

An Assessment of Polymer Nano-composite Materials

Sekhar Chakravorty
The Materials Centre
National Physical Laboratory
Teddington
Middlesex TW11 0LW, UK

ABSTRACT

Polymer nano-composites represent a radical alternative to conventionally filled polymers. The science involves the addition of specially treated nano-scale clay particles, such as montmorillonite, to a variety of plastics to produce significantly improved properties. Understanding the structure-properties relationships is crucial for the successful development of new nano-composite materials. A brief review of polymer nano-composite materials, their applications and associated modelling work has been carried out. An assessment of the reported test methods, including NPL's preliminary results from a pilot study of nylon 6 / clay nano-composite material, is presented.

© Crown copyright 2002
Reproduced by permission of the Controller, HMSO

ISSN 1473 2734

National Physical Laboratory
Teddington, Middlesex TW11 0LW, UK

Extracts from this report may be reproduced provided
that the source is acknowledged

Approved on behalf of Managing Director, NPL,
by Dr C Lea, Head, NPL Materials Centre

CONTENTS

1. INTRODUCTION	..1
2. MATERIALS	..1
3. PROPERTIES AND MEASUREMENT NEEDS.....	..2
4. MODELLING	..3
5. PRELIMINARY RESULTS	..3
5.1 Differential Scanning Calorimetry (DSC)	..4
5.2 Thermal Conductivity	..4
5.3 Pressure Volume Temperature (PVT).....	..4
5.4 Viscosity	..4
5.5 Micro- / Nano-hardness and Modulus	..4
6. SUMMARY OF POLYMER NANO-COMPOSITE MATERIALS	..5
7. FUTURE WORK.....	..5
8. ACKNOWLEDGEMENTS.....	..6
9. REFERENCES	..6
TABLES	12
FIGURES	15

1. INTRODUCTION

The reinforcement of polymers using fillers is common in the production and processing of polymers. The use of nano-scale fillers to augment the properties of polymers has led to the development of polymer nano-composites and has provided a radical alternative to conventional polymer composites. Significant interest was generated by the development of nylon 6 layered silicate nano-composites (with as little as 2 vol%) with considerable improvements in tensile strength and heat distortion temperature without any significant loss of impact strength. The recent interest in extending these achievements to layered silicate-based polyolefins [1-130] and thermoset [131-145] nano-composite systems as well as the development of a range of chemically and physically distinct nano-scale fillers has called for a fundamental understanding of polymer nano-composites. An improved knowledge of the properties may be possible by utilizing new techniques and expertise developed in conventional filled polymer composites. Interest in new nano-scale fillers, syntheses approaches, processing techniques, morphological characterisation, structure-property relationships as well as rheology, thermophysical and physics of nanoscopically confined polymers is rapidly growing in Europe and elsewhere [1-24].

Nano-structured and nano-composite materials are expected to be major areas of growth in the U.K. economy in the next 20 years [11]. Currently the world nano-materials market is growing at the rate of 7-15% in various sectors [5, 6]. It is estimated that the market for polymer nano-composites will grow strongly over the next ten years to reach 600,000 tonnes by the end of 2010. The bulk of research has been split between Japan and the USA, with European groups entering the picture more recently (Tables 1 and 2). More than 70 organisations around the world are currently estimated to be working in the field and opportunities are still considered to be abundant. Major sources of funding and opportunities for collaboration are available from the European Commission (Framework VI), UK Basic Technology (DTI), Foresight (EPSRC), Cambridge and Oxford IRCs and the DTI "Studio" projects.

2. MATERIALS

Polymeric nano-composites are commonly based on intercalated or exfoliated layered clays that exhibit improved properties when compared to their bulk polymer constituents and conventional macro-composite counterparts (Figs. 1 and 2). The nano-particles have at least one characteristic length scale that is of the order of nano-meters and can range from essentially isotropic to highly anisotropic needle-like to sheet-like elements. Uniform dispersion leads to ultra-large interfacial area and nano-scopic dimensions between the constituents, which differentiate polymer nano-composites from traditional composites and filled plastics [2-6].

Polymer nano-composites are formed by integrating two divergent organic and mineral materials. Only 2-5% of the "nano-clay" is required to obtain a remarkable boost in properties. The nylon – montmorillonite clay nano-composite is the prime example of this new class of polymeric materials that was first developed by Toyota for use as a timing belt in the automobile industry (Fig. 3). Since then, the number of commercial applications for nano-technology has been growing at a rapid rate and is set to cover the following key areas in the next five years [5, 6] :

- Drug delivery systems
- Anti-corrosion barrier coatings
- UV protection gels
- Lubricants and scratch free paints
- New fire retardant materials
- New scratch / abrasion resistant materials

Superior strength fibres and films

Altered electrical, electronic, magnetic and optical properties

Polymer nano-composites based on PA, PE, PP, PS, PMMA, and PU have been successfully manufactured and commercialised in the recent times [11]. A wide range of nano-component additions, other than clays, has also been reported e.g. intercalated copper and gold, aluminium nitride and oxide, silver sulphide, acicular iron-oxide and graphite [28-42].

The clay that is most commonly used is montmorillonite (MMT), which is an aluminosilicate mineral with sodium counter ions present between the clay layers (Fig. 4). This space between the clay layers is referred to as the clay gallery. Each platelike layer is about 1 nm thick and from 50 to 100 nm in lateral dimension. To make this compatible with organic polymers, the sodium counter ions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert this material into a hydrophobic ammonium- or phosphonium- treated clay. The nano-composites may be prepared either by a blending process, (either melt blending or solution blending), or by a polymerisation process in the presence of the organically modified clay [3, 4, 46, 71].

The most important aspects for the technical development of polymer nano-composites are synthesis, characterisation and modelling. Polymer nano-composites can be synthesized by intercalating polymers in layered inorganic hosts. Graphite, transition metal chalcogenides, metal phosphates, complex oxides, oxychlorides, and mica-type layered silicates are some examples of layered solids capable of intercalation. The structure and properties of the resulting nano-structure can be conveniently mediated by controlling subtle guest-host interactions. Beyond the conventional phase separated polymer/silicate composites, for which the polymer and the inorganic host remain immiscible, two types of hybrids are possible (Fig. 2) : **intercalated** in which a single, extended polymer chain is intercalated between the host layers resulting in a well ordered multiplayer with alternating polymer/inorganic layers and a repeat distance of a few nanometers, and **exfoliated or delaminated**, in which the silicate layers (1 nm thick) are exfoliated and dispersed in a continuous polymer matrix [1-4].

3. PROPERTIES AND MEASUREMENT NEEDS

Three major characteristics define and form the basis of polymer nano-composites performance: nanoscopically confined matrix polymer, nano-scale inorganic constituents and nano-scale arrangement of these constituents. The driver for current research is to develop the tools – synthesis, processing, characterisation and theory – to optimise and enable full exploitation of the potential of the combination of these unique characteristics.

In general, polymer nano-composites exhibit large increases in tensile strength, modulus and heat distortion temperature (Table 3) with little loss in impact resistance [22]. An addition of 5% clay has been reported to show an increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength and 126% in flexural modulus, while the heat distortion temperature increased from 65° to 152°C at the loss of ~10% in impact strength [72]. They also give lower water sensitivity, permeability to gases (Figs 5 and 6) and thermal co-efficient of expansion. In addition, they could also show flame retardancy (Fig. 7), UV resistance (Fig. 8) and excellent barrier properties (Figs. 9A and 9B) with significant practical and commercial potential without losing clarity in both thermoplastics and thermosets. By contrast, conventional polymer composites show poor ductility and mouldability with degradation and inferior surface smoothness and are difficult to process as films or fibres.

Measurement and modelling of the materials structure and properties at the nano-scale (100 nm or less) as well as linking these to the macro- and micro- scale performance of the material are critically important. The National Physical Laboratory (NPL) in the UK is actively developing novel test methods

and mathematical models to provide a sound interpretation of the experimental results. NPL's micro- and nano- testing facilities include techniques such as TEM, SEM, AFM, SAM, SIMM, AES, XPS, SNOM, X-ray Diffraction, Nano-indentation, thermal and rheological property measurements.

The test methods that have been widely reported in the literature in order to understand the structure-property relationship in polymer nano-composites are:

- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Scanning Force Microscopy (SFM)
- Wide Angle X-ray Diffraction (WAXD)
- Small Angle X-ray Scattering (SAXS)
- Plasma Atomic Emission Spectroscopy
- NMR Spectroscopy
- Small Angle Neutron Scattering (SANS)
- Differential Scanning Calorimetry (DSC)
- Thermo Gravimetric Analysis (TGA)
- Heat Deflection / Distortion Temperature
- Dielectric Properties
- Shear Viscosity
- Melt Flow Index (MFI)
- Nano-indentation
- Nano-scratch technique
- Dynamic Mechanical Analysis (DMA)
- Ultimate Tensile Strength / Modulus
- Young's Modulus
- Stress Relaxation
- Flexural Strength / Modulus
- Impact Resistance

4. MODELLING

Even though significant progress has been made in developing polymer nano-composites with varying polymer matrices and inorganic nano-particles, a general understanding has yet to emerge. A major challenge in developing nano-composites for systems ranging from high performance to commodity polymers is the lack of simple structure-property models. In the absence of such models coupled with the complex role of processing in affecting the structure and properties, the progress in the engineering of nano-composites has remained largely empirical [146-161]. Similarly, predicting the ultimate material limits or maximum performance for different classes of nano-composites remains quite complex at present.

