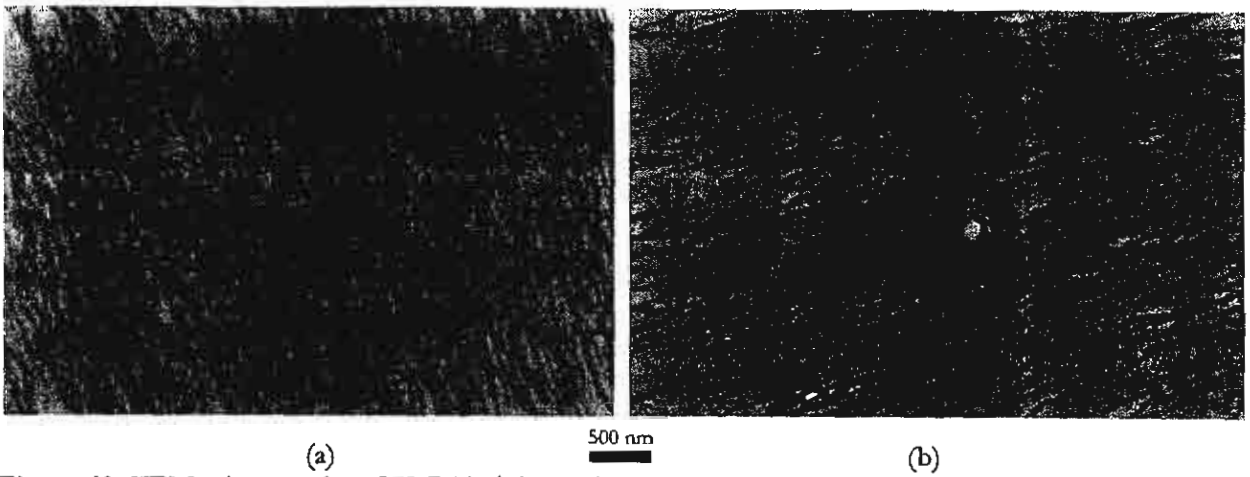


Figure 10. TEM micrographs of PMMA / dodecylammonium-clay composites, containing 20 phr of clay: (a) melt processed polymerisation and (b) melt intercalation composites.

The polymerisation reactions took place in a dispersion of modified clay in methyl methacrylate dissolved in hexane in which the monomer was able to penetrate the clay galleries causing the clay to swell to a separation beyond the detection limit of the X-ray diffraction analysis; i.e. greater than 80 Å. As the molecular weight of the polymer increased during polymerisation, the chains precipitated from solution becoming trapped between the silicate sheets, thereby fixing their separation.

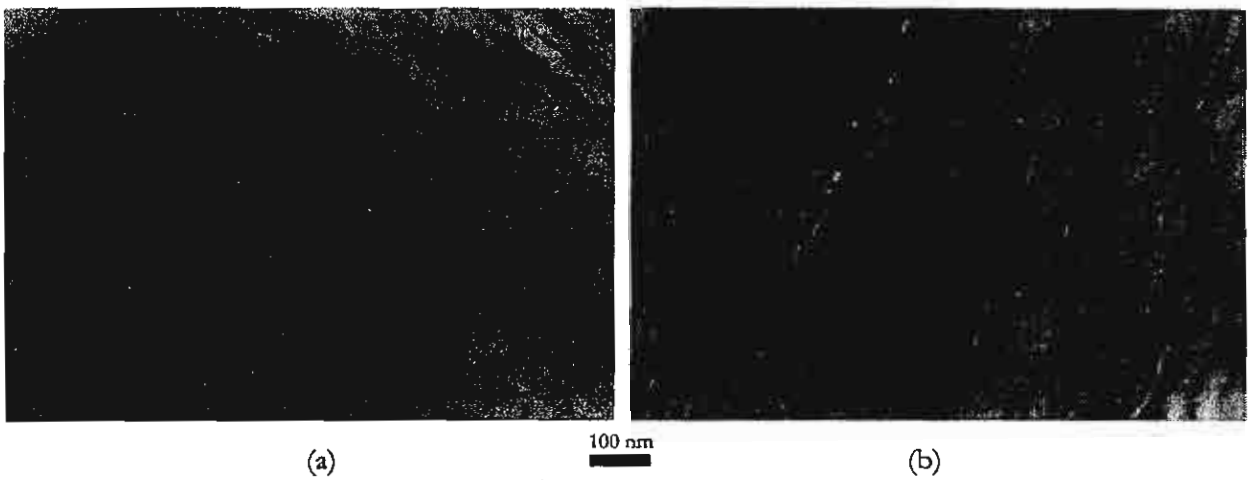


Figure 11. TEM micrographs of PMMA / dodecylammonium-clay composites: (a) melt processed polymerisation and (b) melt intercalation samples; clay content is 50 phr in both.

It is probable that some long-range order between the clay sheets was maintained, however. During subsequent melt processing, some of the PMMA chains moved out from between the layers and the silicate sheets aggregated into more thermodynamically favoured arrangements. The silicate sheets may not have returned wholly to their original positions, with sheet misalignment resultant in the newly formed aggregates. In the melt intercalated sample, the aggregates appear to be well separated from one another, in discrete aggregates. During melt intercalation, the PMMA intercalates the clay crystal aggregates causing them to expand in the [001] direction, i.e. normal to the (001) plane, without causing the layers to loose the vertical alignment of the crystal lamellae. Consequently, more of the original order is maintained in the melt intercalation composites.

Relaxation characteristics

Plots of T_g, determined from DMA, against dodecylammonium-clay content are shown in figure 12. Typical storage modulus curves are shown in figure 13. T_g values of the melt-intercalation composites were close to that of the unfilled PMMA; i.e. around 105°C. The polymerisation composites exhibited pronounced increases in T_g, typically 20°C, in comparison with pure PMMA that were slightly affected by

clay concentration, although the rate of increase in T_g decreased with increasing clay content. Moreover, the storage moduli of the solution-polymerised composites were substantially greater, at every temperature, in comparison with the other formulations. T_g, determined through DSC analyses, of the polymers extracted from the composites showed essentially the same result, although the values obtained from DSC were typically 5°C lower than those obtained from DMA due mainly to the static versus dynamic nature of the DSC and DMA analyses. Thus, changes in T_g may be traced to structural differences in the polymer. Modulus may be affected to some extent by the greater dispersion of the clay in the polymerisation composites due to hydrodynamic effects.

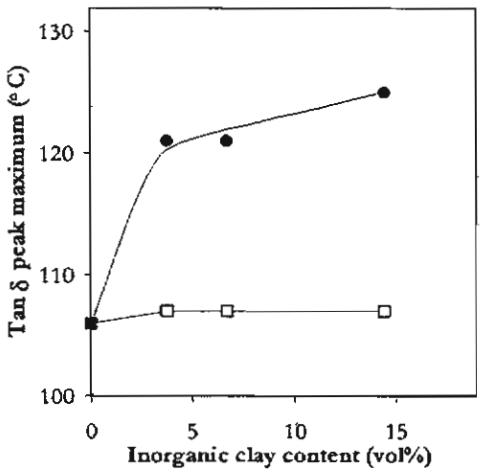


Figure 12. Temperature of tan δ maximum versus inorganic clay content: (□) melt intercalation and (●) melt processed polymerisation composites, containing dodecylammonium-clay.

The NMR results showed that PMMA prepared in the presence of clay was branched. Chain structure affects T_g in PMMA markedly, for example, for the isotactic form T_g = 45°C, for syndiotactic T_g = 115°C, and for statistical polymers prepared through free radical polymerisation T_g = 99°C [14]. Moreover, Krigas et al. [15] observed an increase in T_g with increasing branch content of model polyethylenes.

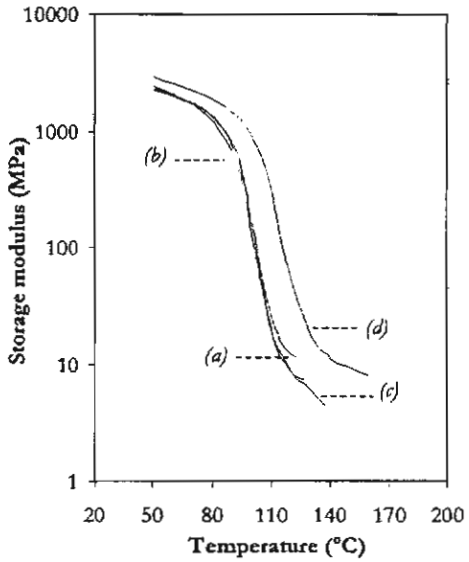


Figure 13. Storage modulus versus temperature for (a) unfilled PMMA and (b) PMMA with unmodified clay. Curve (c) and (d) are from the melt intercalation and melt processed polymerisation composites, respectively, containing 10 phr of dodecylammonium-clay.

It is likely that the chain branching is the cause in the modified relaxation characteristics of the PMMA in the polymerisation composites. The effect of branching may be more pronounced in PMMA due to the

bulkiness of the branch points that restricts the main chain relaxation in comparison with the less sterically hindered polyethylene. From the results of Cowie [16], changes in molecular weight over the range found in this work are not expected to alter T_g.

Vaia *et al.* [5] observed that whilst the main chain relaxation of intercalated polystyrene in montmorillonite composites was suppressed, a transition due to the unintercalated bulk polymer was observed at the same temperature as the glass transition of the unfilled polymer resin. For the intercalated polymer, the relaxation process is limited by the restrictions imposed upon the chains through their confinement between the clay layers. The available free volume may be insufficient to permit co-operative jump processes [17], with the consequence that the relaxation of the intercalated polymer is suppressed, at least within the time and temperature conditions of the analysis. The experimentally observed relaxations in this work originate from the polymer in the bulk.

CONCLUSIONS

- Montmorillonite clay modified with dodecylammonium and hexadecyltrimethylammonium ions can be intercalated through melt mixing with PMMA.
- The length and orientation of the extended alkylammonium ions principally control the interlayer spacings of the clay in both the melt-intercalation and the melt processed polymerisation composites.
- The clay aggregates in the melt processed polymerisation composites are more finely dispersed and are more misaligned than in the melt intercalation composites.
- PMMA synthesised in the presence of the clay was branched and this led to an increase the glass transition temperature of the polymer and the storage moduli of the polymerisation composites in comparison with the melt intercalation samples.

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Part III

Compounding of poly(methyl methacrylate) / clay composites with poly(vinyl chloride)

Abstract

Poly(methyl methacrylate) (PMMA) / clay composites were prepared through solution polymerisation of methyl methacrylate in the presence of dodecylammonium-modified clay. These samples were compounded into poly(vinyl chloride) (PVC) formulations. In comparison with the unmodified clay, the PMMA / clay hybrids conferred pronounced increases in dimensional stability to the products at very low clay contents, as indicated by enhanced tensile modulus at 25°C and flexural modulus at elevated temperatures. This effect was thought to be related to the enhanced clay dispersion in the hybrid containing formulations and to the branching of the PMMA. Even distributive mixing of the clay aggregates in the PVC matrix was found from TEM micrographs; the fine mixing was related to the miscibility of PMMA with the PVC, as inferred from a single glass transition intermediate between that of the pure PMMA and the base PVC compound. The enhanced moduli in the hybrid systems were obtained at the expense of some of the compound toughness. The hydrodynamic effects of the enhanced clay dispersion were the probable cause of both effects.

Experimental

Composite preparation

The PMMA / clay polymerisation composites described in part I and II were prepared and compounded with the PVC resin in a Haake Rheocord 90 at 180°C for 10 min, with a rotor speed of 50 rpm. Blank samples were also prepared by mixing unmodified clay, herein referred to as pristine clay, with PVC or in combination with PMMA. All samples were compression moulded at 180°C to form plaques for characterisation.

Characterisation

X-ray diffraction (WAXD), transmission electron microscopy (TEM), and dynamic mechanical analyses (DMA) were carried out as reported in part I and II. Tensile testing was at 25°C with a crosshead speed of 5 mm/min.

Results and discussion

Clay dispersion in the PVC compounds

PVC blended directly with the unmodified clay had poorly dispersed clay, since the clay aggregates could be seen easily with the naked eye. The XRD pattern of the PVC compound had peaks at $2\theta = 9.4^{\circ}$ and 28.5° corresponding to d-spacings of 9.4 Å and 3.1 Å, respectively; a halo, due to the scattering by amorphous material, was seen between $2\theta = 10$ to 25° in addition to two poorly defined diffractions from the PVC crystalline phase. The maximum of the (001) plane diffraction of clay in the XRD pattern for PVC melt mixed with 2.5 vol% clay was observed at $2\theta = 5.9^{\circ}$. This corresponded to the d-spacing of 15 Å. Increasing the amount of clay to 5.0 vol% did not change the XRD patterns of the composite, except that the peak intensities were higher. The d_{001} of the clay at both filler contents was little changed from that of the pristine clay. Therefore, no intercalation occurred in this system. PVC / clay composites prepared by melt mixing with pristine clay were the conventional filled composites. PVC melt mixed with PMMA and pristine clay had the same appearance as the PVC / clay composites. Therefore, the PMMA did not affect the dispersion of clay in this composition. From the XRD data, the peak maximum of the (001) plane peak was little changed from that of the pristine clay. Therefore, there was no intercalation of PMMA or PVC into the clay layers. Adding PMMA did not affect the dispersion of clay agglomerates because the polymer molecules did not intercalate into the clay layers. The inter-clay particle attraction was too strong to permit intercalation of the polymer into the clay sheets. Moreover, the forces of dispersive mixing were insufficient to break the forces binding the clay agglomerates together, and hence dispersion was poor.

The PVC compounds containing the PMMA / clay hybrids compounds had a homogeneous appearance to the naked eye; i.e., they were transparent, although coloured. This indicates that the dispersion of clay in PVC was better when using the clay in the PMMA clay hybrid form than in the pristine form. The clay aggregates in these materials were small relative to the wavelengths of visible light, and hence little scattering occurred. For PVC with unmodified clay, in the presence or absence of PMMA, the materials contained large unintercalated clay agglomerates. As discussed in part I and II, the solution polymerised PMMA / clay hybrids in powder form had no peaks in the range 2θ = 1-10°. Therefore, they were classified as delaminated nano-composites. After mixing, peaks were observed at 2θ = 3.0° and 6.1°, arising from (001) plane diffraction and the *002* reflection for the (001) plane of clay, respectively. The corresponding d-spacing was 29 Å. The delaminated structure rearranged into the intercalated form during melt processing. The same sequence of events occurred when the hybrids were mixed with the PVC; i.e., the clay layers rearranged to an intercalated hybrid configuration. Upon increasing the hybrid concentration in the PVC formulations to 16.1 vol%, the appearance of the composite became similar to that of the melt processed hybrid samples.

Excess dodecylamine in the organophylic clay

It was thought that the organophylic clay contained some free dodecylammonium ions. Since this may affect the properties of the hybrids, samples containing organophylic clay that was extracted with THF were prepared and characterised. From TGA, the weight loss of organic matter before and after extraction of excess organic matter from the organophylic clay was 17.8 wt% and 12.9 wt%, respectively; i.e., the decreases was 4.9 wt% after the extraction. This fraction was suspected to be composed of the excess dodecylammonium ions. The d_{001} of clay was not changed by extraction as the XRD patterns of the clay before and after extraction were identical. The excess dodecylammonium ions may be adsorbed upon the external surface of the clay, and hence extraction of these non-bonded dodecylammonium ions did not affect the d_{001} of the clay. This result also indicates that the quantity of dodecylammonium ions inside the clay galleries was unchanged, since the basal spacing was not altered. FTIR analysis confirmed that the dodecylammonium ions were present in the extracted organophylic clay. The IR spectra of organophylic clay before and after were essentially the same. Most of dodecylammonium ions were ionically bound to the clay, and only the excess protonated dodecylamine was washed out, confirming the XRD results. The XRD patterns of the hybrids prepared with the extracted clay had no peaks in the range of 2θ = 2-10°. Therefore, they were classified as delaminated nano-composites.

Torque rheometry

Since PVC has inadequate thermal stability, it cannot be truly melted before degradation in the same way that other thermoplastics, such as polyethylene and polypropylene can. Combined shearing and heating to form a 'gel' that retains some of the crystal structure of the original grains must be employed to fuse PVC.

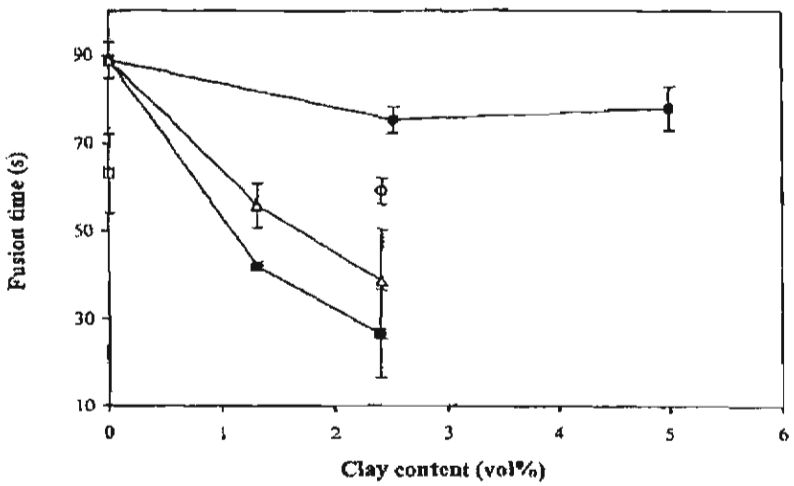

Figure 1. Fusion time for PVC composites containing (•) unmodified clay only, (□) PMMA only, (o) PMMA and unmodified clay, (■) solution polymerised PMMA / clay hybrid, and (Δ) the hybrid prepared with extracted clay.

This process is characterised by the fusion, or gelation, peak in the plot of torque versus time obtained from a torque rheometer. Figure 1 shows the fusion time of the PVC composites. The fusion time of the basic PVC dry blend was about 90 seconds. Incorporation of unmodified clay slightly reduced the fusion time. This minor decrease of fusion time may result from the increase in viscosity of the system, due to the disruption of the melt flow by the filler particles. Therefore, more heat and higher melt stresses were generated, and hence the fusion time of the PVC decreased. Addition of PMMA alone decreased the fusion time by about 30 seconds. PMMA is used commercially as a processing aid for PVC. It has been reported that the PMMA dissolves into the PVC grains causing them to swell and fuse more quickly. The PMMA is essentially miscible with the PVC. The PMMA may also improve the transfer of heat to the compound. PVC formulations containing the PMMA / clay hybrids had shorter fusion times than pure PVC; moreover, increasing the hybrid content reduced the fusion time. Extraction of the excess dodecylammonium ions from the organophylic clay resulted in longer fusion times of the PVC formulations in comparison with the corresponding unextracted materials. This is probably related to the lubricating effect of the excess dodecylammonium ions in the unextracted clay.

Since the PMMA / clay hybrid samples comprised clay layers that were delaminated and dispersed in PMMA, when the hybrids were melt mixed with PVC, the clay was dispersed in PVC more homogeneously than in the formulations containing unmodified clay. Therefore, the number of clay aggregates in was higher in the former system. The larger numbers of particles disturbed the melt flow to a greater extent, and hence increased viscosity of the system, and more heat was generated. Consequently, the temperature of the system was higher, and the PVC fusion took place sooner. In the compounds with unextracted clay, excess dodecylamine acted as an internal lubricant thereby counteracting the rise in viscosity, and hence extended the fusion time.

Mechanical properties

Tensile initial tangent modulus data are shown in Figure 2. The unmodified clay resulted in a small increase in the modulus of the PVC formulation. The modulus of the sample containing PMMA only was not much different from that of PVC, and hence the PMMA did not greatly affect the modulus at the level used. The presence of the PMMA / clay hybrids had a more pronounced effect upon modulus than any combination of PMMA and the unmodified clay at equal additive content.

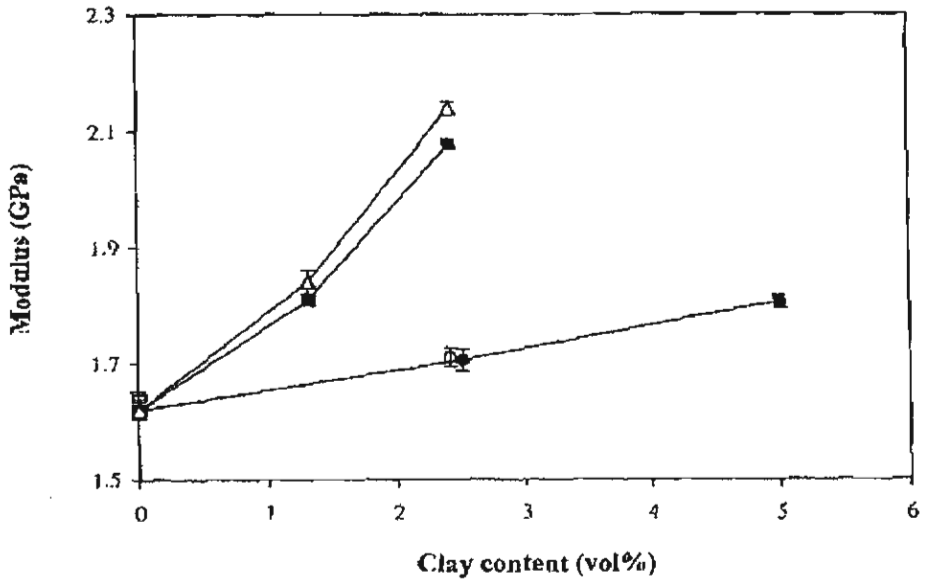

Figure 2. Initial tangent modulus of PVC compounds containing (•) unmodified clay only, (□) PMMA only, (o) PMMA and unmodified clay, (■) the solution polymerised PMMA / clay hybrid, and (Δ) the PMMA / clay hybrid containing extracted clay.

Extraction of the excess DDA from the clay, led to a small further increase in modulus the moduli; again this, this is probably related to the lubricating effect of the excess DDA. The finer clay dispersion, and the branched structure if the PMMA in the hybrid, confers enhanced modulus to the compounds at very low clay contents.

Thermomechanical behaviour

The unmodified clay did not alter the relaxation of PVC at all filler loadings. There was an upward shift of the tan delta peak maximum to a higher temperature of the PMMA containing formulations in comparison with the base PVC compound. No relaxation event was seen for a separate a PMMA phase. These observations were the result of the miscibility of PVC with PMMA. For a miscible blend, the Tg can be calculated by the average of the component Tg values:

$$Tg_{(blend)} = Tg_{(PMMA)}\phi_{(PMMA)} + Tg_{(PVC)}\phi_{(PVC)}$$

where ϕ_i is the volume fractions of component i. Since the volume fraction of PMMA in the blend was low, the shift in Tg was small. The experimentally observed Tg data are compared with the predicted values in table 1.

Table 1. Experimentally determined Tg values of the PVC composites and their corresponding predicted values.

Additive present	Tg (°C)		
	Measured	Theory	Difference
PMMA only	86.5	86.0	+ 0.5
PMMA and unmodified clay	86.6	86.0	+ 0.6
Solution polymerised hybrid; 1.2 vol% clay	87.7	86.4	+ 1.3
Solution polymerised hybrid; 2.2 vol% clay	89.2	87.8	+ 1.4
Solution polymerised hybrid; 1.2 vol% extracted clay	88.0	86.4	+ 1.6
Solution polymerised hybrid; 2.2 vol% extracted clay	89.7	87.8	+ 1.9

Since the measured Tg's of the composites were similar to the calculated Tg's, this suggests that PVC and PMMA formed a mixed amorphous phase in all formulations. An example of a TEM micrograph of a PVC compound containing 16.1 vol% of the solution polymerised PMMA / clay hybrid is shown in figure 3. The clay is arranged into aggregates that are randomly distributed in the matrix, although there is some preferred orientation due to the compression moulding operation. The XRD results showed that the gallery spacings within these aggregates are, on average, 20Å. Moreover, the evenness of the clay distribution indicates that the PMMA does not exist in dispersed domains within the PVC matrix, but rather it is dissolved into the continuous phase thereby facilitating the distributive mixing of the clay aggregates. Hence, PVC and PMMA should be miscible in the composition range studied.

Figure 3. TEM micrograph of a PVC formulation containing a solution polymerised PMMA / clay hybrid (16.1 vol%).

All PVC composites had higher storage moduli than the unfilled PVC formulation at all temperatures, as shown in Figure 4. At the same clay content, the formulations containing the PMMA / clay hybrids exhibited near two-fold increases in storage moduli in comparison with the compounds containing unmodified clay. The storage moduli of the compounds containing extracted clay were marginally higher than those containing unextracted clay.

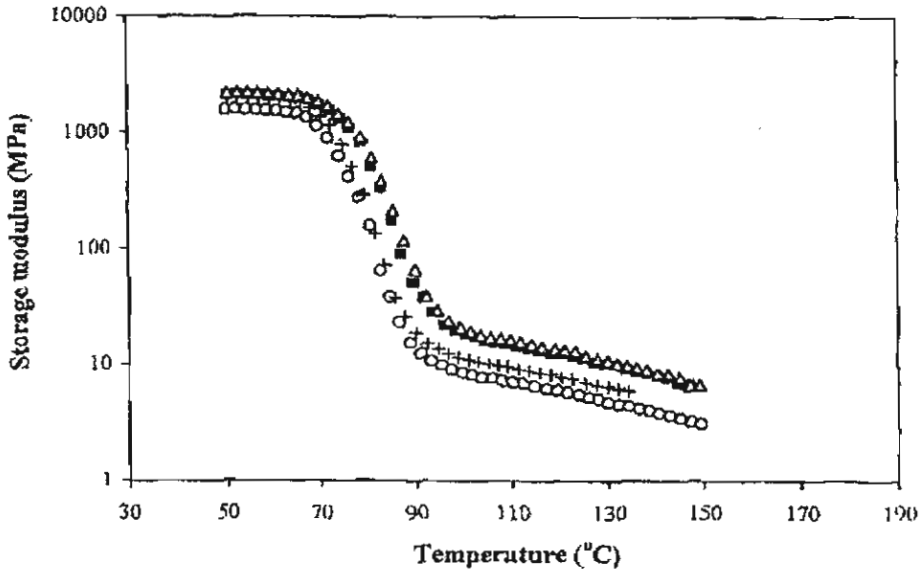

Figure 4. Storage moduli of (o) unfilled PVC and PVC compounds with (+) unmodified clay (2.5 vol% of clay), (■) solution polymerised PMMA / clay hybrid (16.1 vol% of the hybrid), and (Δ) the hybrid prepared with extracted clay (16.1 vol%).

The deflection temperature under load (DTUL) test or heat distortion temperature (HDT) test is commonly used to indicate the relative elevated temperature capabilities of plastic materials. HDT is the temperature that a polymer achieves a certain flexural modulus value; i.e., 971 MPa. In this report, the HDT equivalent is the temperature at which the sample modulus equals 971 MPa. The HDT equivalent was determined from the storage modulus versus temperature curve in figure 4. These data are shown in Table 2. The moduli of the filled composites were higher than those of the unfilled PVC formulation at both 50°C and 80°C.

Table 2. HDT equivalents and storage moduli of PVC composites at 50°C and 80°C; compounds with clay contain 2.2 vol% of inorganic clay material.

Formulation	Storage modulus (MPa) at 50°C	Storage modulus (MPa) at 80°C	HDT equivalent (°C)
PVC base	1593	159	71
PVC with unmodified clay	2006	292	74
PVC with the solution polymerised PMMA / clay hybrid	2225	513	77
PVC with the hybrid prepared with extracted clay	2225	612	78

In table 2, at equivalent clay content, the PMMA/clay hybrids provided a more pronounced increase in storage moduli at the elevated temperature, in comparison with the conventional filled material. The practical consequence of this was that the dimensional stability of the material was enhanced, and the service temperature range was extended.

Compound toughness

Toughness related properties, such as tensile strain at break and energy to failure, detailed in Table 3 were decreased as clay content was increased for all PVC formulations. Thus, the dimensional stability of the compounds was achieved at the expense of some of the toughness. The decrease was more pronounced for the formulations containing the PMMA / clay hybrids. The major effect of the addition of filler to the matrix was to cause strain inhomogeneity in the matrix by restricting the mobility of the polymer at the edges of the particles. When the unfilled resin was placed under a tensile load, the specimen can contract laterally and extend relatively uniformly. When the filled material was stressed, strain, and hence stress, concentrations were present in the matrix in the vicinity of the filler particles,

with failure presumably initiating at these points, causing the filled materials to fail at reduced macroscopic strains.

Table 3. Toughness related properties of the PVC formulations from tensile testing.

Additive present	Clay content (vol%)	Failure energy (J)	Strain at break (%)
none; PVC base	0.0	8.2	15.0
PMMA and unmodified clay	2.5	2.5	7.0
"	5.0	1.8	6.5
Solution polymerised hybrid	1.2	1.0	4.0
"	2.2	0.5	3.0
Solution polymerised hybrid; extracted clay	1.2	1.0	4.2
"	2.2	0.5	2.8

The enhanced dispersion of the clay particles in the hybrid containing formulations may have increased the quantity of the stress concentrations, thereby promoting fracture of the specimens. The unmodified clay particles were present in large agglomerates, and hence the number of aggregates to act as strain concentrators available was lower. Therefore, the formulations with unmodified clay failed at higher strains than the hybrids systems, but had lower moduli.

CONCLUSIONS

The use of the PMMA / clay hybrids in the PVC formulations resulted in the enhanced dimensional stability at elevated temperatures and to increased modulus at room temperature, in comparison with the formulations containing unmodified clay. The finer dispersion of clay conferred a hydrodynamic effect upon the viscosity of the system, but resulted in an increase in the number of stress concentration points. The latter led to reduced toughness of the materials.

Part IV

Stabilisation of the clay dispersion in the poly(methyl methacrylate) / clay hybrids through the use of functional co-monomers

Abstract

Polymer / clay hybrids were prepared through the copolymerisation of methyl methacrylate and glycidyl methacrylate (GMA). The latter was included as a functional monomer in an attempt to stabilise the clay dispersion during melt processing. It was found that the presence of GMA could limit the re-aggregation of the clay. The highly reactive oxirane groups of the GMA led to the formation of a gelled structure during polymerisation.

Introduction

Initially, poly(methyl methacrylate) / clay nano-composites were prepared through the solution polymerisation of methyl methacrylate in the presence of dodecylammonium ion exchanged clays. Figure 1 displays the XRD patterns of the original clay, organophylic clay, and the poly(methyl methacrylate) / clay hybrid reaction product. The trace of the hybrid showed only the halo effect of the amorphous polymer. From the disappearance of 001 reflection in the X-ray diffraction pattern, it was determined that the hybrids were exfoliated to a distance of more than 80 Å.

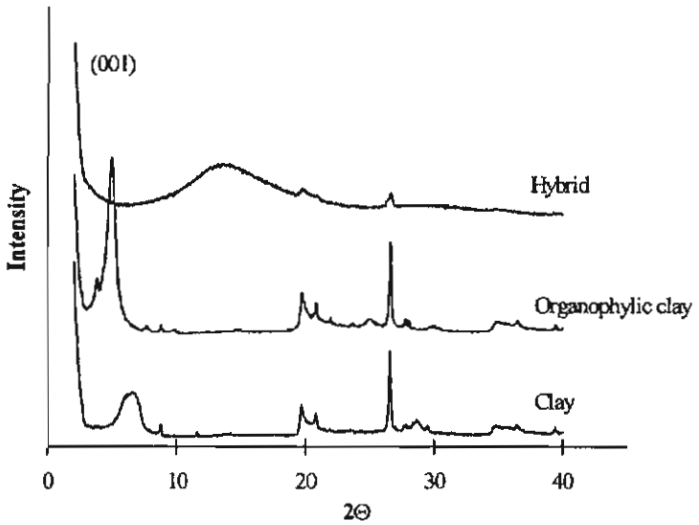

Figure 1. XRD patterns of the original clay, organophylic clay, and the reaction product of the PMMA / clay hybrid (50 phr clay).

After melt processing, the structure of the composite was changed from the exfoliated to intercalated structure. In an attempt to reduce the reordering of the clay during processing, glycidyl methacrylate (GMA) and maleic anhydride (MA) were copolymerised with the methyl methacrylate (MMA). It was anticipated that the GMA or MA functional monomers could strengthen the attraction between the modified clay and polymer, thereby reducing reordering of the nano composite during melt processing. The organophylic clay content of 50 phr was chosen in this phase of the work. GMA contents were in the range 0 to 10 wt% of the total monomers.

Results and discussion

The X-ray diffraction patterns of the reaction products of the hybrids prepared with GMA contents in the range 1 to 10 wt% are shown in figure 2. The X-ray diffraction patterns of the samples containing 0 and 1 wt% GMA show diffuse scattering in the range 1 to 4°2θ, due to the

irregular arrangements of the clay layers in these samples. No distinct peak of the (001) plane in the measurement range of 1-10°2θ is discernible. In the traces of hybrids with increasing GMA content in the range from 3 to 10 wt%, broad peaks due to the constructive scattering of the (001) plane are observed. The corresponding d-spacing is 35 Å.