5. PRELIMINARY RESULTS

A pilot study was conducted to examine thermal, rheological and mechanical properties of a nylon 6 / clay nano-composite material by utilising a selection of experimental techniques available at NPL. The objective of this exploratory work was to make an assessment of the basic properties, which may help to improve the understanding of the materials behaviour in polymer nano-composites. It was also hoped that this study would enable NPL to identify suitable test methods for characterising this new class of

materials. Several experimental techniques (e.g. DSC, Thermal Conductivity, PVT, Viscosity, Micro/Nano-hardness and Modulus) were therefore considered for this investigation and the preliminary results from that work are reported below.

5.1 Differential Scanning Calorimetry (DSC)

Fig. 10 represents the DSC plots of both unfilled and nano-clay filled nylon 6 materials at 5°C/min, 20°C/min and 80°C/min cooling rates respectively. The peak temperatures and the enthalpy data are shown in each case, which appeared to be noticeably different in the two materials. This shift in crystallisation temperature is in the opposite direction to that observed with traditional fillers, where nucleation of crystallisation is often seen. In the current study it is believed that a different nylon crystal structure (with a lower crystallisation temperature) is promoted by the presence of the clay.

5.2 Thermal Conductivity

No significant difference in thermal conductivity between the two materials was observed in the present study (Fig. 11). However, both materials showed significant pressure dependency. Tests conducted at 150 bar gave thermal conductivity values about 80% to 100% higher than the values obtained at 1 bar in the temperature range 50°C to 300°C.

5.3 Pressure Volume Temperature (PVT)

Iso-baric PVT tests were carried out at 150 and 800 bar on both unfilled and filled samples at cooling rates of 5°C/min, 20°C/min and 80°C/min. The change in specific volume (i.e. shrinkage values) was measured as a function of temperature in the range 300°C to 50°C (Figs. 12-13). In all cases, the nylon 6-clay nano-composite material showed an overall shrinkage of ~15%, compared to ~18% in the unfilled nylon 6. Melt compressibility was found to be of the same order in both cases i.e. ~5% at 300°C and ~2% at 50°C. The crystallisation temperatures were, as expected, found to be pressure dependant (varied by ~10°C), but in the case of nano-composite these crystallisation temperatures were reduced by about 10° - 15°C. These results suggest that the relatively low onset temperatures of crystallisation in nylon 6-clay nano-composite could lead to a longer processing time than unfilled nylon 6. These observations also agree reasonably well with the DSC results despite the difference of applied pressure between the experiments.

5.4 Viscosity

The visco-elastic properties of both materials are presented in Figs. 14-16. The storage/elastic modulus (G') and the loss/viscous modulus (G'') values of the nano-composite material were found to be about two orders of magnitude higher than the unfilled nylon 6 material at low frequency, e.g. at 1 rad/sec (Figs. 14 and 15), but the difference gradually reduced at higher frequency (e.g. at 100 rad/sec). The viscosity vs. % strain plots in Fig. 16 show the viscosity values an order of magnitude higher in the nano-composite material than in the unfilled nylon 6 under the test conditions.

5.5 Micro- / Nano-hardness and Modulus

Attempts have been made to determine micro-hardness values of these materials using 0.5 kg and 1.0 kg

loads. The measurement of indentation size proved difficult at this initial attempt as the material around the impression relaxed during examination.

A MTS Nano-instrument II was subsequently used to determine nano-hardness (and modulus) values in both unfilled and nano-clay filled nylon 6 using a Berkovich diamond shaped nano-indenter. Initially a small load was applied (<1mN) to the specimen; the load was then increased at a constant rate for 30s to a maximum value of 1mN (that penetrated to a depth of ~600 nm) where it was held for 60s before taking the measurement during unloading. Ten such readings were taken to form an average. The measured nano-hardness and the corresponding modulus data with their standard deviation values are presented in Table 4 for both unfilled and filled materials pre-compacted at 50 and 800 bar pressures respectively. The nylon 6 / clay nano-composite shows relatively higher hardness and modulus values in both conditions than the unfilled nylon 6 material. The results also suggest that the pre-compacted pressure has negligible effect on the properties of the filled material.

6. SUMMARY OF POLYMER NANO-COMPOSITE MATERIALS

Although intercalated layered silicates (clay) have been known in inorganic chemistry for decades, it took the pioneering work of Toyota on nylon 6 nano-composites at the end of the 1980s to reawaken interest in this class of materials. While nano-composites are not yet in a position to compete directly with glass fibre-reinforced plastics, they do present an unusually multi-faceted potential, especially with regard to in-situ generation of silicate nano-fillers that extends far beyond modification of mechanical properties.

With the “active” filler concept of nano-composites, barrier characteristics, electrical and optical properties, surface/interface modification and flame retardant properties can be achieved. Even today new additive classes based on layered silicates are appearing. Low percentages of nanolayer silicates (~2% by volume) suffice to cause massive changes in property profiles. Control of inter-particle interactions represents a particular challenge on the path to higher loading without sacrificing processability and property synergies. Cooperation among filler manufacturers, the plastics industry and materials research and modelling can yield innovative solutions to the problems associated with increasing the value of established plastics, application-specific customisation of property profiles and development of new applications. Important changes in behaviour are caused not only by continuous modifications of characteristics with diminishing size, but also by the emergence of totally new phenomena such as quantum size confinement, wave-like transport and predominance of interfacial phenomena. Once it becomes possible to control feature size and shape, it would also then become possible to enhance material properties and device functions beyond what are already established.

7. FUTURE WORK

An opportunity for collaborative research work currently exists at NPL with financial support available from the DTI. U.K. companies interested in joint research work with NPL are invited to take part in the “Studio” projects, where 50% of the funding is available from the DTI (companies are expected to pay 15% in cash and provide a 35% in-kind contribution). Further information on this DTI initiative and NPL’s nano-research activities are available from the following websites or from the author.

Nano research	http://nanomaterials.npl.co.uk
Studio project	www.npl.co.uk/npl/cmmmt/collaborative.html

8. ACKNOWLEDGEMENTS

This project is part of a programme of underpinning research financed by the National Measurement System Directorate (NMSD) of the Department of Trade and Industry on measurements related to the processability of materials.

The author is grateful to the following staff of NPL for their helpful discussion and assistance in this work: Chris Brown, David Mendels, Angela Dawson, Crispin Allen, Eric Bennett, Tony Maxwell, Uvais Sheriff, Barbara Sanger and Lydia Solomon.

9. REFERENCES

- 1 E.P. Giannelis, R. Krishnamoorti and E. Manias: *Advances in Polymer Science*, vol 138, p107-147, 1999.
- 2 E P Giannelis: "Antec'99", New York, Vol. III, p3966, 1999.
- 3 "Polymer-clay nano-composites", Eds. T J Pinnavaia and G W Beall, Wiley, 2001.
- 4 "Polymer Nanocomposites- Synthesis, Characterisation and Modelling", ACS Symposium series 804, Eds. R Krishnamoorti and R A Vaia, 2001.
- 5 "Nanotechnology", technology alert, a DTI, Eureka and Inst. Of Nano-technology publication, 2001.
- 6 K Strafford: "Expanding awareness of the nanoworld", *Materials world*, p24, April 2002.
- 7 H S Jeon, J K Rameshwaram and Y H Kim: "Characterisation and processing of polymer nano-composites", PPS-18 Conf. Proceedings, Portugal, 16-20 June 2002.
- 8 A.A. Voevodin and J.S. Zabinski: *Journal of Materials Science*, vol 33, p319-327, 1998.
- 9 H.J. Choi, S.G. Kim, Y.H.Hyun and M.S. Jhon: *Polymer Reprints*, vol 41, p1183-1184, 2000.
- 10 R. Leaversuch: "Nano-composites", *Plastics Technology*, vol 47, p64-69, Oct 2001.
- 11 Anon: "Nanocomposites technology takes off", *European Plastics News*, p31, Sept 2000.
- 12 R Muhlaupt: "Polymer Nanocomposites", *Polymers in Europe Quo Vadis ?*, European Polymer Federation, Special Issue, p 50, July 2001.
- 13 C.Zilg, P.Reichert, F.Dietsche, T.Engelhardt and R.Muelhaupt: *Kunststoffe Plast Europe*, vol 88, p65-67, 1998.
- 14 L.M. Sherman: *Plastics Technology*, vol 44, p21-23, January 1998.
- 15 M.Okamoto, P.H. Nam, P.Maiti, T.Kotaka, N.Hasegawa and A.Usuki: *Nano Letters*, vol 1, p295-298, 2001.
- 16 X.Chen, K.Gonsalves and R.S. Rounds: *Mat. Res. Soc. Symp. Proc.* vol 501, p209-214, 1998.
- 17 C. Saujanya, Ashamol, S. Padalkar and S. Radhakrishnan: *Polymer*, vol 42, p2255-2258, 2001.
- 18 J.A. Nairn and D.A. Mendels: *Mechanics of Materials*, vol 33, p335-362, 2001.
- 19 G. Jannerfeldt, L. Boogh and J.-A.E. Månson: *Journal of Polymer Science*, vol 37, p2069-2077, 1999.
- 20 G. Jannerfeldt, L. Boogh and J.-A.E. Månson: *Polymer*, vol 41, p7627-7634, 2000.
- 21 C.J.G. Plummer, L. Garamszegi, Y. Leterrier, M. Rodlert and J.-A.E. Månson: *Chem. Mater.*, vol 14, p486-488, 2002.