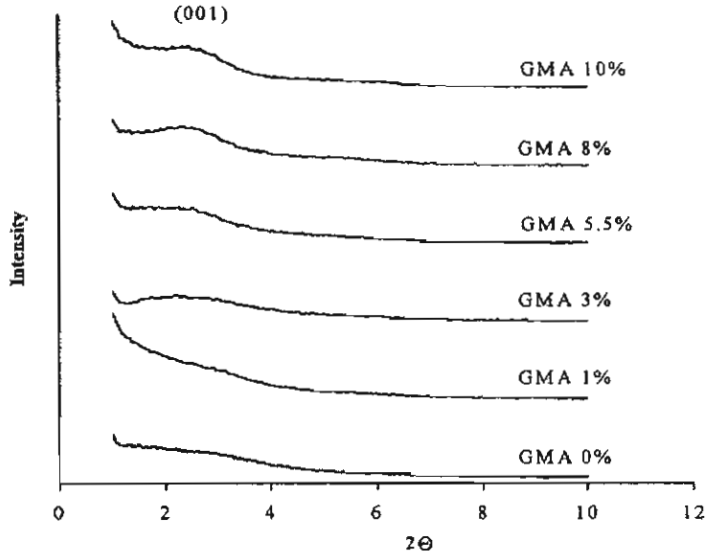

Figure 2. XRD patterns of the reaction products of the poly(methyl methacrylate-co-glycidyl methacrylate) / clay hybrids containing 50 phr of clay.

The XRD patterns of hybrids containing GMA, after melt shaping into plaques, are shown in figure 3. As reported in part I and II of this work, the sample containing MMA alone, labelled GMA 0% in figure 3, displayed a sharp diffraction peak of the (001) plane with a d-spacing of 27.6 Å.

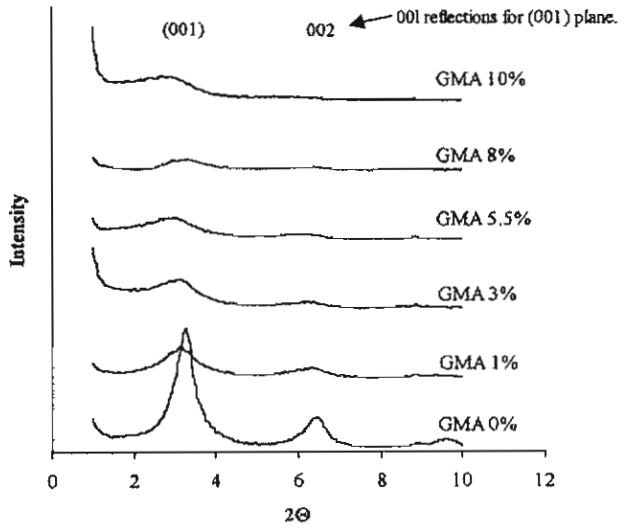

Figure 3. XRD patterns of the poly(methyl methacrylate-co-glycidyl methacrylate) / clay hybrids containing 50 phr of clay after compression moulding.

The appearance of this reflection was brought about by the reordering of the microstructure through narrowing of the clay galleries with the partial exclusion of the polymer. The compression moulded samples containing GMA had boarder, less intense reflections of the (001) plane in comparison with the plaques that did not contain GMA. The corresponding d-spacings were 27.6, 27.8, 28.3, 29.0, 27.6, and 30.2 Å for samples with 0, 1, 3, 5.5, 8, and 10 wt% GMA content, respectively. Moreover, the X-ray traces of the melt processed GMA containing samples were little different from those of

the corresponding reaction products before melt processing. Evidently, the presence of GMA in the polymer reduced the degree of reordering of the clay particles during melt processing.

The XRD patterns of the reaction products before melt processing and the same materials after compression moulding, for samples containing no GMA and 1 wt% GMA, are compared in figure 4. The intensity of the reflections is proportional to the mass fraction of clay resident in agglomerates of regularly spaced clay sheets.

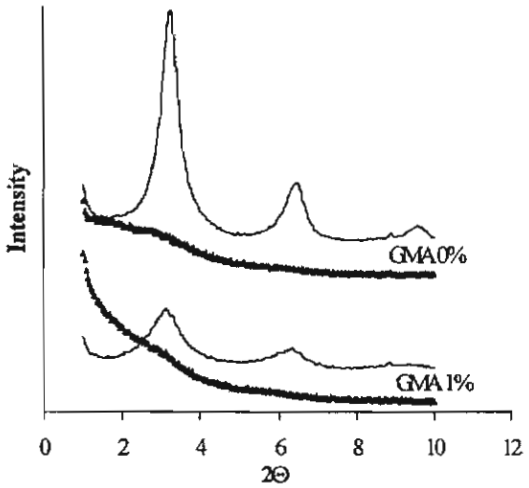

Figure 4. X-ray patterns of (Δ) the powdered reaction products and (-) the compression moulded plaques containing 50 phr of organophylic clay.

The lower peak intensities of the compression moulded sample containing GMA in comparison with the sample without GMA shows the reduced level of re-aggregation in the former sample. The GMA does not completely prevent the change, however. As detailed in part II of this work, the level of the clay dispersion may be characterised by the average aggregate thickness, L_c, and the average number layers in each aggregate, N_c.

Table 1. L_c and N_c values of the compression moulded plaques for hybrids with MMA only and the MMA / GMA sample containing 1 wt% GMA.

GMA content (wt%)	L_c (Å)	N_c
0	172	7
1	112	5

Table 1 shows that the clay aggregates in the hybrid containing 1 wt% GMA were smaller than those of hybrid containing PMMA homopolymer; i.e., the dispersion of the clay is superior in the hybrid containing GMA at the 1 wt% level.

The effects of clay content.

The poly(glycidyl methacrylate-co-methyl methacrylate) /clay hybrids were subsequently prepared with a range of organophylic clay contents; the GMA content was fixed at 1 or 10 wt% of the total monomer. The products were characterised through X-ray diffraction. The XRD traces of the reaction products and the melt processed plaques of samples containing 1 wt% GMA are shown in figure 5. The samples containing 1 wt% GMA appeared to contain delaminated clay both before melt processing for all clay contents. For organophylic clay contents of 20 and 50 phr, the reflection of the (001) plane, with d-spacings of 31.0, 27.8 Å, respectively, could be detected. Probably there is insufficient matrix polymer present to disperse the higher clay contents completely.

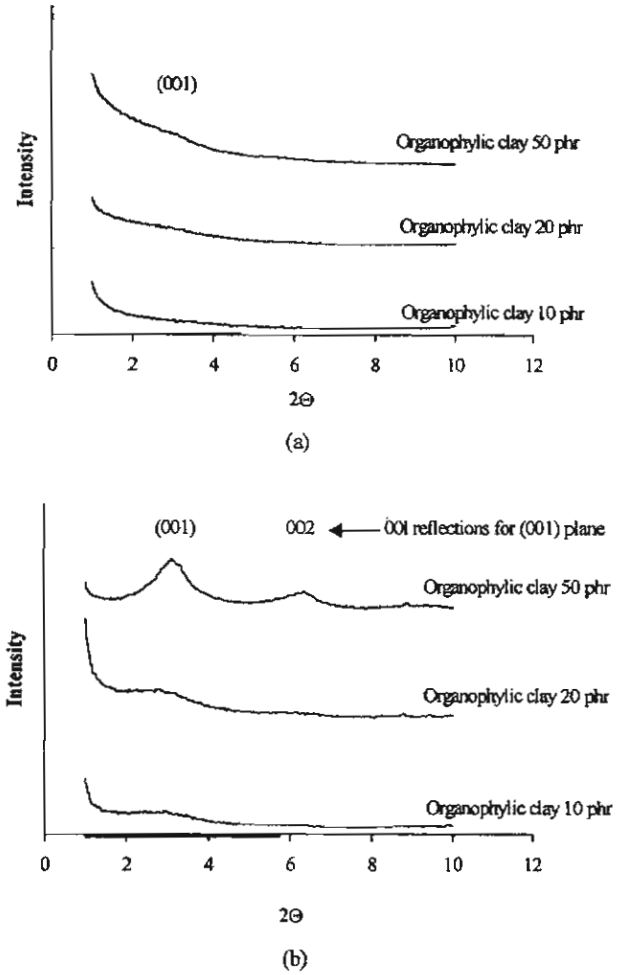

Figure 5. X-ray diffraction patterns of (a) the reaction products of the hybrids and (b) the compression moulded plaques containing 1 wt% GMA.

The L_c and N_c values for the compression moulded samples containing 1 wt% GMA are plotted as functions of clay content in figure 6. The mean clay aggregates size increases as the clay content increases. That is, the level of clay dispersion decreases for the higher clay contents. As stated previously, the quantity of polymer present at the higher filler loading is insufficient to efficiently disperse the clay.

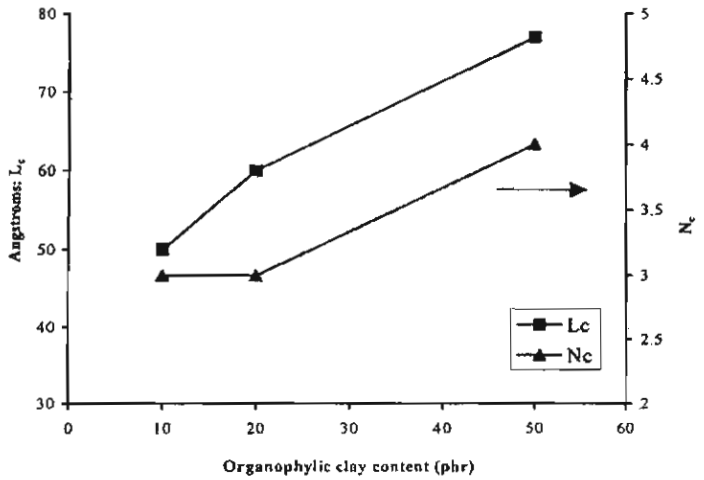

Figure 6. N_c of the compression moulded plaques containing 1 wt% GMA.

Samples containing 10 wt% GMA

The XRD traces of the hybrids and plaques containing 10 wt% GMA are shown in figure 7. Organophylic clay contents lower than 30 phr resulted in delaminated structures. Samples with clay contents of 40 and 50 phr exhibited low intensity 00l reflections for the (001) plane with corresponding d-spacings of 36.0 and 35.0 Å. After compression moulding, theses peaks became sharper.

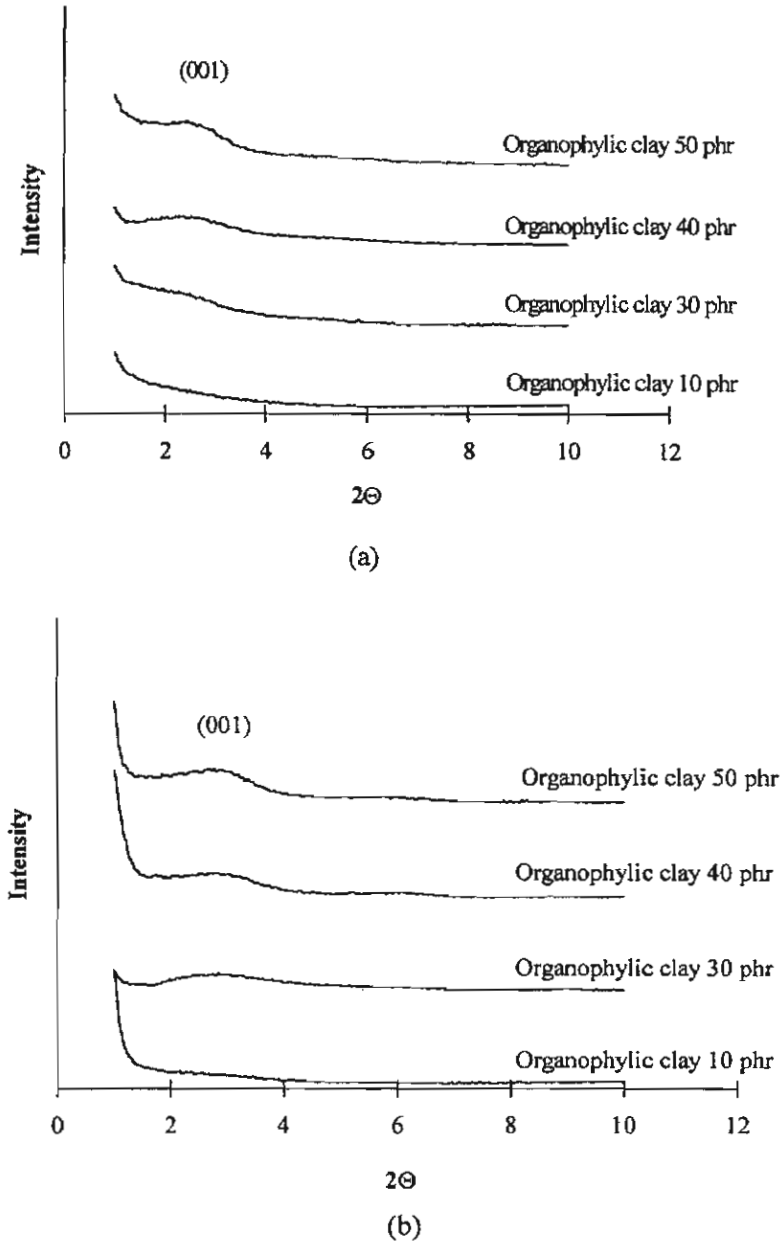

Figure 7. X-ray pattern of (a) the reaction products of the hybrids and (b) compression moulded plaques containing 10 wt% GMA.

CONCLUSIONS

The copolymerisation of MMA with GMA led to the partial stabilisation of the clay dispersion in the hybrids. However, due to the reactivity of the GMA a gelled product with an uncontrolled structure was obtained. In the subsequent work presented in part V, the GMA was replaced with maleic anhydride in attempt to maintain the thermoplasticity of matrix.

Part V

The use of maleic anhydride as a co-monomer to stabilise the clay dispersion

Abstract

Polymer / clay hybrids were prepared through the copolymerisation of methyl methacrylate and maleic anhydride. The latter was included as a functional monomer in an attempt to stabilise the clay dispersion during melt processing. It was found that maleic anhydride contents of 10 wt% in the copolymer could limit the re-aggregation of the clay. When prepared in the presence of clay, the relaxation characteristics of the copolymer were altered, probably due to the reaction of succinic anhydride groups with the amine that was bound to the organophylic clay. The product of this reaction was heterogeneous resulting in the formation of copolymer fractions with different glass-rubber transition temperatures.

Experimental

Sample preparation

Polymerisations were carried as before, except that MA was added to the reaction system. The solvent was changed from hexane to methanol due to the limited solubility of MA in hexane.

Results and discussion

Effect of MA content upon clay dispersion and stability

Samples were prepared with MA contents in the range from 1 wt% to 10 wt% of the total monomer at the constant organophylic clay content of 10 phr. The WAXD patterns of the hybrids are shown in figure 5.1. In each analysis, a small peak at from the (001) plane reflection was detected in the X-ray diffraction trace. The corresponding d-spacings of the (001) plane are 27.9, 27.9, 28.3, 28.7, and 29.4 Å, corresponding to the 0, 1, 2, 5, and 10 wt% MA content, respectively.

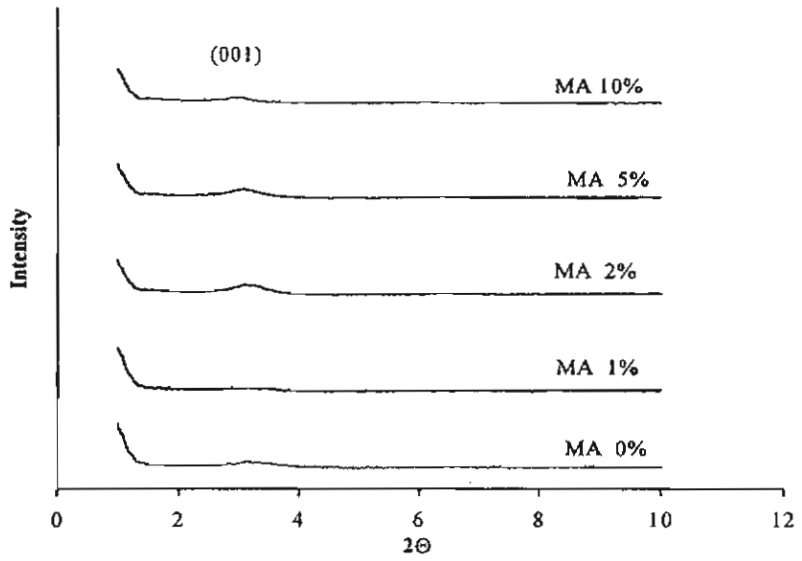

Figure 5.1 X-ray diffraction of traces of the reaction products of the poly(methyl methacrylate-co-maleic anhydride) / clay hybrids; clay content is 10 phr in each.