22. L.M. Sherman: *Plastics Technology*, vol 45, p 52-57, June1999.
23. L.M. Bronstein, C. Joo, R. Karlinsey, A. Ryder and J.W. Zwanziger: *Chem. Mater.*, vol 13, p3678-3684, 2001.
24. J.-H.Chang, K.M. Park and D. Cho: *Polymer Eng. and Science*, vol 41, p1514-1520, 2001.
25. T. Takeichi, R. Zeidam and T. Agag: *Polymer*, vol 43, p45-53, 2002.
26. K.H. Wang, M.H. Choi, C.M. Koo, Y.S.Choi and I.J. Chung: *Polymer*, vol 42, p9819-9826, 2001.
P.H. Nam, P. Maiti, M. Okamoto, T. Kotaka, N. Hasegawa and A. Usuki: *Polymer*, vol 42, p9633-9640, 2001.
H. Yanagimoto, K. Akamatsu, K. Gotoh and S. Deki: *J. of Materials Chemistry*, vol 11, p2387-2389, 2001.
X.-F. Qian, J. Yin, S. Feng, S.-H. Liu and Z.-K. Zhu: *J. of Materials Chemistry*, vol 11, p2504-2506, 2001.
30. A.V. Murugun, B.B. Kale, C.-W. Kwon, G.Campet and K. Vijayamohanan: *J. of Materials Chemistry*, vol 11, p2470-2475, 2001.
31. Z.-K. Xu, L.Xiao, J. Wang and Y.-Y. Xu: *Polymeric Mater. Sci. & Eng.*, vol 85, p92-93, 2001.
32. G.Y. Yang, R.M. Briber, E.Huang, P.M. Rice, W. Volksen and R.D. Miller: *Polymeric Mater. Sci. & Eng.*, vol 85, p 18-19, 2001.
33. O. Rios, R. Jones and K. Lozano: *Antec'01*, vol 665, p3292-3294, 2001.
34. B.R. Hsieh and A.R. Melnyk: *Polymeric Mater. Sci. & Eng.*, vol 74, p412-413, 1996.
35. M. Ganter, W. Gronski, P. Reichert and R. Mülhaupt: *Rubber Chemistry & Technology*, vol 74, p221-235, 2001.
36. X. Deng, J. Hao and C. Wang: *Biomaterials*, vol 22, p2867-2873, 2001.
37. H. Wang, C. Zeng, P. Svoboda and L.J. Lee: *Antec*, vol 431, p2203-2207, 2001.
38. D.Merinska, Z.Malac, J.Hrncirik, J. Simonik, J.Trlica, M.Pospisil, P. Capkova and Z.Weiss: *Antec*, vol 416, p2166-2170, 2001.
39. S. Bagrodia, L.T. Germinario, J.W. Gilmer and M.R. Tant: *Antec*, vol 410, p2116-2119, 2001.
40. D.L. VanderHart, A.Asano and J.W. Gilman: *Chemistry of Materials*, vol 13, p3796-3809, 2001.
41. M.J. Solomon, A.S. Almussallam, K.F. Seefeldt and P. Varadan: *Polymeric Mater. Sci. & Eng.*, p263-265, 2000.
42. R.S. Guico, A.G. Richter, J.Wang and K.R. Shull: *Polymeric Mater. Sci. & Eng.*, vol 85, p27, 2001.
43. A.F Thünemann, A.Lieske and B.-R. Paulke: *Advanced Materials*, vol 11, p321-324, 1999.
44. E. Bourgeat-Lami, P. Espiard and A. Guyot: *Polymer*, vol 36, p4385-4389, 1995.
45. X. Chen, K.E. Gonsalves, G.-M. Chow and T.D. Xiao: *Advanced Materials*, vol 6, p481-484, 1994.
46. J. Zhu, F. Lamelas and C.A. Wilkie: *Polymeric Mater. Sci. & Eng.*, vol 83, p55, 2000.
47. A.B. Morgan, J.M. Antonucci, M.R. VanLandingham, R.H. Harris Jr and T. Kashiwagi: *Polymeric Mater. Sci. & Eng.*, vol 83, p57-58, 2000.
48. W. Liu, Z. Wu and D.H. Reneker: *Polymer Reprints*, vol 41, p1193-1194, 2000.
49. J. Zhu and C.A. Wilkie: *Polymer Int.*, vol 49, p1158-1163, 2000.
50. B. Hoffmann, J. Kressler, G. Stöppelmann: *Polymeric Mater. Sci. & Eng.*, vol 82, p286-287, 2000.
51. J. Murphy: *Plastics Additives & Compounding*, vol 2, p30-32, 2000.

52. J.W. Gilman and T. Kashiwagi: *SAMPE Journal*, vol 33, p40-46, 1997.
53. A. Antonov, M. Yablokova, L. Costa, A. Balabanovich, G. Levchik and S. Levchik: *Mol. Cryst. And Liq. Cryst.*, vol 353, p203-210, 2000.
54. J.W. Gilman, T. Kashiwagi, E.P. Giannelis, E. Manias, S. Lomakin, J.D. Lichenhan and P. Jones: *Fire Retardancy of Polymers*: p203-221, 1998.
55. D. Shia, C.Y. Hui, S.D. Burnside and E.P. Giannelis: *Polymer Composites*, vol 19, p608-617, 1998.
56. S.J. Jana and S. Jain: *Antec'01*, vol 419, p2180-2184, 2001.
57. D. Choi and N. D'Souza: *Antec'01*, vol 567, p3619-3623, 2001.
58. A.J. Hsieh, J.W. Song, J. Nebo and A. Singh: *Antec'01*, vol 420, p2185-2189, 2001.
59. W. Zhou, J.E Mark, M.R. Unroe and F.E. Arnold: *J. Macromol.Sci.-Pure Appl.Chem.*, vol A38, p1-9, 2001.
60. W. Niedermeier and B. Schwaiger: *TyreTech*, vol 14, p1-5, 1999.
61. R.A. Vaia, J.W. Lee, C.S. Wang, B. Click and G. Price: *Chemistry of Materials*, vol. 10, p2030-2032, 1998.
62. P. Breton, X. Guillon, D. Roy, F. Lescure, G. Riess, N. Bru and C. Roques-Carnes: *Biomaterials*, vol 19, p271-281, 1998.
63. S. Maeda, S.P. Armes: *Synthetic Metals*, vol 73, p151-155, 1995.
64. P.A. Drake and P.W. Bohn: *Analytical Chemistry*, vol 67, p1766-1771, 1995.
65. A. Wawkuszewski, H.-J. Cantow, S.N. Magonov, S.S. Sheiko and M. Möller: *Polymer Bulletin*, vol 31, p699-705, 1993.
66. D.M. Delozier, R.A. Orwoll, J.F. Cahoon, N.J. Johnston, J.G. Smith Jr and J.W. Connell: *Polymer*, vol 43, p813-822, 2002.
67. R.L. Cook, B. Elliott, S. Luebben, A.W. Myers and B. Smith: *Polymeric Mater. Sci. & Eng.*, vol 85, p159, 2001.
68. Z. Yang, L. Yonglai, L. Li, F. Yuxing, Z. Liqun: *China Synthetic Rubber Industry*, vol 24, p350-353, 2001.
69. H.Y. Byun, M.H. Choi and I.J. Chung: *Chemistry of Materials*, vol 13, p4221-4226, 2001.
70. R.S. Underhill and G. Liu: *Chemistry of Materials*, vol 12, p3633-3641, 2000.
71. J.Zhu, A.B. Morgan, F.J. Lamelas and C.A. Wilkie: *Chemistry of Materials*, vol 13, p3774-3780, 2001.
72. E.P. Giannelis: *Antec'96*, vol 3, p2998-3003, 1996.
73. L. Lehoczki: *Int. Polymer Science & Tech.*, vol 28, p1-5, 2001.
74. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, Jr., E. Manias, E.P. Giannelis, M. Wuthenow, D. Hilton and S. Phillips: *Flame Retardants*, p49-68, 2000.
75. L. Lehoczki: *Muanyag Es Gumi*, vol 37, p257-260, 2000.
76. C. Zilg, F. Dietsche, B. Hoffmann, C. Dietrich and R. Mülhaupt: *Macromol. Symp.*, vol 169, p65-77.
77. Y Katahira: *Kobunshi Ronbunshu*, vol 55, p477-482, 1998.
78. R. Müller-Mall: *Macromol. Symp.*, vol 100, p159-162, 1995.
79. S. Deki, K. Sayo, T. Fujita, A. Yamada and S. Hayashi: *J. Mater. Chem.*, vol 9, p943-947, 1999.
80. B.M. Sergeev, V.A. Kasaikin, E.A. Litmanovich, G.B. Sergeev and A.N. Prusov: *Mendeleeev Commun.*, vol 4, p130-132, 1999.
81. G.D. Barber, C.M. Carter and R.B. Moore: *Antec 2000*, vol 710, p3763-3767, 2000.
82. S.T. Smith, S. Harb and D.G. Chetwynd: *J. Phys. D: Appl. Phys.*, vol 25, p240-248, 1992.
83. C.J. O'Neil, L.A. Acquarulo, Jr. and J. Xu: *Antec*, vol 318, p1518-1522, 2000.