The clay was probably not completely delaminated in the reaction vessel since the a gel formed as the molecular weight of the polymer increased due to the limited solubility of the polymer in methanol. Figure 5.2 shows the XRD patterns of the reaction products after compression moulding. For 0, 1, 2, and 5 wt% MA contents, the XRD patterns displayed distinct reflections for the (001) plane; the

corresponding d_{001} values were 28.7, 27.6, 28.1, and 27.6 Å, respectively. The sample containing 10 wt% MA had a board 001 reflection with a d_{001} of 27.6 Å. The reordering of the hybrids decreased when the MA content increased.

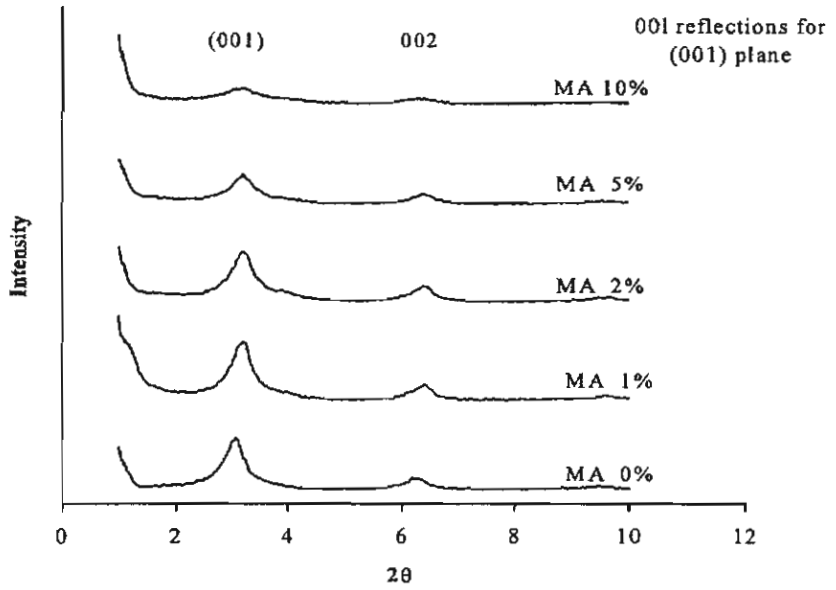

Figure 5.2 X-ray diffraction of traces of the compression moulded reaction products of the poly(methyl methacrylate-co-maleic anhydride) / clay hybrids; clay content is 10 phr in each.

The XRD patterns of the reaction products and the corresponding compression moulded plaques are compared in figure 5.3.

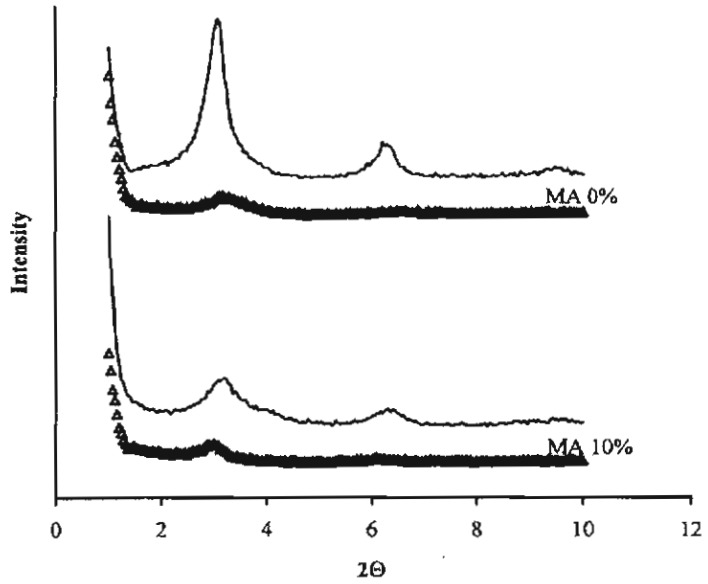

Figure 5.3 XRD traces of the poly(methyl methacrylate-co-maleic anhydride) / clay hybrids; clay content is 10 phr in each: (Δ) hybrid and (–) plaque.

Effect of clay content in the poly(maleic anhydride-co-methyl methacrylate)/clay hybrids

The copolymer containing 10 wt% was used to investigate the effect of clay content. Materials were synthesised containing organophylic clay contents in the range 10 to 50 phr. The XRD traces of the hybrids are shown in figure 5.4. The d_{001} values were 29.4, 30.7, 30.2, and 28.7 Å for 10, 20, 30, and 50 phr organophylic clay content, respectively. The 001 reflection intensity increased when the organophylic clay content increased.

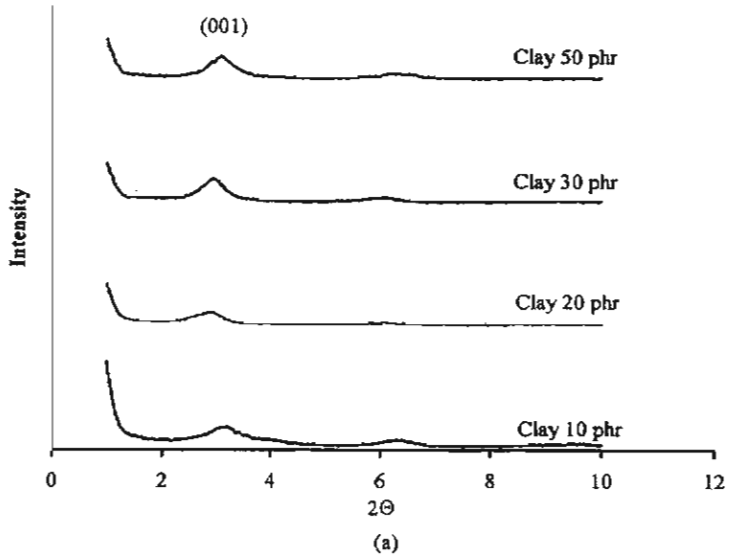

Figure 5.4 X-ray diffraction of traces of the reaction products of the poly(methyl methacrylate-co-maleic anhydride) / clay hybrids containing 10 wt% of MA.

The XRD traces of the corresponding plaques are displayed in figure 5.5. The d-spacing of the (001) plane in the plaques was 27.6, 27.9, 28.3, and 28.3 Å when the organophylic clay content was 10, 20, 30, and 50 phr, respectively. The intensity of the 001 reflection increased when the organophylic clay content increased.

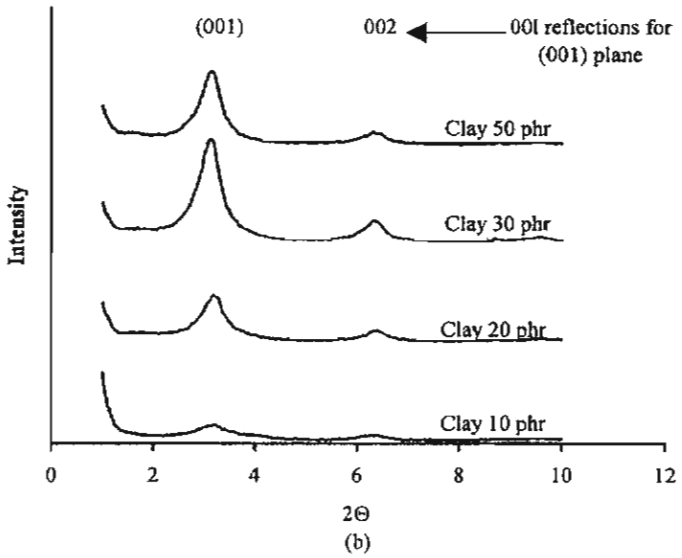

Figure 5.5 X-ray diffraction of traces of the compression moulded poly(methyl methacrylate-co-maleic anhydride) / clay hybrids containing 10 wt% of MA.

The Scherrer crystal thickness values, L_c, calculated from the 001 reflection of the moulded poly(methyl methacrylate-co-maleic anhydride) / clay hybrids plaques are shown in table 5.1; these data are plotted in figure 5.6. The FWHM decreased when the organophylic clay content increased and therefore L_c increased.

Table 5.1 L_c values associated with the (001) plane for the plaques containing 10 wt% MA.

The organophylic clay content (phr)	FWHM (°2θ)	L_c (Å)
10	0.639	138
20	0.501	177
30	0.485	182
50	0.461	192

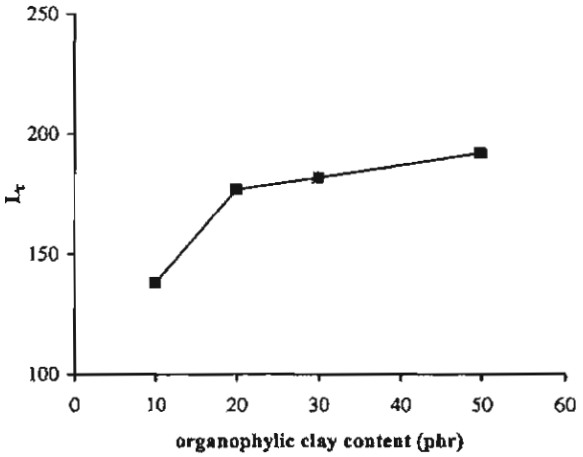

Figure 5.6 Scherrer crystal thickness, L_c, from peak width of 001 reflection of the moulded poly(methyl methacrylate-co-maleic anhydride) / clay hybrids containing 10 wt% MA.

Relaxation characteristics

The relaxation characteristics of the compression moulded poly(methyl methacrylate-co-maleic anhydride) containing 10 wt% of MA were determined through DMA; the data are plotted in 5.7.

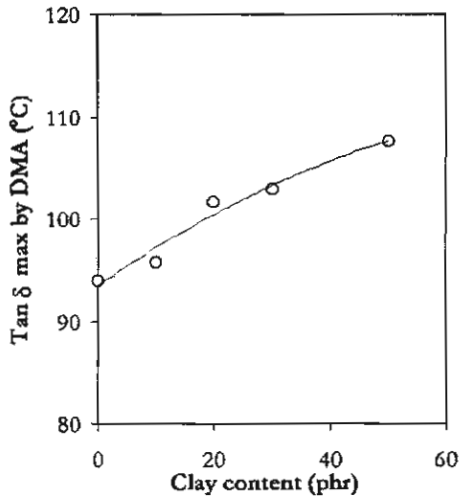

Figure 5.7 Relaxation temperatures, by DMA, of the compression poly(methyl methacrylate-co-maleic anhydride) containing 10 wt% MA.

Apparently, the temperature of the main relaxation event is a function of the clay content. To investigate this further, the poly(methyl methacrylate-co-maleic anhydride) copolymers containing 10 wt% of MA were extracted from the reaction products and the compression moulded hybrids; the extracts were characterised through DSC. The thermograms had two relaxation events, indicating a heterogeneous structure of the copolymer. The temperatures of these relaxations are plotted as functions of clay content in figure 5.8.

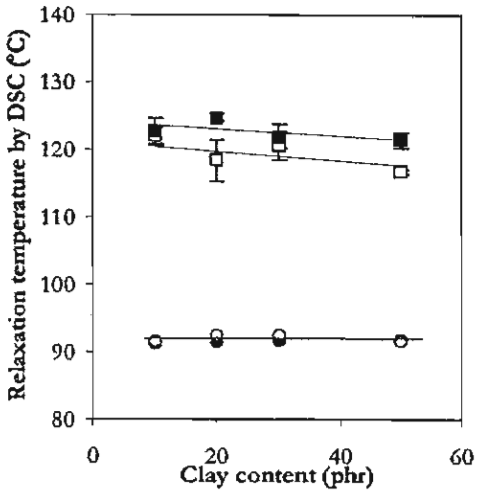

Figure 5.8 Relaxation temperatures, by DSC, of the poly(methyl methacrylate-co-maleic anhydride) containing 10 wt% MA: extracted from mouldings (1st transition ●, 2nd transition ■) and (1st transition ○, 2nd transition □) of the reaction products.

The differences in relaxation characteristics must be related to changes in polymer microstructure. ^{1}H-NMR analysis revealed that the copolymer extracted from the composites containing higher clay contents had an additional resonance at 6.7 ppm that was not detected in the copolymer prepared in the absence of clay. This resonance may be due to the presence of amide resulting from the reaction of MA with the amine that was used to modify the clay. It is possible that the structure produced as a consequence of this reaction has a higher Tg than the poly(methyl methacrylate-co-maleic anhydride). The two relaxation events seen in the DSC analysis suggest that the solvent extraction process resulted in the fractionation of the polymer due to solubility differences of components. It is speculated that the copolymer in close proximity to the clay reacts to a greater extent with the amine than copolymer in the bulk, the former creating a higher Tg fraction and the latter a lower Tg fraction. The dependence of Tg by DMA upon clay content implies that the copolymer fractions were at least partially mixed in the melt-pressed plaques. The relaxation events observed around 120° C, by DSC, of the copolymer extracted from the reaction products were approximately 5°C lower than the corresponding events in the copolymers that were extracted from the compression mouldings. This may be the result of the further reaction of the MA in the copolymer upon pressing to form the plaques. Further characterisation tests are needed to clarify these details.

Conclusions

The presence of MA in the copolymer led to enhanced stability of the clay dispersion of the moulded samples. The reactivity of the anhydride groups caused microstructure changes in the polymer that resulted in changes in the relaxation characteristics of the polymers. The details of the process must be clarified, and quantified, through further analysis of the characterisation data.

Out put from the PROJECT
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1. Tabtiang, A., Lumlong, S., and Venables, R. A., *'The influence of preparation method upon the thermomechanical characteristics of poly(methyl methacrylate) / clay composites'*, ***Eur. Polym. J.***, **36**(12), pp. 2559-2568 (2000)
2. Tabtiang, A., Lumlong, S., and Venables, R. A., *'The effects of shear and thermal history upon the microstructure of solution polymerised poly(methyl methacrylate) / clay composites'*, ***Polym.-Plast. Technol. Eng.***, **39**(2), pp. 293-303 (2000)
3. Tabtiang, A. and Venables, R. A., *'The stabilisation of the clay dispersion in poly(methyl methacrylate) / clay hybrids through the use of functional co-monomers'*, in preparation.

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EFFECTS OF SHEAR AND THERMAL HISTORY ON THE MICROSTRUCTURE OF SOLUTION POLYMERIZED POLY(METHYL METHACRYLATE)–CLAY COMPOSITES

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Abstract

Poly(methyl methacrylate)–clay composites were synthesized through free-radical solution polymerization of methyl methacrylate in the presence of clay that was preintercalated with dodecylammonium or hexadecyltrimethylammonium ions. Neither the diffraction peak from the (001) plane nor the 00*l* reflections for the (001) plane were observed during x-ray characterization, showing that the clay particles were greatly expanded (i.e., exfoliated) in the reaction products, due to the presence of large quantities of polymer between the clay layers. Syntheses carried out with high clay loadings resulted in reductions in the weight and number-average molecular weights and increases in the polydispersities of the polymers, caused by chain transfer to active sites on the surface of the clay. It was found that heat and shear, during subsequent processing of the reaction products, resulted in reordering of the microstructure through narrowing of the clay galleries with the partial exclusion of the polymer. The final interlayer spacings were determined by the orienta-

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tion and lengths of the preintercalated alkylammonium ions. It was concluded that the exfoliated structure created during polymerization was unstable under the processing conditions and, consequently, reordered into a more stable form.

Key Words: Poly(methyl methacrylate); Clay; Composite; Hybrid.

INTRODUCTION

Polymer–clay composites with fine dispersions of reinforcing particles may be prepared by using the swelling properties of smectite clays (1), whereby a polar molecule intercalates the clay layers and, consequently, increases the interlayer spacing. This process may be carried out in several steps, the essential features of which are the following: (1) exchange of the clay's sodium ions with alkylammonium ions to partially expand the clay galleries and to reduce the hydrophilicity of the clay's surface, yielding a modified clay; (2) swelling of the modified clay with monomer; and (3) polymerization of the monomer. An example of this type of system is the polyimide–clay hybrid described by Yano et al. (2), where a film containing montmorillonite clay was synthesized from a dimethylacetamide solution of poly(amic acid) and a dimethylacetamide dispersion of montmorillonite, intercalated with an ammonium salt of dodecylamine. The final product showed improved barrier properties to the permeation of vapors, in comparison with the unmodified polyimide. Other systems have shown improved mechanical properties at elevated temperatures (3).