84. G. Qian, J.W. Cho and T. Lan: Polyolefins, p553-559, 2001.
85. F.M. Uhl, F.J. Lamelas and C.A. Wilkie: ACS Polymeric Mat. Sci. & Eng., vol 83, p56, 2000.
86. A.B. Morgan, J.W. Gilman, R.H. Harris, C.L. Jackson, C.A. Wilkie and J. Zhu: ACS Polymeric Mat. Sci. & Eng., vol 83, p53-54, 2000.
87. A. Dekar, H. Stretz and J. Koo: ACS Polymeric Mat. Sci. & Eng., vol 83, p105-106, 2000.
88. W. Niedermeier and B.F. Hürth: Kautchuk und Gummi Kunststoffe, vol 52, p670-676, 1999.
89. J. Ma, S. Zhang and Z. Qi: J. Appl. Polymer Sci., vol 82, p1444-1448, 2001.
90. W.-J. Zhou and D.L. Gin: Polymer Reprints, vol 41, p1330-1331, 2000.
91. X. Li, T. Kang, W.-J. Cho, J.-K. Lee and C.-S. Ha: Macromol. Rapid Commun., vol 22, p1306-1312, 2001.
92. E. Mäder and S. Gao: J. Adhesion Sci. Technol., vol 15, p1015-1037, 2001.
93. L. Zheng, R.J. Farris and E.B. Coughlin: Macromolecules, vol 34, p8034-8039, 2001.
94. Y.I. Tien and K.H. Wei: Macromolecules, vol 34, p9045-9052, 2001.
95. D. Lopez, I. Cendoya, F. Torres, J. Tejada and C. Mijangos: J. Appl. Polymer Sci., vol 82, p3215-3222, 2001.
96. P. Kodgire, R. Kalgaonkar, S. Hambir, N. Bulakh and J.P. Jog: J. Appl. Polymer Sci., vol 81, p1786-1792, 2001.
97. D. Smock: Modern Plastics, vol 28, p28-29, 1998.
98. N. Freestone: Chemistry & Industry, vol 1, p32-33, 2000.
99. D. Porter, E. Metcalfe and M.J.K. Thomas: Fire & Materials, vol 24, p45-52, 2000.
100. S. Bourbigot, M. Le Bras, F. Dabrowski, J.W. Gilman and T. Kashiwagi: Fire & Materials, vol 24, p201-208, 2000.
101. G. Beyer: Gummi Fasern Kunststoffe, vol 38, p321-325, 2001.
102. E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu and T.C. Chung: Chemistry of Materials, vol 13, p3516-3523, 2001.
103. G. Beyer: Int. Polymer Sci. & Tech., vol 28, p1-5, 2001.
104. S. De Vito and C.R. Martin: Chemistry of Materials, vol 10, p1738-1741, 1998.
105. E. Reynaud, M.H. Klopffer, J.Y. Cavaille, C. Gauthier, J. Varlet and G. Vigier: ACS Polymeric Mat. Sci. & Eng., vol. 36, p219, 2000.
- M.A.S. Pedroso, M.L. Dias, C. Azuma and C.G. Mothé: Colloid Polym. Sci., vol 278, p1180-1186, 2000.
- A.B. Morgan, J.W. Gilman and C.L. Jackson: Macromolecules, vol 34, p2735-2738, 2001.
- A. Strojny, X. Xia, A. Tsou and W.W. Gerberich: J. Adhesion Sci. Technol., vol 12, p1299-1321, 1998.
- D.L. VanderHart, A. Asano and J.W. Gilman: Macromolecules, vol 34, p3819-3822, 2001.
- R. Dhamodharan, J.D. Jeyaprakash, S. Samuel, M.K. Rajeswari: J. Appl. Polymer Sci., vol 82, p555-561, 2001.
- I. Cendoya, D. Lopez, A. Alegria and C. Mijangos: J. Polymer Sci., vol 39, p1968-1975, 2001.
- S.A. Ozerin, S.A. Zav'yalov and S.N. Chvalun: Polymer Sci., vol A43, p1171-1176, 2001.
- H. Wang, C. Zeng, M. Elkovitch, L. James Lee and K.W. Koelling: Polymer Eng. & Sci., vol. 41, p2036-2046, 2001.
- O Dufaud, E Favre and C Vu: Int. Symp. of Eurofillers, paper Cm36, Villeurbanne,

- France, 6-9 Sept 1999.
115. D. Lopez, I. Cendoya, F. Torres, J. Tejada and C. Mijangos: *Polymer Eng. & Sci.*, vol 41, p1845-1852, 2001.
 116. J.-H. Chang and K.M. Park: *Polymer Eng. & Sci.*, vol 41, p2226-2230, 2001.
 117. G.-H. Chen, D.-J. Wu, W.-G. Weng and W.-L. Yan: *Polymer Eng. & Sci.*, vol 41, 2148-2154, 2001.
 118. R. W. Carpick, D.Y. Sasaki and A.R. Burns: *Polymer Preprints*, vol 41, p1458-1459, 2000.
 119. A. Hodzic, J.K. Kim and Z.H. Stachurski: *J. Mat. Sci. Letters.*, vol 19, p1665-1667, 2000.
 120. A. Paiva and M.D. Foster: *Polymer Preprints*, vol 41, p1433-1444, 2000.
 121. G.-H. Chen, D.-J. Wu, W.-G. Weng and W.-L. Yan: *Polymer Eng. & Sci.*, vol 41, p2148-2154, 2001.
 122. K.E. Gonsalves, H. Li, and P. Santiago: *J. Mat. Sci.*, vol 36, p2461-2471, 2001.
 123. B. Wessling: *Synthetic Metals*, vol 102, p1396-1399, 1999.
 124. J. Sandler, M.S.P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte and A.H. Windle: *Polymer*, vol 40, p5967-5971, 1999.
 125. Anon: *Additives for Polymers*, p10-11, 2001.
 126. A. Tidjani and C.A. Wilkie: *Polymer Degradation & Stability*, vol 74, p33-37, 2001.
 127. S. Bourbigot, E. Devaux and X. Flambard: *Polymer Degradation & Stability*, vol 75, p397-402, 2002.
 - P. Beck, J. Kreuter, R. Reszka and I. Fichtner: *J. Microencapsulation*, vol 10, p101-114, 1993.
 - F.B. Landry, D.V. Bazile, G. Spenlehauer, M. Veillard and J. Kreuter: *Biomaterials*, vol 17, p715-723, 1996.
 130. N. Behan and C. Birkinshaw: *Macromol. Rapid Commun.*, vol 22, p41-43, 2001.

Epoxy based nano-composites

- Y. Ke, J. Lu, X. Yi, J. Zhao and Z. Qi: *Journal of Applied Polymer Science*, vol 78, p808-815, 2000.
- A. Lee and J.D. Lichtenhan: *Journal of Applied Polymer Science*, vol 73, p1993-2001, 1999.
133. C.J.G. Plummer, R. Mezzenga, L.Boogh and J.-A.E. Månson: *Polymer Eng. and Science*, vol 41, p43-52, 2001.
134. R. Mezzenga and J.-A.E. Månson: *Journal of Materials Science*, vol 36, p4883-4891, 2001.
135. R. Mezzenga, L. Boogh and J.-A.E. Månson: *Composites Science & Technology*, vol 61, p787-795, 2001.
136. A. Lee and J.D. Lichtenhan: *Macromolecules*, vol 31, p4970-4974, 1998.
137. X. Kornmann, H. Lindberg and L.A. Berglund, *Polymer*, vol 42, p1303-1310, 2001.
138. P. Butzloff: *Bell Helicopter Textron, Inc.*, N.A. D'Souza: *University of North Texas*, p1-3, 1999.
- R. Mezzenga, L. Boogh and J.-A.E. Månson: *Macromolecules*, vol 33, p4373-4379, 2000.
140. C.B. Ng, B.J. Ash, L.S. Schadler and R.W. Siegel: *Advanced Composites Letters*, vol 10, p101-111, 2001.
141. P.O. Henk, T.W. Kortsen and T. Kvarts: *High Perfm. Polymers*, vol 11, p281-296, 1999.

- G.Z. Li, L. Wang, H. Toghiani, T.L. Daulton, K. Koyama and C.U. Pittman, Jr.: *Macromolecules*, vol 34, p8686-8693, 2001.
143. Y.M. Cao, J. Sun, D.H. Yu: *J. Appl. Polymer Sci.*, vol 83, p70-77, 2002.
144. G.H. Hsiue, Y.L. Liu and H.H. Liao: *J. Appl. Polymer Sci.*, vol 39, p986-996, 2001.
145. K.T. Gam, L. Bonnaud, H.-J. Sue, H. Kawai and M. Miyamoto: *Antec*, vol 418, p2176-2179, 2001.

Modelling work

- J.U. Otaigbe, M.D. Barnes, K. Fukui, B.G. Sumpter and D.W. Noid: *Advances in Polymer Science*, vol 154, p1-86, 2001.
147. A C Balazs: "Antec' 99", New York, vol III, p3969-3970, 1999.
148. M.M.N. Gibbons, J.N. Hay and B.J. Howlin: *ACS Polymeric Mat. Sci. & Eng.*, p447-448, 1999.
- D A Mendels: "Trends in Nano-technology: TNT 2001 symposium", Spain, 3-7 September, 2001.
150. G.W. Beall: *Antec*, vol 11, p2398-2401, 1999.
151. D.H. Cole, K.R. Shull, P. Baldo and L. Rehn: *Macromolecules*, vol 32, p771-779, 1999.
152. R.K. Bharadwaj: *Macromolecules*, vol 34, p9189-9192, 2001.
153. A. Heise, J.L. Hedrick, M. Trollsas, J.G. Hilborn, C.W. Frank and R.D. Miller: *Polymer Reprints*, vol 40, p452-453, 1999.
154. A. Hodzic, J.K. Kim, and Z.H. Stachurski: *Polymer*, vol 42, p5701-5710, 2001.
155. A.B. Kaiser, G.U. Flanagan, D.M. Stewart, D. Beaglehole: *Synthetic Metals*, vol 117, p67-73, 2001.
- T.A. Bogetti, T.Wang, M.R. VanLandingham and J.W. Gillespie, Jr.: *Composites*, vol A30, p85-94, 1999.
157. A. Dufresne, J.-Y. Cavallé and W. Helbert: *Polymer Composites*, vol 18, p198-210, 1997.
158. G. Tanaka, L.A. Goettler: *Polymer*, vol 43, p541-553, 2002.
159. D.A. Brune and J. Bicerano: *Polymer*, vol 43, p369-387, 2002.
160. G.W. Beall: *Antec'01*, vol. 430, p2195-2202, 2001.
161. B.G. Sumpter, K. Fukui, M.D. Barnes and D.W. Noid: *Materials Today*, vol 2, p3-6, 2000.