Although poly(vinyl chloride) (PVC) is a low-cost material with versatile properties, its performance is limited in some applications where elevated temperatures are experienced, due to its low softening temperature. Properties may be improved, however, by blending the PVC with engineering resins that possess high glass transition temperatures (T_g). These resins have been referred to as HT additives (4). Examples include those based on poly(methyl methacrylate) (PMMA), styrene–maleic anhydride copolymer, and brominated polycarbonate. The HT additive should be miscible or partially miscible with the PVC to maintain optical clarity. Because of the outstanding heat distortion temperature properties of polymer–clay hybrids (3), a hybrid may perform suitably as a HT additive for PVC. Thus, in this work, an additive of this type was prepared through solution polymerization of methyl methacrylate in the presence of modified clays, for use in rigid PVC formulations. PMMA was chosen because of its known compatibility with PVC (5) and inherently high T_g. The PMMA is intended to act as a carrier polymer to bring the dispersed clay layers into the PVC matrix. The objectives of the work described herein were to establish the initial structure of the additive and, because it will experience heat and hydrodynamic stresses during processing, to determine the processing effects on the final structure.

EXPERIMENT

Materials

The inhibitor was extracted from methyl methacrylate (MMA) (Fluka) with $NaOH_{(aq)}$, then washed with distilled water, and subsequently dried over anhydrous Na_2SO_4. Bentonite clay, containing a minimum of 90% montmorillonite, was from Colloid Environmental Technologies Co., Ltd. Dodecylamine was from Fluka, hexadecyltrimethylammonium chloride from Merck, and 2,2′-azo-bis(isobutyric-nitrile) (AIBN) initiator was supplied by TPI Co., Ltd., Thailand.

Synthesis of Modified Clay

Clay (20 g) was dispersed in distilled water (600 mL) at 80°C. To this was added a solution of dodecylamine or hexadecyltrimethylammonium chloride (0.05 mol) and concentrated hydrochloric acid (4.8 mL) in distilled water (100 mL). Heating and stirring was continued for 1 h while maintaining the temperature at 80°C. The suspension was then filtered and the solid residue washed with hot distilled water until no chloride was left, as determined by using the silver nitrate test. The product was dried at 60°C for several days in a fan oven, then milled in a ball mill, and subsequently dried at 60°C under vacuum for 24 h, yielding the dodecylammonium–clay (DDA–clay) and hexadecyltrimethylammonium–clay (HDA–clay).

Composite Preparation

2,2′-Azo-bis(isobutyric-nitrile) (0.1 g) was dissolved in the extracted MMA (10 g), followed by the addition of the modified clay (1, 2, 5, or 10 g) and distilled hexane (40 mL). For the highest clay contents, 100 mL of hexane was needed to disperse the clay. The reaction flask was suspended in a thermostated water bath at 68°C for 5 h, with a condenser fitted. The powdered product was recovered from the reaction mixture by evaporation of the solvent, followed by drying under vacuum at 60°C. Portions of the products were either melt fluxed in a Haake Rheocord 90 at 180°C for 5 min, with a rotor speed of 50 rpm, to give the samples a melt processing history, or statically annealed in a fan oven for 30 min at 175°C. All melt-fluxed samples were compression molded at 180°C to form plaques for characterization.

Characterization

Wide-angle x-ray diffraction (WAXD) measurements were carried out using a JEOL JDX-3530. The Cu K_α radiation source was operated at 30 kV and 30 mA. The scanning speed, step angle, and count time were 1.2°2θ/min,

0.04°2θ, and 2 s, respectively. For the scan range 1–10°2θ, the divergence slit, receiving slit, and scattering slit were 0.5°, 0.1 mm, and 0.5°, respectively, whereas for the range 3–40°2θ, these values were 1°, 0.2 mm, and 1°, respectively. Infrared data were collected using a Perkin Elmer FT2000 and diffuse reflectance (DRIFT) accessory. Gel permeation chromatography (GPC) was carried out on the polymer extracted from the composites with tetrahydrofuran at room temperature, using a Waters 150-CV Plus. Thermogravimetric analyses (TGA) were carried out using a Perkin Elmer TGA7.

RESULTS AND DISCUSSION

Characterization of Modified Clay

Figure 1 shows DRIFT spectra of the unmodified clay and DDA–clay. The presence of protonated dodecylamine in the clay galleries is shown by the

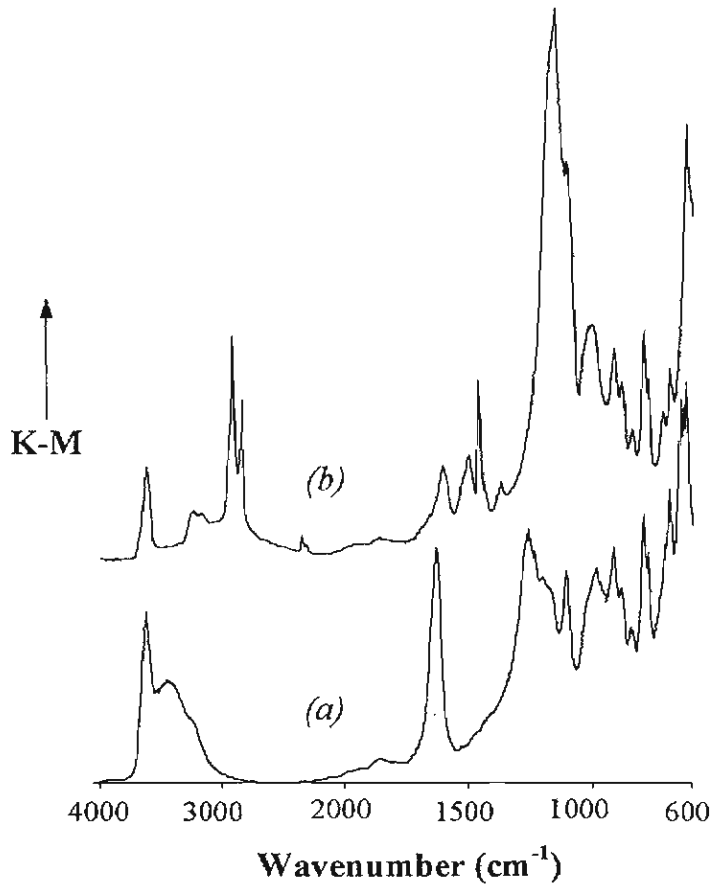

FIG. 1. DRIFT spectra of (a) unmodified clay and (b) DDA–clay.

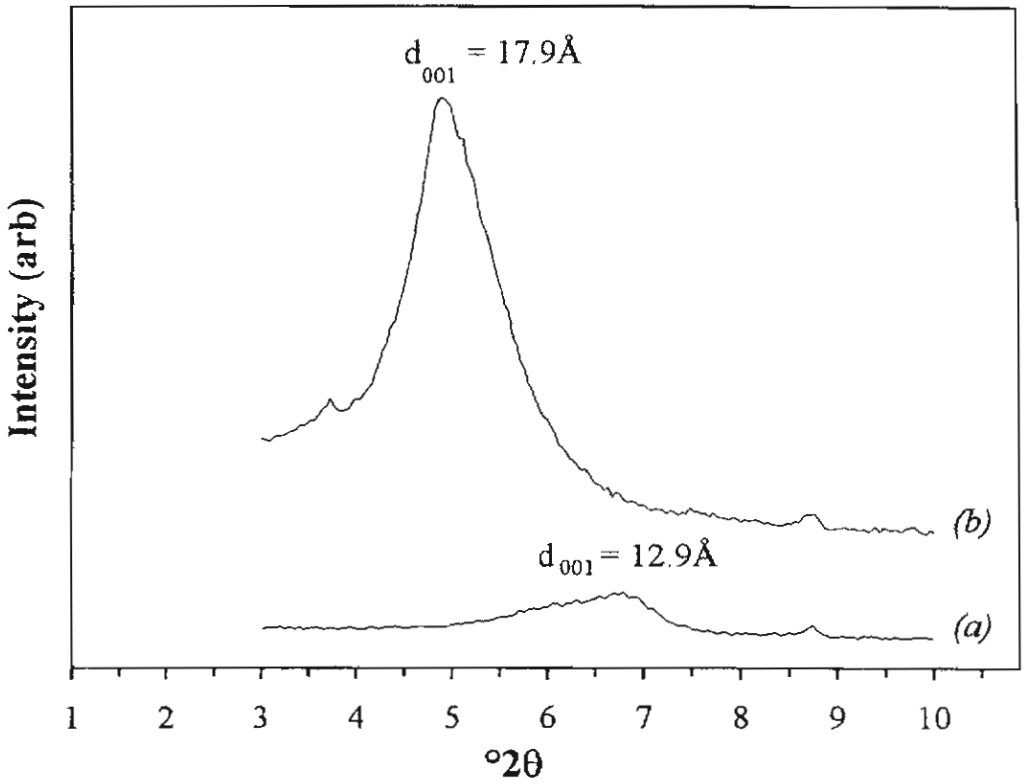

FIG. 2. X-ray diffraction traces of (a) unmodified clay and (b) DDA–clay.

N—H stretching of the NH_3^+ group in the region 3260–3181 cm^{-1} and the CH stretching peaks in the range 2925–2852 cm^{-1}. The O—H stretching bands at 3400–3200 cm^{-1} and the HOH bending peak at 1641 cm^{-1} of adsorbed interlayer water (6) found in the original clay were absent in the modified sample, because of the reduced hydrophilicity of the internal surfaces of the clay. The average quantity of intercalated dodecylammonium ions, from four replicated TGA analyses of the modified clay, was 17.7 wt%. The x-ray diffraction patterns of the unmodified and modified clays are displayed in Fig. 2. The *d*-spacing of the (001) plane, d_{001}, in the original clay was 12.9 Å, whereas that of the DDA–clay was 17.9 Å. The gallery spacing (i.e., the distance between the internal surfaces of neighboring clay layers) is calculated from the difference between d_{001} and the van der Waal's thickness of the clay layer. This thickness is estimated at 9.6 Å (7). For the DDA–clay, the gallery spacing was 17.9 − 9.6 = 8.3 Å. This gallery spacing is too small to accommodate the dodecylammonium ions standing perpendicular to the surface of the clay, as the total length of the extended ion is around 20 Å (7). The more probable orientation is that one molecule lies parallel to each of the internal surfaces of the clay, in a bilayer orientation (8). Similar results were obtained for HDA–clay.

Characterization of Polymerization Products

In the x-ray traces of the reaction products from solution polymerization containing DDA–clay, neither peaks from the montmorillonite's (001) plane nor the 00*l* reflections for the (001) plane were seen in the range 1–10°2θ. The absence of the (001) diffraction peak shows that during polymerization, d_{001} increased to a distance greater than that measurable with the minimum scan angle of the powder diffractometer (i.e., greater than around 88 Å). This may be considered an exfoliated arrangement of the clay layers (9). In the x-ray trace for the PMMA without clay, an increase in intensity at low angles was observed that was caused by the primary beam contribution to the signal. For the clay-containing samples, the onset of a very broad scattering signal, from the (001) plane, associated with the clay sheets at distant irregular spacings was superimposed on the primary beam signal. The original structure of the modified clay is largely destroyed, however.

The dispersion force, dipole–dipole interaction, and hydrogen-bonding contributions to the solubility parameter (10) of MMA are around 15.7, 8.2, and 6.7 $(MPa)^{1/2}$, respectively, compared to the corresponding values of 16.7, 0.0, and 0.0 $(MPa)^{1/2}$, respectively, for hexane, and hence the MMA monomer will tend to displace the hexane from the clay galleries, due to its more favorable specific interactions with the surface of the clay, causing the clay to swell. The gain in freedom of the dodecylammonium ions and hexane molecules as the interlayer spaces enlarge counterbalances the loss in entropy of the monomer. As the polymer precipitates from the solution, it is trapped in the interlayer, thereby fixing the distant separation of the clay sheets. The quantity of clay present during polymerization did not affect the extent of clay delamination.

Gel permeation chromatography data showed that DDA–clay contents up to 7 vol% did not significantly affect the molecular weight or the polydispersity. Clay contents of 15 vol% or more caused reductions in molecular weight and increased polydispersity. When the ratio of clay to monomer is high, chain transfer to the clay due to interactions with Brönsted sites on the clay's surface may become significant, with consequent alterations to the molecular-weight parameters. This may be related to the larger quantities of solvent that were required during synthesis in the presence of high clay contents, resulting in more dilute reaction conditions. Chain transfer to the solvent itself may not be the predominant mechanism, however, because *n*-hexane cannot form sufficiently stable radical intermediates (11).

Effects of Shear and Thermal History

X-ray traces of the melt-processed polymerization products containing DDA–clay are shown in Fig. 3. It is apparent that the (001) diffraction, fol-

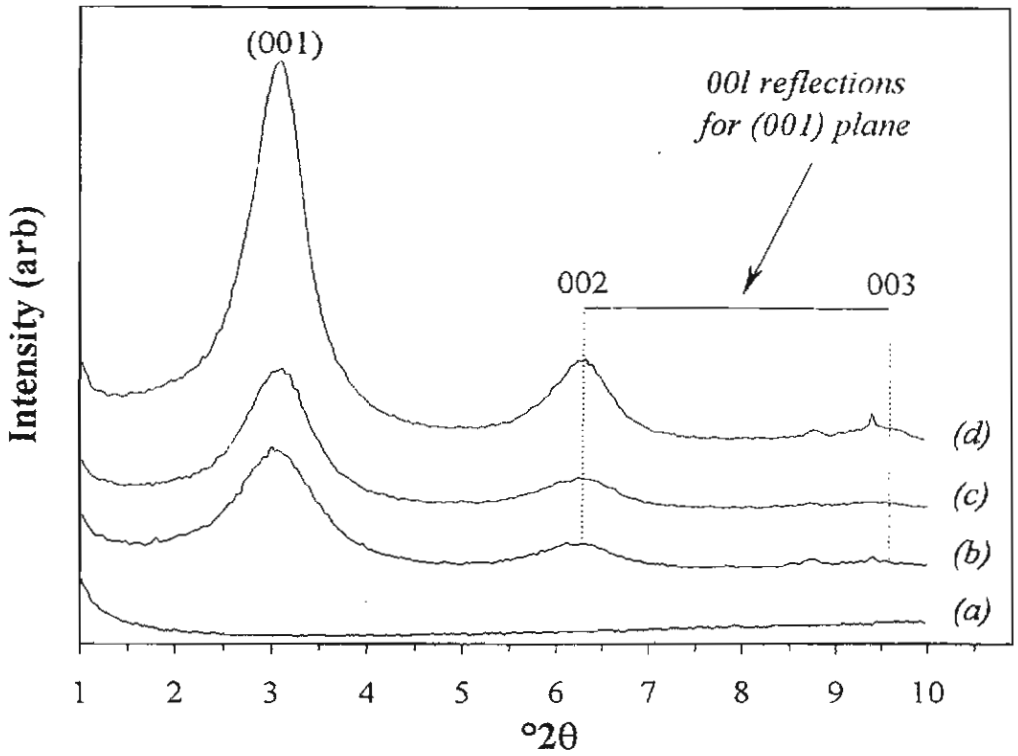

FIG. 3. X-ray diffraction traces of (a) PMMA without clay and the melt-processed DDA–clay composites containing (b) 10, (c) 20, and (d) 50 phr of clay.

lowed by two less intense signals with regular displacement along the °2θ axis, is present. The less intense signals are the 00*l* reflections for the (001) plane; the corresponding *d*-spacing is around 29 Å. Thus, at least some of the clay layers change from the expanded arrangement that is created during solution polymerization to a closer-packed configuration after melt processing. Moreover, the resultant d_{001} changes little with increasing clay content.

To assess the effect of heat alone without the concurrent application of pressure and stress, the powdered reaction products were statically annealed. The presence of the 00*l* reflections for the (001) plane implied that some thermally induced reordering of the clay layers occurs upon static annealing. The peaks were less intense than in the melt-fluxed samples, showing that the extent of reordering was lower. This difference may simply be kinetic in origin, whereby the mechanical work during mixing greatly accelerates the system toward the thermodynamic equilibrium position. The structural changes may also be influenced by the melt-elasticity contribution to the free energy of the system, however. This is analogous to the situation in partially miscible blends where the temperatures of phase dissolution or separation are altered under shear; both enhanced and reduced miscibility has been ob-

served (12). The absence of the (100) peak, at $^{\circ}2\theta = 19.5$, in the melt-processed sample shows that during compression molding, the silicate sheets move under pressure to lie parallel to the mold surface. In the powdered reaction products, the clay is randomly oriented; hence, the (100) plane is detected.