TABLES

Table 1 Institutes and companies involved in nano-composites research [refs. 73, 97]

Company	Matrix polymer	Role
	Polyamide 6	Developer of the original nanocomposite technology: currently they do not use nanocomposites
Ube Industries, Japan	Polyamide 6 Polyamide 66 Polyamide 12	The first Toyota licensee and developer of polyamide 6 mixes for automotive applications
Nanocor, USA	Polyamide Polyester Polypropylene	Daughter company of Amcol International, involved in the development of nanocomposite technology on the basis of its own patents and the Toyota licence
Dow Chemical, USA	Not reported	Together with Magna International is studying the application of nanocomposites in vehicles
ICI Polyester, UK	Polyester	Coating of nanocomposites for gas-impermeable sheets
	Polypropylene	Nanocomposites for interior and exterior automotive components
Allied Signal, USA	Polyamide 6	Nanocomposite patents
	Polyamide 6 Polyamide 66 Polyamide copolymers	Technology development, for use in car industry
Claytec, USA	Epoxy resin	Use of epoxy resin matrix products
	Fluoropolymers	Patents for the use of nanocomposites as coating materials
Industrial Technology Research Institute, Taiwan	Conductive polymers Polystyrene Polyester	Development of compounds with improved antistatic, gas-impermeability and mechanical properties

Table 2 A brief list of nano-composites suppliers [ref. 10]

Supplier & Tradename	Matrix Resin	Nano-Filler	Target Market
Bayer AG (Durethan LPDU)	Nylon 6	Organo-clay	Barrier films
Clariant	PP	Organo-clay	Packaging
Creanova (Vestamid)	Nylon 12	Nano-tubes	Electrically conductive
GE Plastics (Noryl GTX)	PPG/Nylon	Nano-tube	Automotive painted parts
Honeywell (Aegis)	Nylon 6 Barrier Nylon	Organo-clay Organo-clay	Multi-purpose Bottles and film
Hyperion	PETG, PBT PPS, PC, PP	Nano-tube	Electrically conductive
Kabelwerk Eupen of Belgium	EVA	Organo-clay	Wire & cable
Nanocor (Imperm)	Nylon 6 PP Nylon MDX6	Organo-clay Organo-clay Organo-clay	Multi-purpose Molding PET beer bottles
Polymeric Supply	Unsaturated polyester	Organo-clay	Marine, transportation
RTP	Nylon 6, PP	Organo-clay	Multi-purpose, electrically conductive
Showa Denko (Systemer)	Nylon 6 Acetal	Clay, mica Clay, mica	Flame retardance Multi-purpose
Ube (Ecobesta)	Nylon 6, 12 Nylon 6, 66	Organo-clay Organo-Clay	Multi-purpose Auto fuel systems
Unitika	Nylon 6	Organo-clay	Multi-purpose
Yantai Haili Ind. & Commerce of China	UHMWPE	Organo-clay	Earthquake-resistant pipe

Source: Bins & Associates, Sheyboygan, Wis.

Table 3 A comparison of properties between a nylon 6 nano-composite and standard nylon [ref. 22]

	Unfilled	5% Nanoclay	30% Mineral	30% Glass
Tensile Strength, psi	7250	11,800	8000	23,000
Flexural Modulus, psi	120,000	500,000	650,000	1,100,000
Notched Izod, ft-lb/in.	1.2	1.2	1.6	1.8
HDT @ 264 psi, F	150	230	248	380
Specific Gravity	1.13	1.14	1.36	1.35

Table 4 Results of NPL's nano-hardness and modulus measurements

Material	Nano-hardness (GPa)	Standard Deviation	Modulus (GPa)	Standard Deviation
nylon 6/clay nano-composite compacted at 50 bar	0.119	0.010	2173	0.087
nylon 6/clay nano-composite compacted at 800 bar	0.121	0.007	2170	0.079
nylon 6 unfilled, compacted at 50 bar	0.068	0.012	2080	0.039
nylon 6 unfilled, compacted at 800 bar	0.109	0.006	2067	0.048

FIGURES

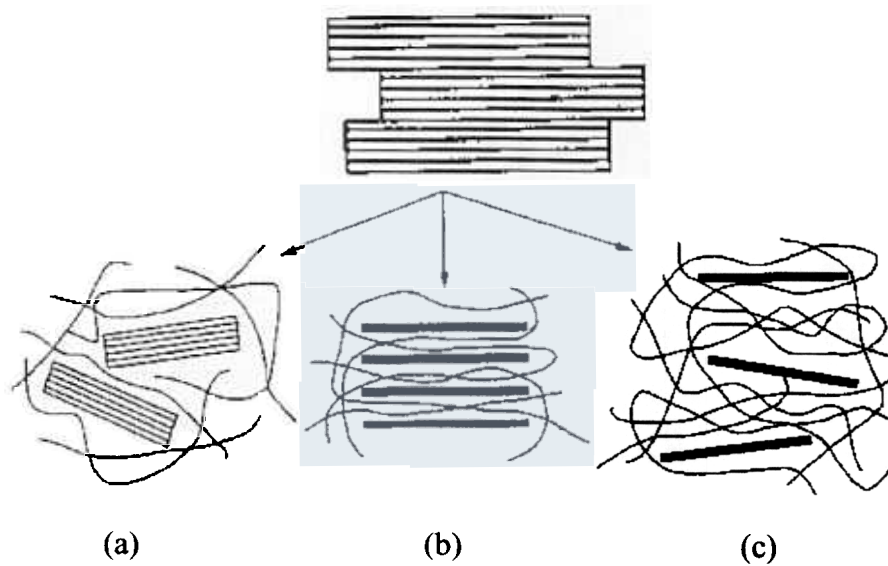


Figure 1 Schematic illustrations of the structures (a) conventional, (b) inter-calated and (c) exfoliated polymer clay nanocomposites. The clay layers adopt an aggregated, intercalated and exfoliated morphology, respectively, in each type of composite. The clay interlayer spacing is fixed in an intercalated nanocomposite and independent of the polymer-clay ratio, but in an exfoliated nanocomposite the average separation between nanolayers is variable and determined by the clay loading in the polymer [from ref. 3].

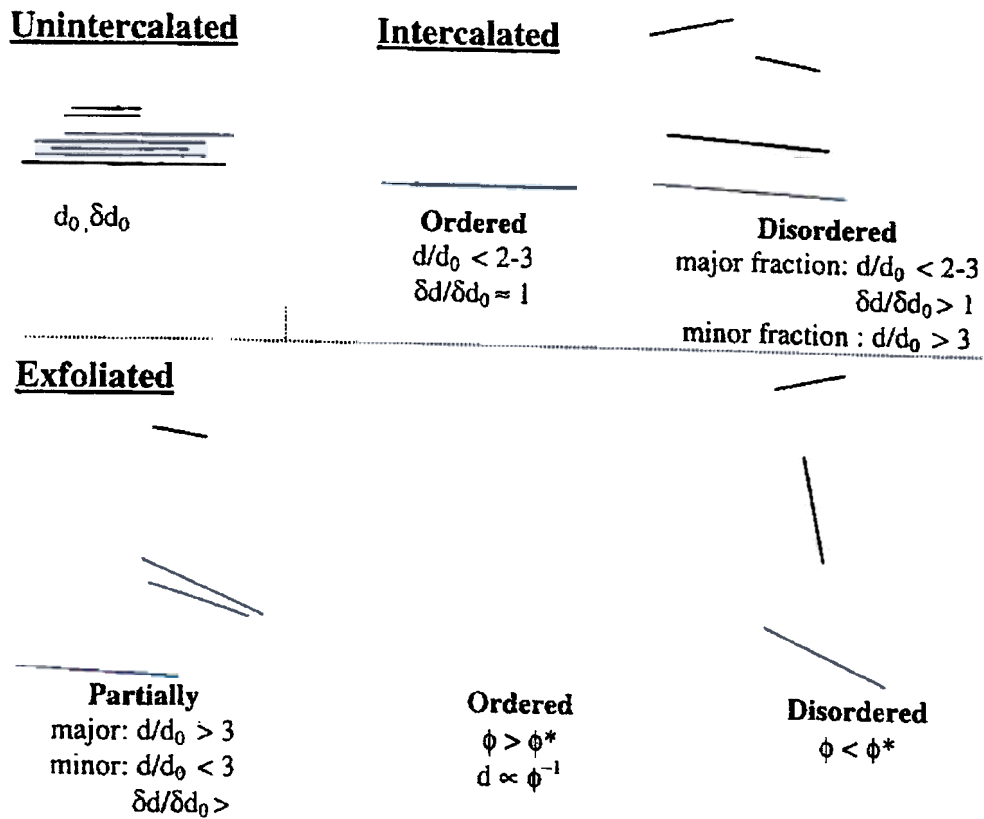


Figure 2 Idealized representations of various nanoscale arrangements of layered silicate in PLSN. Empty space represents polymer and dark lines represent layers oriented perpendicular to the surface of the page d_0 and δd_0 are the initial spacing and variation in layer spacing of unintercalated crystallites, respectively. The classes can be differentiated based on the relative change and variation of layer spacing upon combination with polymer (d and δd), relative volume fraction of single layers and layer stacks, and the dependence of single layer separation on silicate volume fraction (ϕ). Differentiation ($d/d_0 > 3$) is qualitatively based on experimental observations [ref. 4].

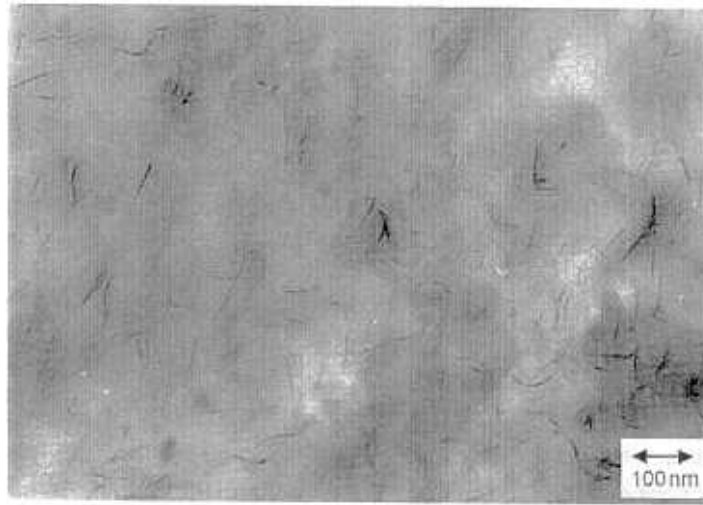


Figure 3 TEM micrograph of Nylon 6-clay nano-composite material [ref. 3].

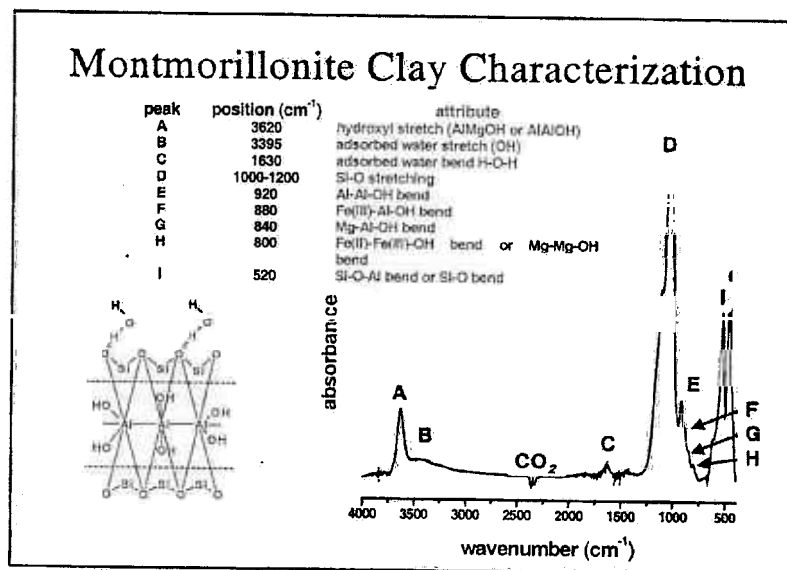


Figure 4 The *FTIR* spectral characteristics of a montmorillonite clay [ref. 4].

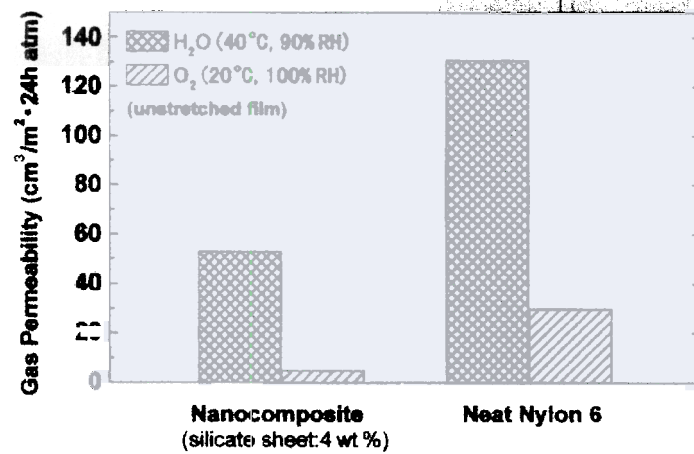


Figure 5 Gas permeability of the nano-composite film (150 μm thickness) [ref. 3].

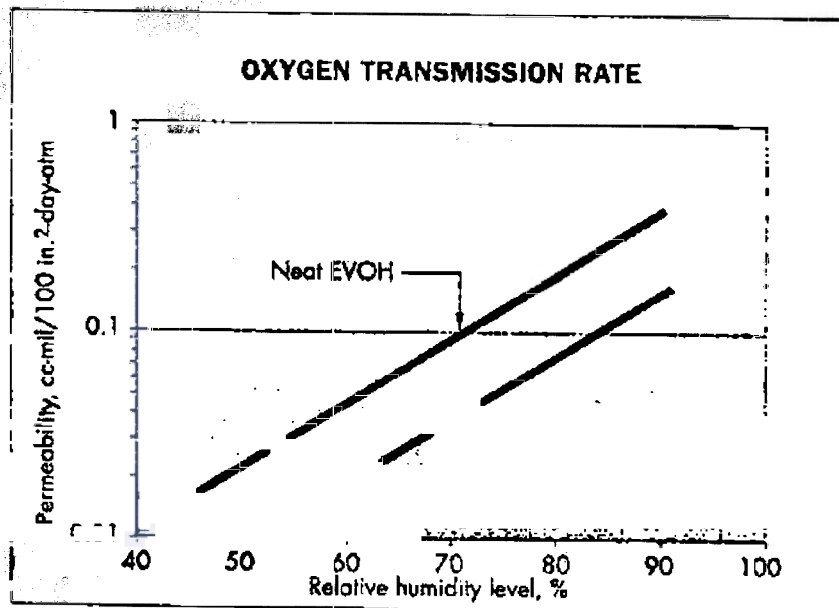


Figure 6

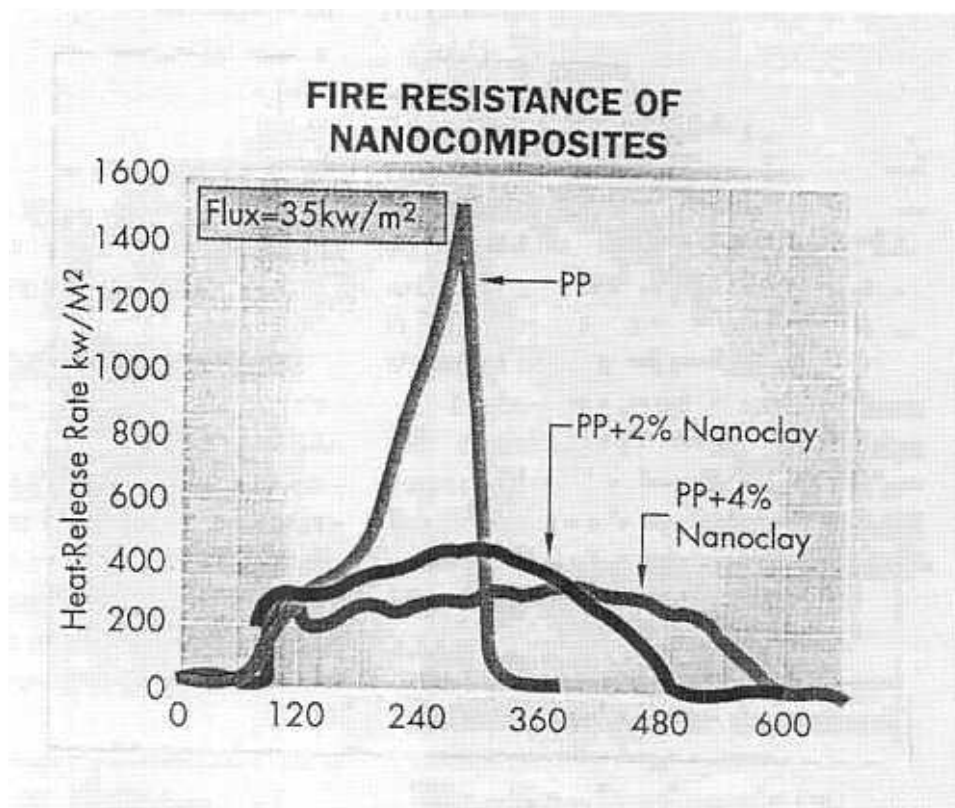


Figure 7 Cone-calorimeter tests by NIST show much lower peak heat-release rates from PP nanocomposites than from neat PP [ref. 22].

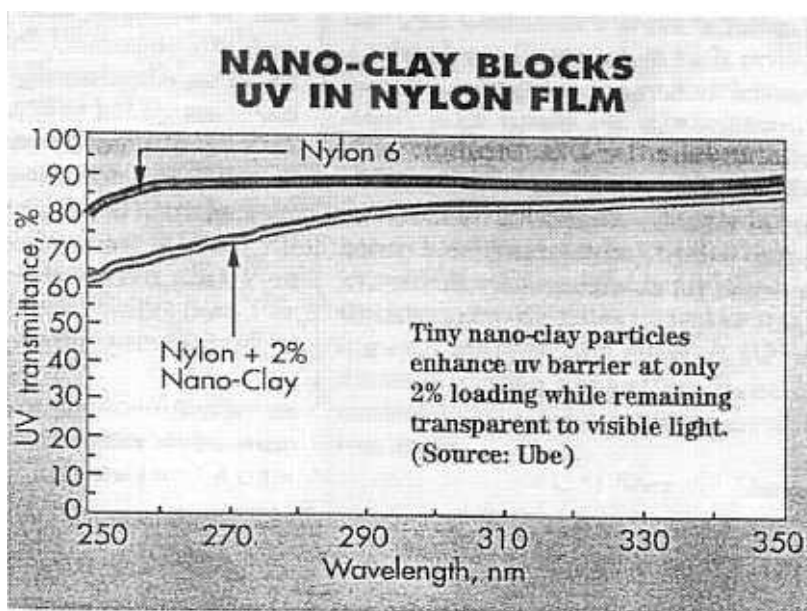


Figure 8 UV barrier properties of nano-clay filled nylon film [ref. 14].