At the processing temperature, the specific interactions between the PMMA and the clay surface become weakened by the increased thermal motion of the molecules. The clay particles rearrange to a more thermodynamically stable state. This occurs through the expulsion of some of the PMMA chains from between the silicate sheets, allowing the layers to approach one another more closely. The driving force may be the gain in entropy of the polymer chains as they are freed from their confinement. The d_{001} values in the melt-processed DDA–clay composites were typically around 29 Å, giving an interlayer spacing of 19.4 Å. The length of the extended dodecylammonium ion is estimated to be 20.2 Å (7); that is, its length is approximately the same as the gallery spacing. This suggests that the gallery ions adopt a near-perpendicular orientation to the clay sheets in the presence of the PMMA melt and span the gallery from one clay layer to the next, thereby partially controlling the interlayer distance. This phenomenon was investigated further by using HDA–clay, containing the longer alkylammonium ion, to prepare the composites. The x-ray data for these materials show that the polymerization products (Fig. 4a) similarly contained greatly expanded clay, inferred from the absence of the (001) peak and the 00*l* reflections from the (001) plane. The statically annealed and melt-processed HDA–clay composites (Figs. 4b and 4c, respectively) both show series of 00*l* reflections, which correspond to a d_{001} of 38.8 Å and gallery spacing of 29.2 Å. The extended chain length of the hexadecyltrimethylammonium ion is around 29 Å; hence, it is reasonable to infer that the aliphatic chains of the ion are oriented perpendicular to the surface of the clay and, therefore, control the gallery spacing. This indicates that the same reordering of the dispersed clay layers occurs for both of the modified clays.

The d_{001} in the melt-processed composites can be explained qualitatively through consideration of the thermodynamic forces that drive the system (13,14). The gallery spacing is restricted through the loss in entropy due to the confinement of the polymer and by any unfavorable pairways interactions among the clay surface, polymer, and alkylammonium ions. It is driven to expand through the gain in entropy of the alkylammonium chains and the exothermic interactions between the clay and PMMA. Upon melt fluxing, the distance between the clay layers reduces, as the PMMA chains move out from between the clay layers to gain entropy, until the distance that is equal to the length of the extended alkylammonium ions is reached. At this point, the con-

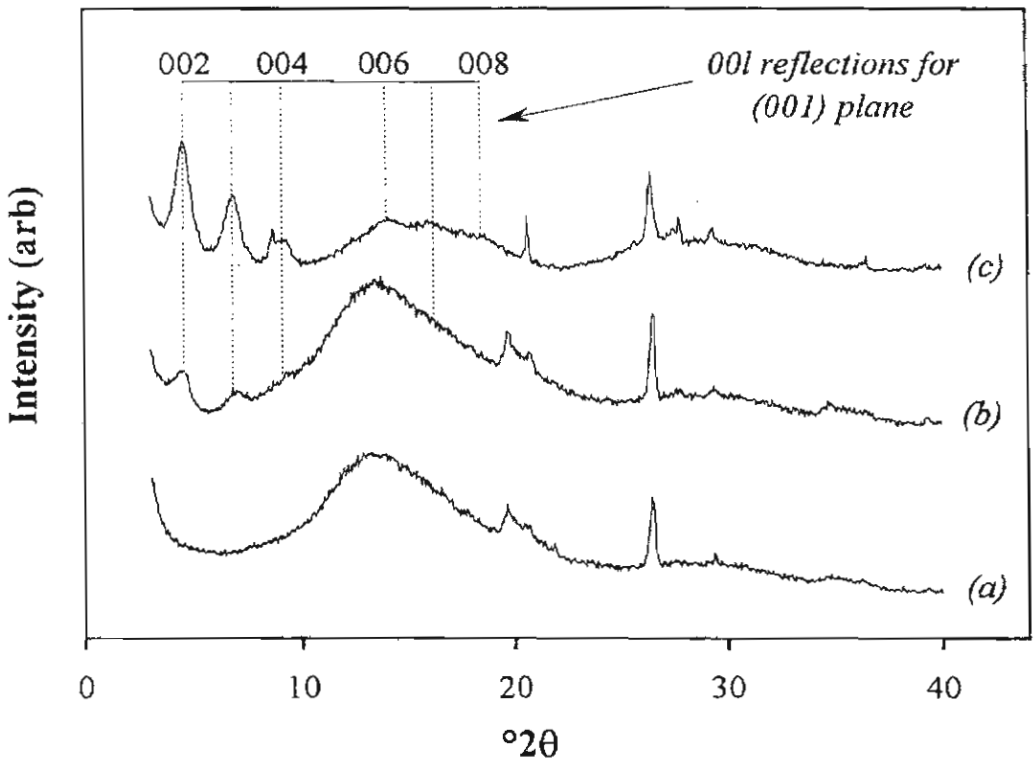

FIG. 4. X-ray diffraction traces of HDA–clay composites: (a) powder reaction product; (b) reaction product after static annealing; (c) the reaction product after melt processing.

traction is arrested, because further narrowing of the galleries would result in the unfavorable loss in entropy of the alkylammonium ions. The final gallery spacing is therefore approximately the same as the length of the alkylammonium ions. The heat of polymer–clay interaction under these conditions is sufficient to overcome the loss in entropy of the remaining confined polymer. Hence, some of the PMMA remains in the galleries, causing the alkylammonium ions to maintain their perpendicular orientation.

In the transmission electron micrograph of a melt-processed DDA–clay composite, shown in Fig. 5, it can be seen that the silicate sheets are present in aggregates of three to five primary layers; the distances between these aggregates are around 85 Å. Moreover, in the top region of the image, an isolated sheet can be seen. The x-ray analysis described earlier responds to the structure within the aggregates, showing that the interlayer distance within the aggregates is small and is typically 19.4 Å. These observations show that the clay layers are still partially delaminated after melt processing.

FIG. 5. Transmission electron micrograph of DDA–clay aggregates in a melt-processed sample.

CONCLUSIONS

1. Solution polymerization of MMA in hexane, in the presence of DDA–clay and HDA–clay, produces PMMA–clay composites containing silicate sheets that are exfoliated to a separation beyond the detection limit of the x-ray analysis.
2. Free-radical polymerizations in the presence of high clay loadings result in reductions in the weight and number-average molecular weights and increases in the polydispersity of PMMA.
3. The exfoliated structure is unstable under processing conditions and, consequently, reordering of the clay particles, through narrowing of the clay galleries with the exclusion of some of the polymer, takes place. The final clay structure is partially delaminated and comprises small aggregates of sheets, separated by distances of around 85 Å. The interlayer spacing within the aggregates is considerably smaller and is controlled by the orientation and length of the extended preintercalated alkylammonium ions.

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The influence of preparation method upon the structure and relaxation characteristics of poly(methyl methacrylate)/clay composites

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Abstract

Poly(methyl methacrylate) (PMMA)/clay composites were prepared using two methods: through solution polymerisation of methyl methacrylate in the presence of alkylammonium-modified clay and through the direct melt intercalation of PMMA. Both composites were fluxed in an internal mixer to give comparable melt processing histories. In the reaction product of the polymerisation method, the clay layers were separated to a distance greater than 80 Å; after melt processing, the layers were partially re-aggregated. The length and orientation of the alkylammonium ions principally controlled the interlayer spacings within these aggregates. A finer degree of dispersive mixing of the clay in the polymerisation system was observed. The presence of modified clay in the polymerisation system led to branching, reduction of average molecular weight, increase in polydispersity, and to a bimodal molecular weight distribution of the PMMA. The glass–rubber transitions were observed around 120°C in the polymerisation system in comparison with 105°C for the melt intercalation materials and the PMMA resin. Moreover, PMMA extracted from the polymerisation composites had similarly elevated glass transition temperatures. The chain branching in the polymerisation system was the principal reason for the differences in the thermomechanical behaviour of the two composites.

Keywords: Clay; Composite; Relaxation; Poly(methyl methacrylate)

1. Introduction

Polymer/clay composites have been prepared through in-situ polymerisation of monomers within the galleries of modified clays [1] and through intercalation from solution [2]. It has been reported that several of these composites exhibited improved mechanical [3] and barrier properties [4], in comparison with the matrix polymer. Vaia et al. [5] presented a method for the melt intercalation of polymer chains. The process involves mixing a modified layered silicate with the polymer and heating to above the glass transition temperature and melting point, where appropriate, of the polymer. The materials that have been prepared through melt intercalation include polystyrene [6] and polypropylene [7] composites.

In a previous report by the authors [8], the preparation of poly(methyl methacrylate) (PMMA)/clay composites, through solution polymerisation of methyl methacrylate (MMA) in the presence of dodecylammonium and hexadecyltrimethylammonium-modified montmorillonite clay, was described. X-ray diffraction showed that the clay layers were separated by a distance greater than 80 Å in the powdered reaction products, as there were no reflections from the (001) plane of montmorillonite in the range 1–10° 2θ. This resulted from the large expansion of the clay aggregates during

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polymerisation. However, re-aggregation of the clay particles during subsequent melt processing was observed. After melt processing, the interlayer spacings in the clay aggregates were approximately the same as the lengths of the extended pre-intercalated alkylammonium ions, i.e. around 20 Å for dodecylammonium clay and 29 Å for the hexadecyltrimethylammonium clay. From this observation, it was suggested that the alkylammonium ions were fully extended and stood perpendicular to the internal clay surfaces, thereby controlling the interlayer spacings, with the PMMA chains occupying the remaining interlayer volume. Thus, the clay layers changed from the expanded arrangement created during solution polymerisation to a closer packed configuration during the melt processing.

In the work described herein, the PMMA/clay composites were prepared through direct melt intercalation during melt mixing. The microstructures and relaxation characteristics of these samples were compared with those in the solution-polymerised composites. Of particular interest were the thermomechanical properties and how they were affected by the composite preparation methods, the objective being to find the most suitable method of preparing PMMA/composites that gives an enhanced modulus at elevated temperatures.

2. Experimental

2.1. Materials

The hydroquinone inhibitor was extracted from the MMA monomer, from Fluka, with aqueous sodium hydroxide, then washed with distilled water, and dried over anhydrous sodium sulphate. Bentonite clay, containing a minimum of 90% montmorillonite, was from Colloid Environmental Technologies Co., Ltd. Dodecylamine was from Fluka and 2,2′-azo-bis(isobutyric-nitrile) (AIBN) initiator was supplied by TPI Co., Ltd., Thailand.

2.2. Modification of clay

The clay (20 g), possessing a *d*-spacing of the (0 0 1) plane, d_{001}, of 12.9 Å, was dispersed in distilled water (600 ml) at 80°C. A solution of dodecylamine or hexadecyltrimethylammonium chloride (0.05 mol) and concentrated hydrochloric acid (4.8 ml) in distilled water (100 ml) was added; heating and stirring was continued for 1 h. The suspension was filtered, and the solid residue washed with hot distilled water until no chloride was left, as determined by using the silver nitrate test. The product was dried at 60°C for several days in a fan oven, then milled in a ball mill and subsequently dried at 60°C under vacuum for 24 h, yielding the dodecylammonium-modified clay or hexadecyltrimethylammonium clay; d_{001} of these clays were 17.9 and 19.7 Å, respectively.

2.3. Solution polymerisation

AIBN (0.1 g) was dissolved in the extracted MMA (10 g), followed by the addition of the modified clay (1, 2, 5, or 10 g) and distilled hexane (40 ml). For the highest clay contents, 100 ml of hexane was needed to disperse the clay. The reaction flask was suspended in a thermostated water bath at 68°C for 5 h, with a condenser fitted. The solid, powdered product was recovered from the reaction mixture by evaporation of the solvent, followed by drying under vacuum at 60°C.

2.4. Melt processing

Melt-intercalated composites were prepared by melt mixing the PMMA resin with the modified clay (10, 20, and 50 phr) in a Haake Rheocord 90 at 180°C for 10 min, with a rotor speed of 50 rpm. This procedure was repeated with the unmodified clay, for comparison. The products from the solution polymerisations were also melt fluxed to provide a processing history. All samples were compression moulded at 180°C to form plaques for characterisation.

2.5. Characterisation

The X-ray diffraction (WAXD) was carried out using a wide angle a JEOL JDX-3530 diffractometer. The radiation source was operated at 30 kV and 30 mA; all but the CuK_α X-ray photons were filtered out of the beam. The scanning speed, step angle, and count time were 1.2° 2θ/min, 0.04° 2θ, and 2 s, respectively. For the scan range 1–10° 2θ, the divergence slit, receiving slit, and scattering slit were 0.5°, 0.1 mm, and 0.5°, respectively, whilst for the range 3–40° 2θ these values were 1°, 0.2 mm, and 1°, respectively. The precision of the *d*-spacings calculated from the X-ray data was assessed by measuring the *d*-spacing associated with a diffraction due to a biotite impurity in the clay at 10.2° 2θ as an internal standard. The mean *d*-spacing was 8.5 Å, standard deviation 0.08, and coefficient of variation 1%, based upon nine measurements. Transmission electron microscope (TEM) observations of sections were carried out with a JEOL JEM-100CX instrument. To assess the degree of dispersion of the clay particles in the TEM images, a line intersection method was employed. The frequency of the clay aggregate intersections with a line drawn along the micrograph, corresponding with the direction normal to the surfaces of the compression moulded plaque, was determined for each formulation. The results are given in the form of frequencies, expressed as the number of aggregate intersections with the line per μm. Dynamic mechanical analyses (DMA) were obtained with a

Polymer Laboratories DMTA mkII thermal analyser. Glass transition temperature, T_g, was determined from the maximum in the tanδ versus temperature scan. The PMMA was extracted from the compounds with tetrahydrofuran using a Soxhlet apparatus; the polymer was recovered through precipitation with methanol followed by drying. Differential scanning calorimetry (DSC) data were obtained with a Perkin Elmer DSC7 instrument. Samples were heated at 10°C/min to 180°C, cooled at 10°C/min to 50°C and finally heated at 10°C/min to 180°C. The data discussed herein were taken from the second heating phase of the cycle. T_g was determined from the mid-point of the step transition in the heat capacity versus temperature thermogram. Several replicate thermal analyses were carried out for each sample; the data reported are the mean values. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected using a Bruker 300 MHz spectrometer employing $CDCl_3$ as the solvent. Gel permeation chromatography (GPC) was carried out using a Waters 150-CV Plus instrument at room temperature with tetrahydrofuran as the solvent and PMMA calibration standards.

3. Results and discussion

3.1. Clay expansion during composite preparation

Fig. 1 displays the representative X-ray diffraction traces for (a) samples prepared through melt intercalation, (b) polymerisation compounds after melt processing, and (c) reaction products from polymerisation before melt processing, each containing 20 phr of dodecylammonium clay; (d) is PMMA without clay. The abscissa are given in d-spacings calculated from the Bragg equation

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}, \tag{1}$$

where $n = 1$, $\lambda = 1.542$ Å, and angle, θ. The X-ray traces for the unmodified clay filled PMMA were little different from the original unmodified clay, since the unmodified clay particles are simply incorporated into the polymer matrix in an agglomerated state, with no intercalation of the polymer. For both the melt processed polymerisation and melt-intercalation composites, a series of reflections exhibiting periodicity along the d-axis are present in the diffraction traces. These are the 0 0 1 reflections for the (0 0 1) plane and indicate that the clay layers are at least partially arranged into aggregates that comprise regularly spaced layers. The average d_{001} for the melt-intercalation composites was 30.2 Å and changed little with clay content. The corresponding value for the melt processed polymerisation composites was 29.2 Å, and was independent of clay content. The

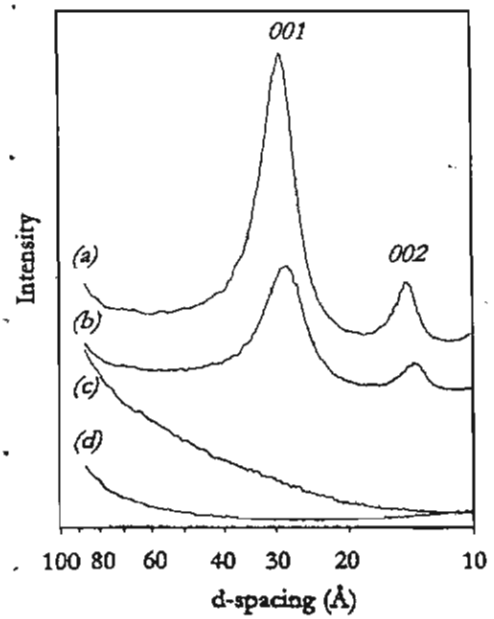

Fig. 1. WAXD traces of composites, containing 20 phr of dodecylammonium clay, prepared through (a) melt intercalation; (b) polymerisation (after melt processing); (c) polymerisation (powder reaction products before processing), and (d) PMMA synthesised in the absence of clay.

gallery spacing, S_g, is the distance between the internal surfaces of neighbouring clay layers; it is calculated

$$S_g = d_{001} - t, \tag{2}$$

where t is the van der Waal's thickness of the clay layer, that is 9.6 Å [9]. The gallery spacings are thus 20.6 and 19.6 Å for the intercalation and melt processed polymerisation composites, respectively. The length of an extended dodecylammonium ion is estimated to be 20.0 Å [9]; and hence, it is inferred that the extended ions stand perpendicular to the surface of the clay with the PMMA chains occupying the remaining space.