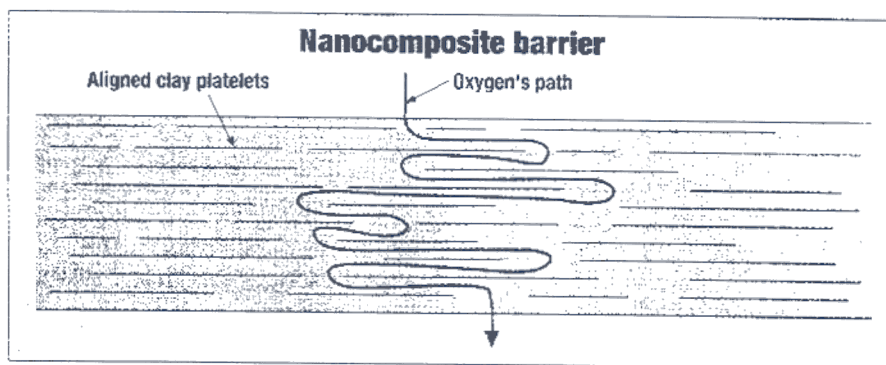


Figure 9A Nanocomposites are able to produce such strong barrier properties because gas molecules must travel a tortuous path through clay platelets [ref. 97].

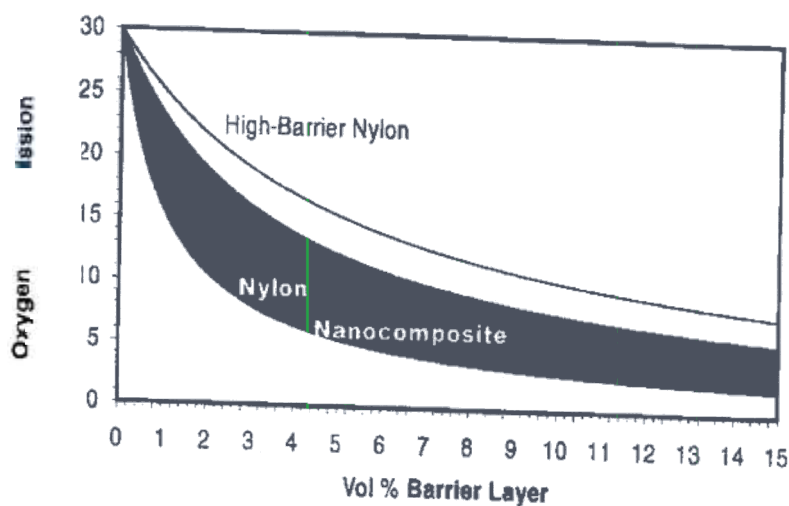


Figure 9B Plots of whole-bottle oxygen transmission rate versus vol % barrier layer consisting of a high-barrier nylon and nylon nano-composites containing 1-3 wt% silicate (ash). The data were measured on 0.5L, 29g, three-layer bottles comprising the barrier material in the centre layer [ref. 3].

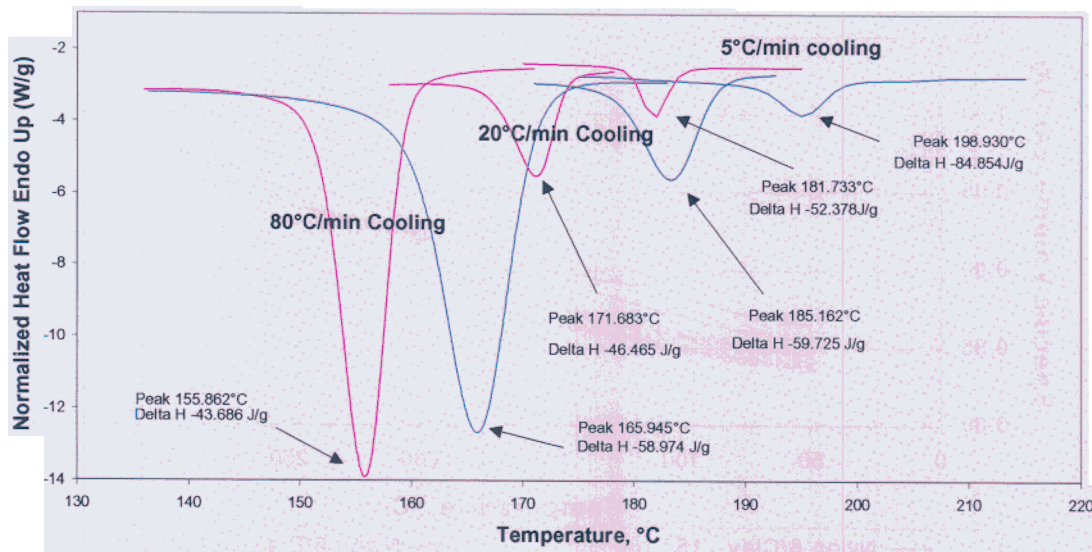


Figure 10 DSC test data of nylon 6 unfilled (blue) and nano-clay filled (pink) materials at 5°C/min, 20°C/min and 80°C/min cooling rates.

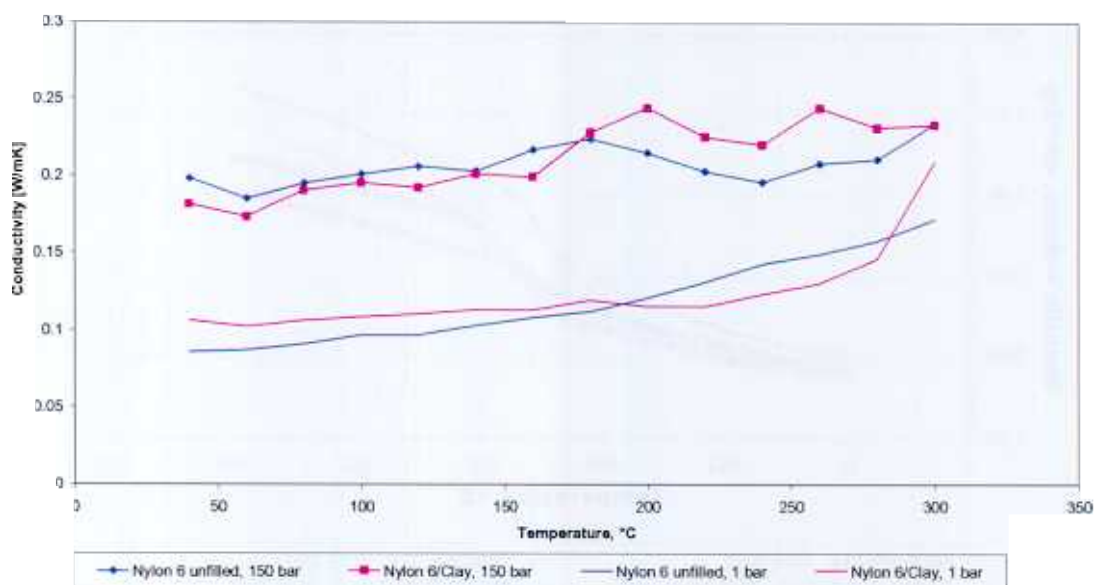


Figure 11 Thermal Conductivity data of unfilled and nano-clay filled nylon 6 at 1 bar and 150 bar.

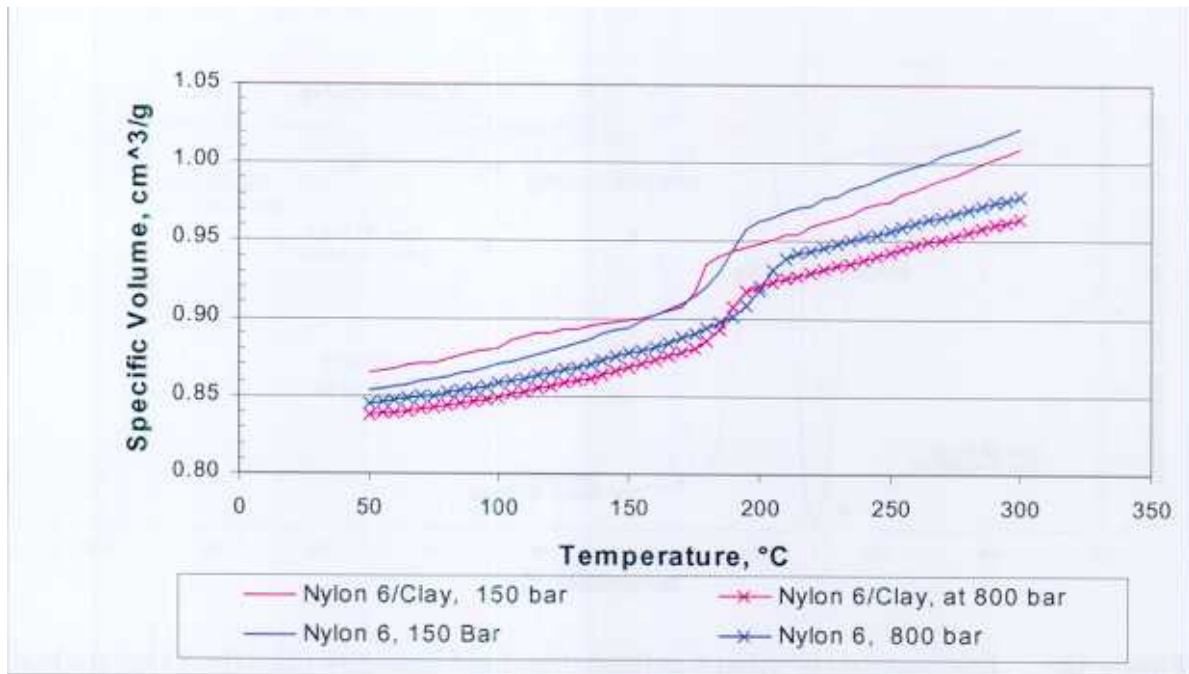


Figure 12 Iso-baric PVT test data of unfilled and nano-size clay filled nylon 6 at 5°C/min cooling rate at 150 bar and 800 bar.