For the melt-intercalation composites, the preparation process may be described qualitatively by the following reasoning: in the dodecylammonium-modified clay, before composite preparation, the d_{001} was 17.9 Å, giving a corresponding interlayer spacing of 8.3 Å. This result suggests that the ions assume a bilayer arrangement [9], that is with one ion lying parallel to each of the internal surfaces of the clay. During melt mixing, the PMMA chains intercalate the clay interlayers, with the alkyl chains of the ions turning through 90° to become oriented perpendicular to the clay surface, thereby providing room to accommodate the PMMA. The favourable interactions between PMMA and the surface of the silicate sheets, and the gain in entropy of the alkyl chains as the interlayer spaces expand, permit an unfavourable

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loss in entropy of the polymer, due to its confinement between the silicate sheets, to be overcome [10,11]. Consequently, intercalation of the PMMA chains takes place during melt mixing. Further polymer intercalation does not occur, however, because once the alkyl chains are fully extended, no further entropy can be gained by the alkylammonium ions with continued layer expansion, and therefore, there is no driving force to overcome the associated loss in entropy as extra polymer is confined in the galleries.

This hypothesis was tested by melt intercalating PMMA into the galleries of a clay sample that had been modified with an ion possessing a different length from the dodecylammonium ions, namely hexadecyltrimethylammonium ions. The d_{001} of the composite was 39.7 Å, and hence, the gallery spacing was 30.1 Å. The estimated extended chain length of the hexadecyltrimethylammonium ion is 29.0 Å, and therefore, it is reasonable to conclude that the extended ions assume a perpendicular orientation to the inner surfaces of the clay, thereby playing a major role in determining the interlayer spacing.

The gallery spacings for all formulations are plotted versus the clay content as shown in Fig. 2. It can be seen that the melt intercalation samples have slightly higher spacings than the melt processed polymerisation materials. This result is obtained for every concentration of the clay, suggesting that the difference is reproducible, and hence significant relative to the estimated 1% error of the measurements. The origin may lie in the microstructure differences of the polymers, as discussed in Section 3.2.

3.2. Polymer microstructure

For both the polymerisation and melt-intercalation composites, all the PMMA could be extracted with tetrahydrofuran in a Soxhlet apparatus. Thus, in each composite, the polymer interacts with the clay through physical bonds that can be displaced through the formation of the tetrahydrofuran-clay specific interactions. Each extracted polymer was characterised through the GPC and NMR spectroscopy. The GPC data for the polymerisation system are displayed in Fig. 3; the melt-intercalation polymer was unchanged from the original resin. Polymerisation of MMA in the presence of higher loadings of modified clay resulted in the formation of polymers with reduced molecular weight and increased polydispersity, in comparison with the PMMA prepared under comparable conditions in the absence of clay. This may be due to the interference of active sites upon the clay surface with the free radical polymerisation; chain transfer to Lewis or Brönsted acid sites may take place.

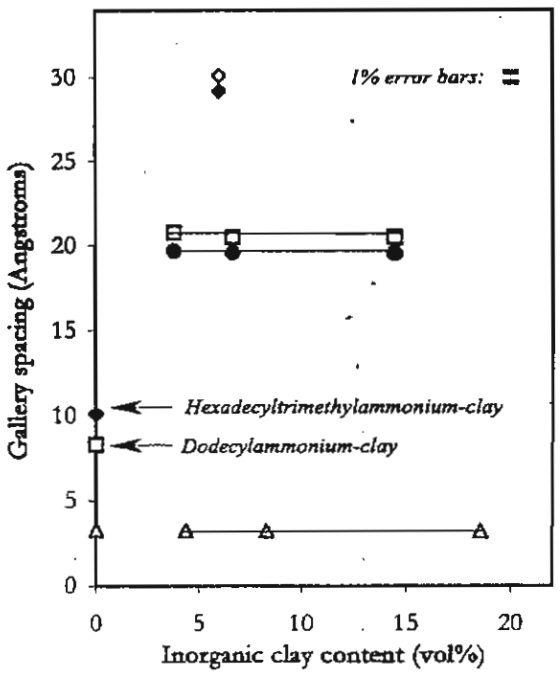

Fig. 2. Gallery spacings for all composites as a function of clay content: (Δ) PMMA/unmodified clay composites; (●) polymerisation composites containing dodecylammonium clay; (□) melt-intercalation composites containing dodecylammonium clay; (◆) polymerisation composites containing hexadecyltrimethylammonium clay, and (◇) melt-intercalation composites containing hexadecyltrimethylammonium clay.

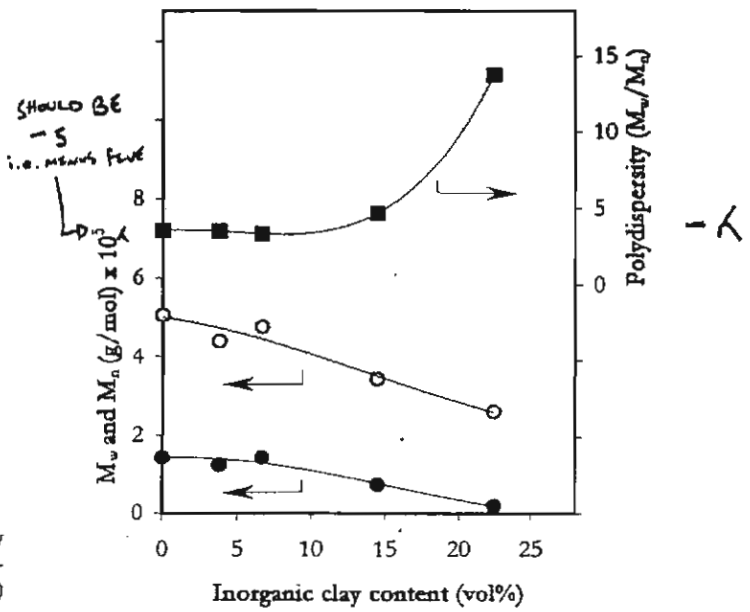

Fig. 3. GPC data for PMMA extracted from polymerisation composites: (○) weight average molecular weight, M_w; (●) number average molecular weight, M_n, and (■) polydispersity.

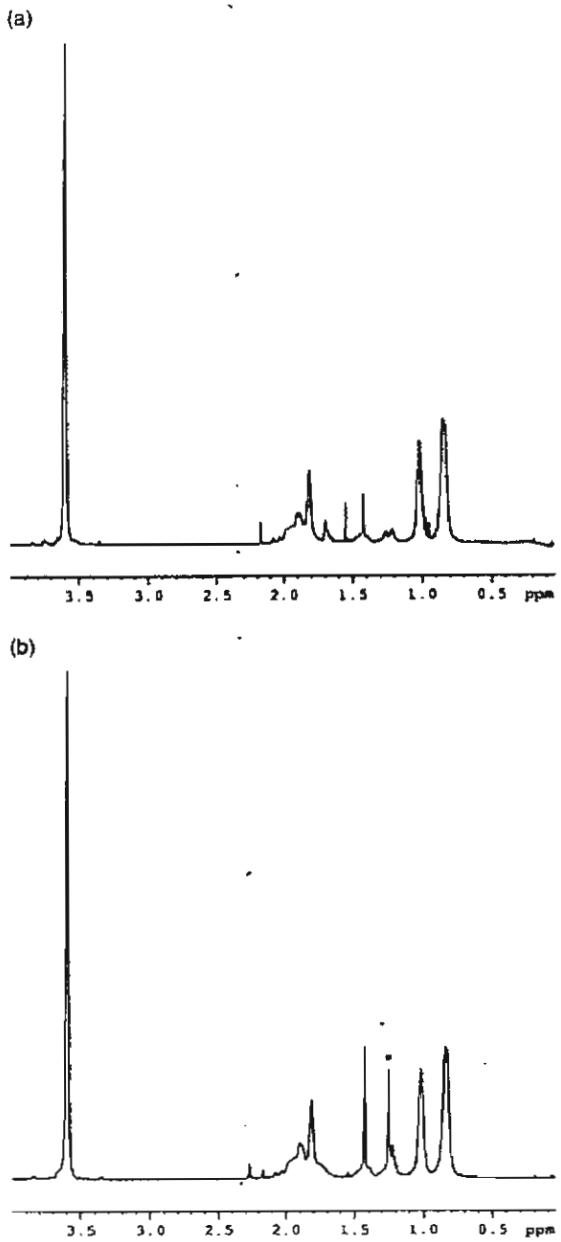

Fig. 4. ^{1}H-NMR spectra of (a) PMMA synthesised in the absence of clay and (b) PMMA extracted from a polymerisation composite containing 20 phr of dodecylammonium clay.

In Fig. 4 the ^{1}H-NMR spectrum of PMMA synthesised in the presence of modified clay is compared with the spectrum of PMMA prepared in the absence of clay; Fig. 5 shows the corresponding ^{13}C-NMR spectra. The resonances observed in the ^{1}H-NMR spectrum of PMMA prepared in the absence of clay may be assigned from previous studies [12]: OCH_3 at $\delta = 3.60$ ppm, CH_2

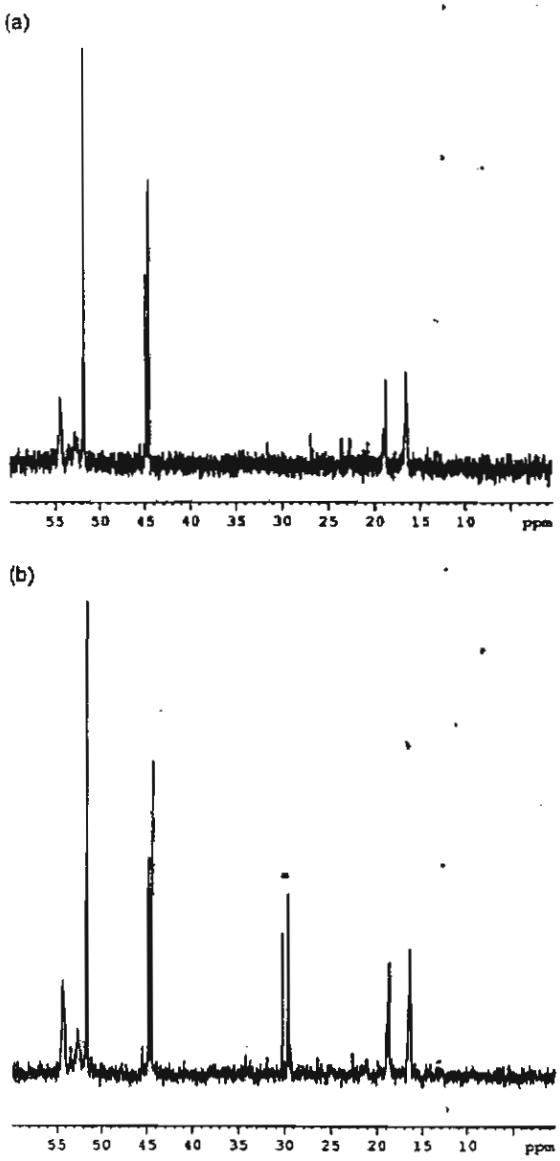

Fig. 5. ^{13}C-NMR spectra of (a) PMMA synthesised in the absence of clay and (b) PMMA extracted from a polymerisation composite containing 20 phr of dodecylammonium clay.

in the range $\delta = 2.50$ to 1.30 ppm, CH_3 at $\delta = 1.21$, 1.02, and 0.85 ppm, from isotactic, heterotactic, and syndiotactic triads, respectively. The PMMA synthesised in the presence of clay has an additional resonance at 1.25 ppm (marked with the symbol '■' in Fig. 4b); the area of this peak increased with increasing quantites of clay in the reaction vessel. Whilst this peak is in close proximity to the CH_3 resonance of the isotactic triads, it can be discounted as resulting from an increase in the fraction of isotacticity, since the splitting pattern of the CH_2 protons are not consistent with this result [12]. The ^{13}C-

NMR spectrum of PMMA synthesised in the presence of clay has chemical shifts of 29.7 and 30.3 ppm, marked with the symbol '■' in Fig. 5b, which are not present in the spectrum of PMMA synthesised in the absence of clay. The ^{13}C-NMR and ^{1}H-NMR results are consistent with the formation of ≡C–H structures, with the 29.7 and 30.3 ppm resonances being assigned to the tertiary carbon and the 1.25 ppm resonance to the methine proton. These results suggest that the polymer prepared in the presence of clay contains branch points, and hence, it is concluded that this is promoted by the active involvement of the clay surface during polymerisation.

In the GPC chromatograms of PMMA extracted from the composites containing 20 phr or more of clay, as exemplified in Fig. 6, it is evident that there is a bimodal distribution of molecular weights. This may result from the heterogeneous conditions of the polymerisations carried out in the presence of clay. Reactions taking place in close proximity of the clay surface may readily interact with the active sites of the clay leading to the formation of the lower molecular weight and more highly branched polymer. Both factors lead to reduced coil dimensions, and therefore longer retention times in the GPC column. Polymerisations progressing at some distance from the clay have lower probabilities of being affected, and hence, a higher molecular weight fraction may be formed. It is possible that the more highly branched polymer, with lower molecular weight, formed near the clay surfaces locates in the clay galleries. It was noted previously that the clay gallery spacings were always smaller in the polymerisation system than in the intercalation system. The observation may be related to the altered microstructure of the PMMA when prepared in the presence of clay. Branching results in reduced coil dimensions, changes in the conformations of the polymer chains, and to an increase in the number of polymer chain ends in comparison with a linear polymer of the same molecular weight [13]. Thus, the free energy of interaction between the PMMA, alkylammonium ions, and the clay is affected resulting in the modification of the clay aggregate structure.

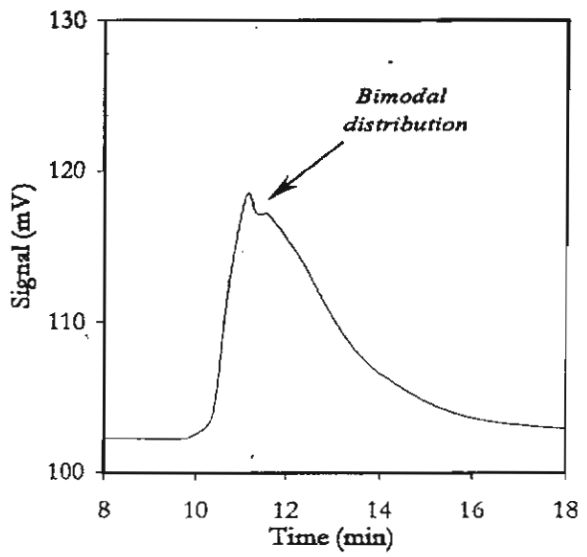

Fig. 6. GPC chromatogram of PMMA extracted from the polymerisation composite containing 50 phr of dodecylammonium clay.

3.3. Clay aggregate dispersion

The appearances of the polymerisation and melt-intercalation composites to the naked eye were similar, in that both were transparent. It may be inferred from the observation that the clay aggregates in these materials are small relative to the wavelengths of visible light and hence, little diffraction occurs. Conversely, the compounds containing unmodified clay were opaque, indicating the presence of large agglomerates that scatter light. The SEM micrographs shown in Fig. 7 confirm the presence of large agglomerates in the composites prepared with the unmodified clay, in comparison with the finer textures seen for the melt-processed polymerisation and melt-intercalation composites. The alkylammonium ions reduce the attractive forces between the clay layers and enable the polymer or monomer to intercalate into the clay galleries thereby aiding the dispersion of the clay. The average thickness of the clay crystal aggregates perpendicular to the (0 0 1) plane, L_c, was calculated using the Scherrer equation

$$L_c = \frac{k\lambda}{\beta_{001}\cos\theta}, \tag{3}$$

where $k = 1$ and β_{001} is the width, in radians, at half maximum intensity of the 0 0 1 reflection.