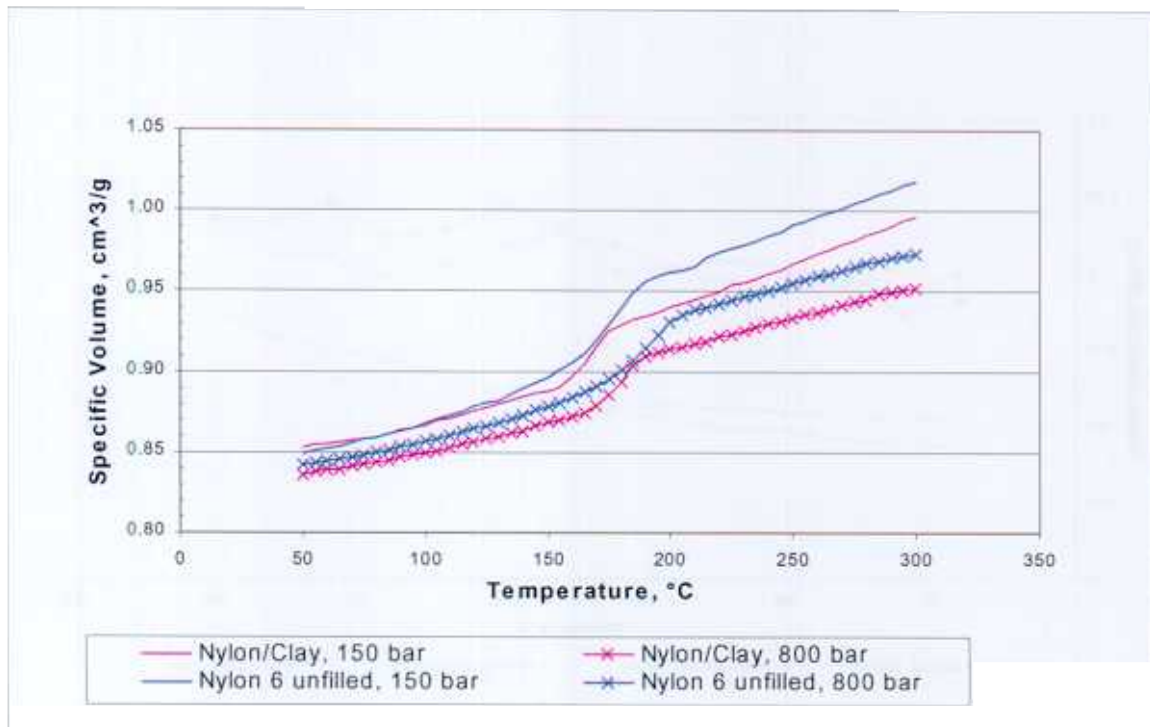


Figure 13 Iso-baric PVT test data of unfilled and nano-size clay filled nylon 6 at 20°C/min cooling rate at 150 and 800 bar.

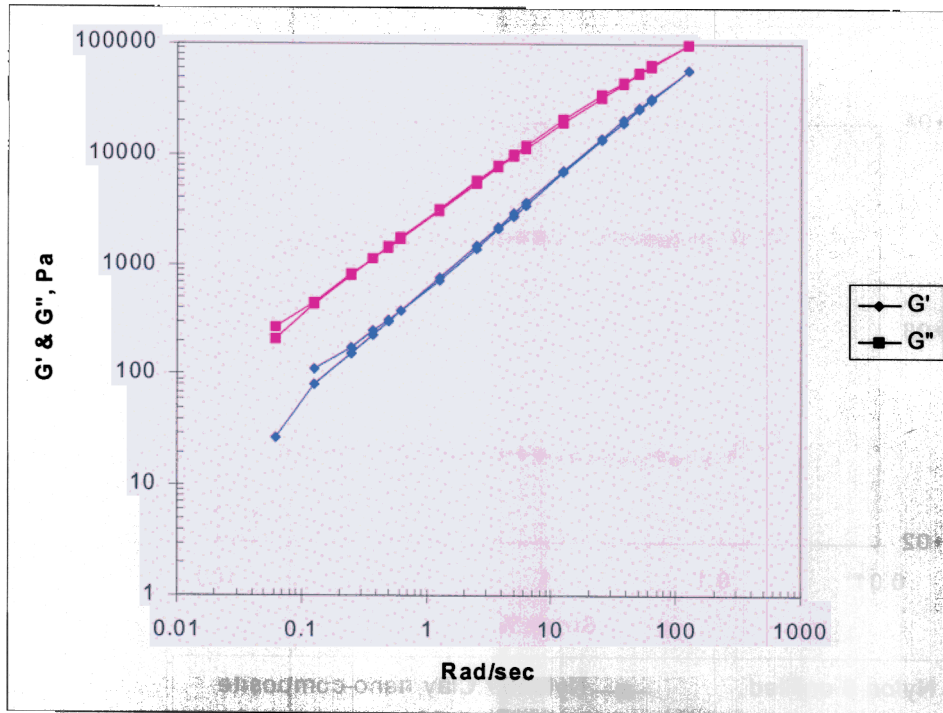


Figure 14 Rheological study of nylon 6/clay nano-composite at 240°C.

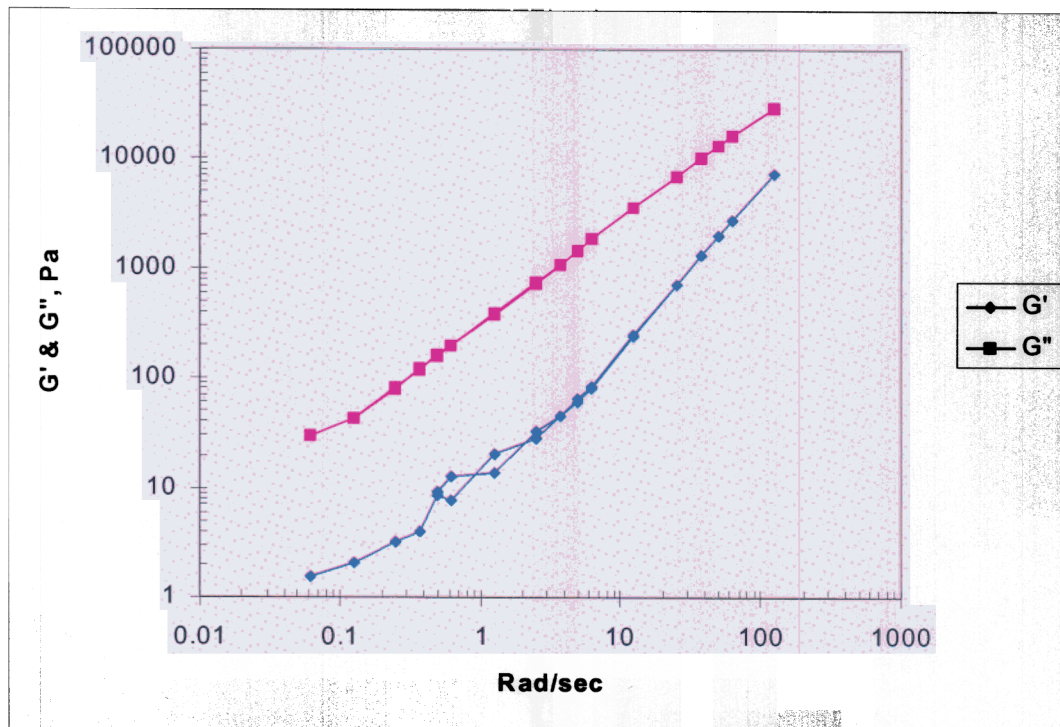


Figure 15 Rheological study of unfilled nylon 6 at 240°C.

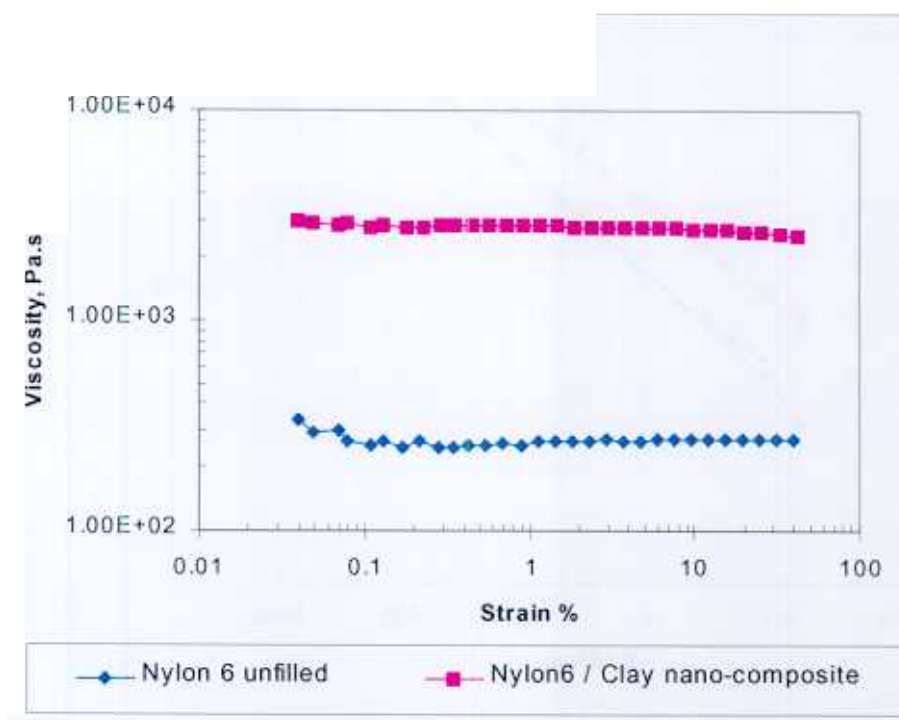


Figure 16 Viscosity data of unfilled and nano-size clay filled nylon 6 at 240°C.