The average number of layers in each aggregate, N_c, was calculated:

$$N_c = \left(\frac{L_c}{d_{001}}\right) + 1. \tag{4}$$

L_c and N_c values for the two types of composite are plotted as functions of the clay content in Fig. 8. It is inferred from the data that in the polymerisation system, for the two lowest clay contents, the clay is dispersed into a larger number of aggregates each comprising fewer silicate sheets than in the melt-intercalation composites. At the highest clay content, however, the X-ray analysis reveals little difference between the two types of composite. The peak width, β_{001}, may be increased due to the disorder in the crystals in addition to the influence of the finite crystallite size, and hence, the calculated L_c may decrease. The TEM measurements plotted in Fig. 9 show that, for a given clay content, there is a larger

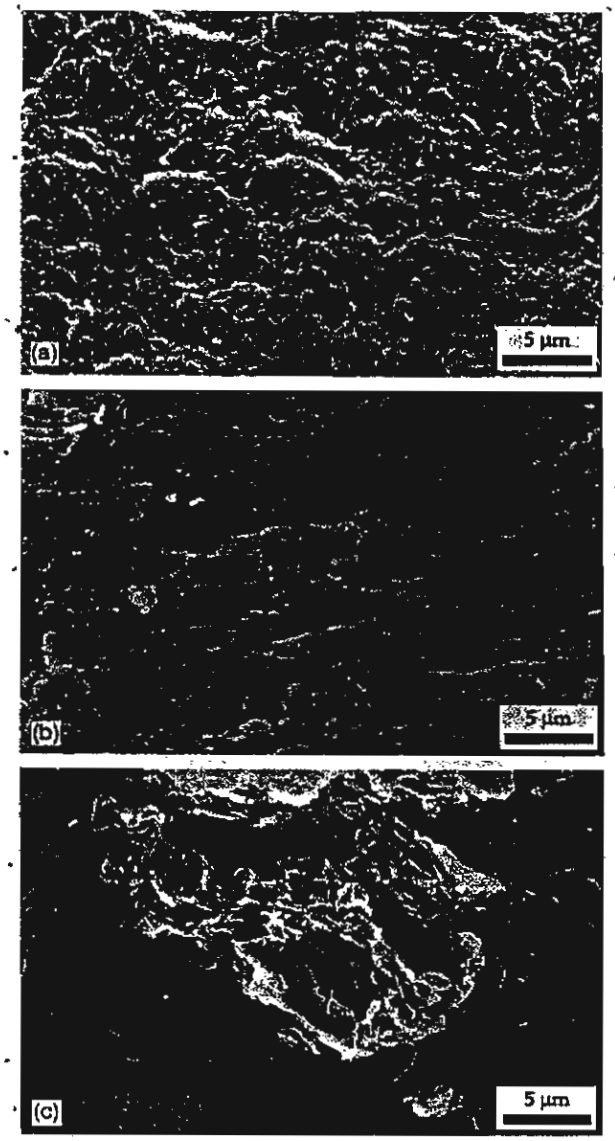

Fig. 7. SEM micrographs of fracture surfaces: (a) melt processed polymerisation PMMA/dodecylammonium clay composite; (b) PMMA/dodecylammonium clay melt-intercalation composite, and (c) unmodified clay filled PMMA; content is 10 phr in each sample.

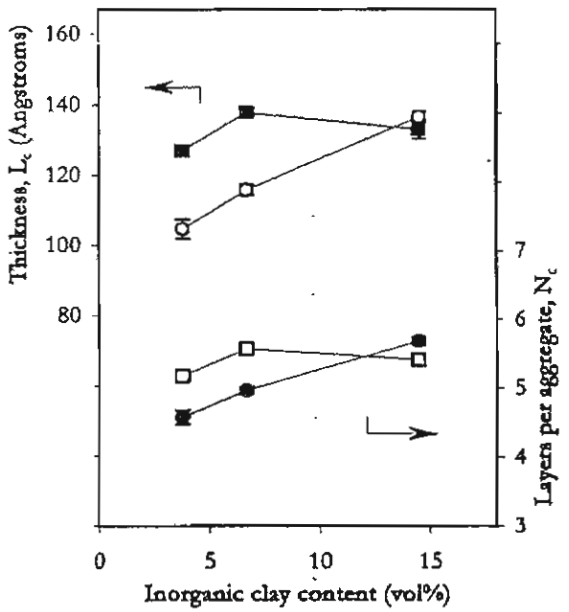

Fig. 8. Average crystallite thickness, L_c, in the (○) melt processed polymerisation and (■) melt intercalation systems containing dodecylammonium clay; average number of clay layers per aggregate, N_c, versus clay content in the same (●) polymerisation and (□) melt-intercalation composites.

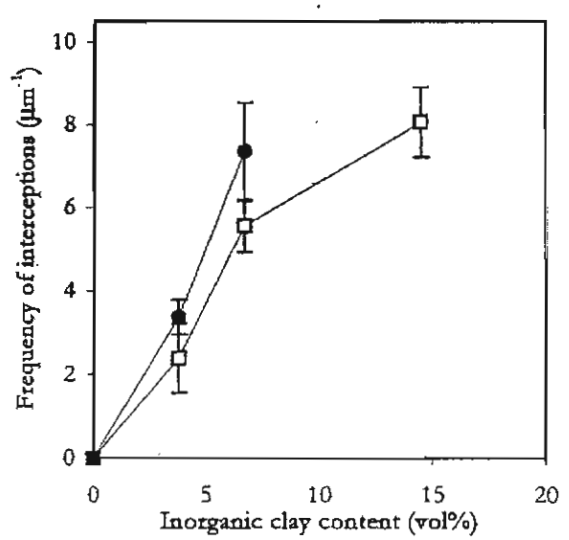

Fig. 9. Plot of number of clay aggregate-line intersections per micron for: (□) melt-intercalation composites and (●) melt processed polymerisation composites, both containing dodecylammonium clay.

number of clay aggregates in the polymerisation composites than in the intercalation composite; i.e. the aggregates are smaller in the former material. This confirms that the increases in β_{001} at least partly reflect reductions in the crystallite thickness. Examples of the TEM micrographs from which the data in Fig. 9 were obtained are displayed in Fig. 10. The clay layers are oriented on one plane, that is, with the basal surfaces, and hence the (0 0 1) plane, parallel to the platens of the compression press. Moreover, the 1 0 0 reflection of the quartz in the clay was not seen in the X-ray diffraction traces of the moulded samples, indicating its perpen-

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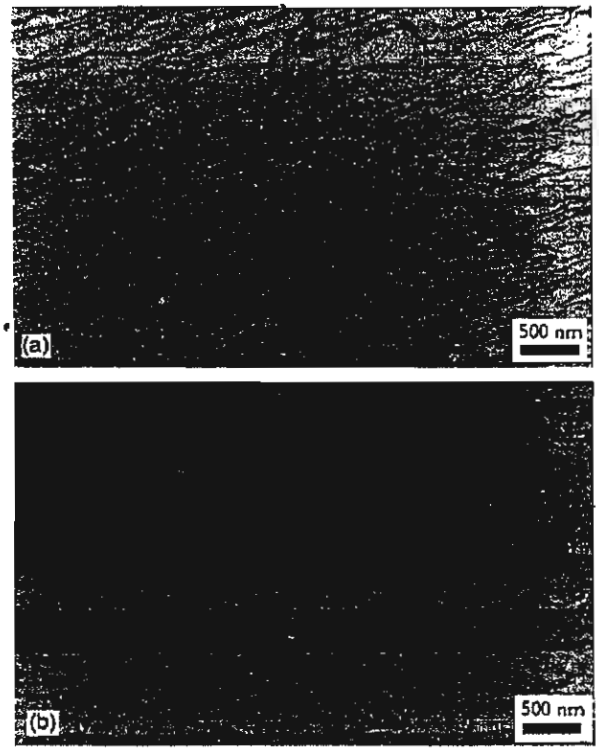

Fig. 10. TEM micrographs of PMMA/dodecylammonium clay composites, containing 20 phr of clay: (a) melt processed polymerisation and (b) melt-intercalation composites.

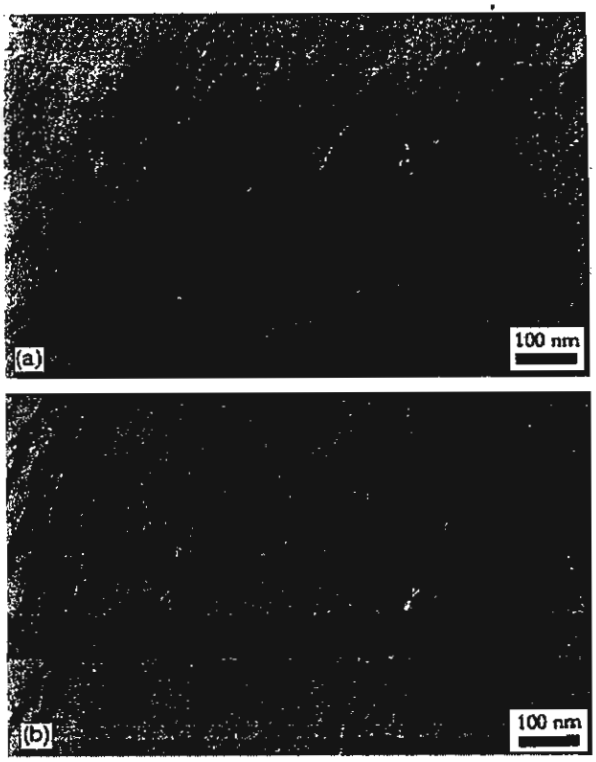

Fig. 11. TEM micrographs of PMMA/dodecylammonium clay composites: (a) melt processed polymerisation and (b) melt intercalation samples; clay content is 50 phr in both.

dicular orientation to the platens. The TEM micrographs of the composites containing the highest clay content, shown in Fig. 11, reveal differences in the arrangement of the clay aggregates in the two composites. In the polymerisation composite, the aggregates form an almost continuous pattern, with a large amount of connectivity, overlap, and misalignment within the aggregates, making differentiation of individual aggregates unclear. The line intersection method was uncertain for this micrograph and consequently no data are given in Fig. 9 for the sample. The melt-intercalation composite has more regular and clearly defined aggregates.

The differences in the polymerisation and melt-intercalation composite structures originate from the conditions during sample preparation. The polymerisation reactions took place in a dispersion of modified clay in MMA dissolved in hexane in which the monomer was able to penetrate the clay galleries causing the clay to swell to a separation beyond the detection limit of the X-ray diffraction analysis; i.e. greater than 80 Å. As the molecular weight of the polymer increased during polymerisation, the chains precipitated from the solution became trapped between the silicate sheets, thereby fixing their separation. However, it is probable that some long-range order between the clay sheets was maintained. During subsequent melt processing, some of the PMMA chains moved out from between the layers and the silicate sheets aggregated into more thermodynamically favoured arrangements. The silicate sheets may not have returned wholly to their original positions, with sheet misalignment resultant in the newly formed aggregates. In the melt intercalated sample, the aggregates appear to be well separated from one another, in discrete aggregates. During melt intercalation, the PMMA intercalates the clay crystal aggregates causing them to expand in the (0 0 1) direction, i.e. normal to the (0 0 1) plane, without causing the layers to loose the vertical alignment of the crystal lamellae. Consequently, more of the original order is maintained in the melt-intercalation composites.

3.4. Relaxation characteristics

The plots of T_g, determined from DMA, against dodecylammonium clay content are shown in Fig. 12. Typical storage modulus curves are shown in Fig. 13. T_g values of the melt-intercalation composites were close to that of the unfilled PMMA, i.e. around 105°C. The

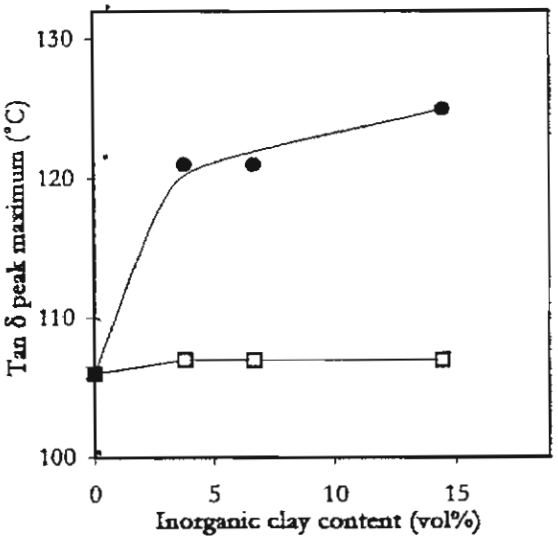

Fig. 12. Temperature of tanδ maximum versus inorganic clay content: (□) melt intercalation and (●) melt processed polymerisation composites, containing dodecylammonium clay.

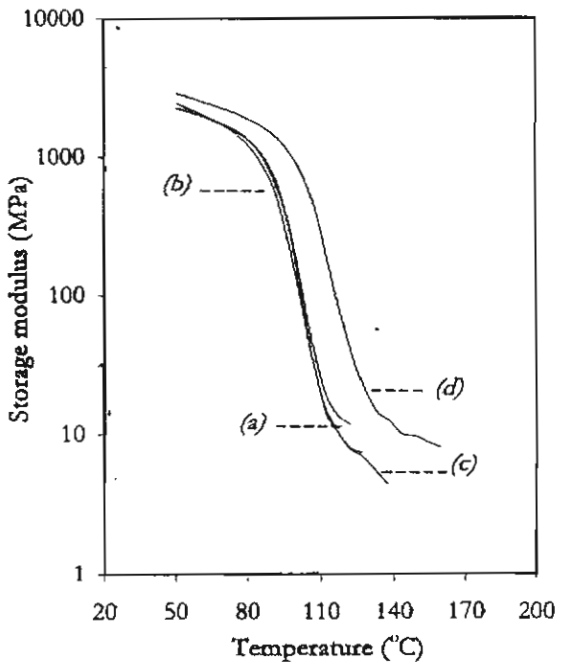

Fig. 13. Storage modulus versus temperature for (a) unfilled PMMA and (b) PMMA with unmodified clay. Curve (c) and (d) are from the melt intercalation and melt processed polymerisation composites, respectively, containing 10 phr of dodecylammonium clay.

polymerisation composites exhibited pronounced increases in T_g, typically of 20°C, in comparison with pure PMMA that was slightly affected by the clay concentration, although the rate of increase in T_g decreased with increasing clay contents. Moreover, the storage moduli of the solution-polymerised composites were substantially greater, at every temperature, in comparison with the other formulations. T_g, determined through DSC analyses, of the polymers extracted from the composites showed essentially the same result, although the values obtained from DSC were typically 5°C lower than those obtained from DMA mainly due to the static versus dynamic nature of the DSC and DMA analyses. Thus, changes in T_g may be traced to structural differences in the polymer. Modulus may be affected to some extent by the greater dispersion of the clay in the polymerisation composites due to the hydrodynamic effects. The NMR results showed that the PMMA prepared in the presence of clay was branched. The chain structure affects T_g in PMMA markedly, e.g. for the isotactic form $T_g = 45$°C, for syndiotactic $T_g = 115$°C, and for statistical polymers prepared through free radical polymerisation $T_g = 99$°C [14]. Moreover, Krigas et al. [15] observed an increase in T_g with increasing branch contents of model polyethylenes. It is likely that the chain branching is the cause in the modified relaxation characteristics of the PMMA in the polymerisation composites. The effect of branching may be more pronounced in PMMA due to the bulkiness of the branch points that restricts the main chain relaxation in comparison with the less sterically hindered polyethylene. From the results of Cowie [16], changes in the molecular weight over the range found in this work are not expected to alter T_g.

Vaia et al. [5] observed that whilst the main chain relaxation of the intercalated polystyrene in montmorillonite composites was suppressed, a transition due to the unintercalated bulk polymer was observed at the same temperature as the glass transition of the unfilled polymer resin. For the intercalated polymer, the relaxation process is limited by the restrictions imposed upon the chains through their confinement between the clay layers.

The available free volume may be insufficient to permit co-operative jump processes [17], with the consequence that the relaxation of the intercalated polymer is suppressed, at least within the time and temperature conditions of the analysis. The experimentally observed relaxations in this work originate from the polymer in the bulk.

4. Conclusions

1. Montmorillonite clay modified with dodecylammonium and hexadecyltrimethylammonium ions can be intercalated through melt mixing with PMMA.

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2. The length and orientation of the extended alkylammonium ions principally control the interlayer spacings of the clay in both the melt intercalation and the melt processed polymerisation composites.
3. The clay aggregates in the melt processed polymerisation composites are more finely dispersed and are more misaligned than in the melt intercalation composites.
4. PMMA synthesised in the presence of the clay was branched and this led to an increase in the glass transition temperature of the polymer and the storage moduli of the polymerisation composites in comparison with the melt intercalation samples.

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