Some issues on toughening, fire retardancy, and wear/scratch damage in polyamide-based nanocomposites

S.-H. Lim, A. Dasari, Z.-Z. Yu and Y.-W. Mai

Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronic Engineering (J07), The University of Sydney, Sydney, NSW 2006, Australia
Tel: +61-2-93512290; Fax: +61-2-93513760; E-mail: ymai@usyd.edu.au

Abstract: Addition of small percentage of nanoclay layers to polymers significantly improves many of their mechanical, physical and transport properties. Despite these improvements, some issues remain with the resultant nanocomposites and include concerns on fracture toughness, flame retardancy (and thermal stability), and scratch-wear resistance. It is the inadequacy of these specified properties that has curtailed potential applications of this class of new materials. Here, we present the efforts and approaches that were made to understand some facets of these issues in achieving a balance between different mechanical and physical properties, with particular emphasis on our recent and current research findings.

Keywords: clay, flame retardancy, nanocomposites, scratch, toughness, wear.

1 Introduction

The great interest generated for micro-composites in scientific and structural applications have finally led to the limits of optimizing composite properties, because the properties achieved usually involve compromises. To overcome the drawbacks from these traditional reinforcements, nano-scale fillers were introduced - where the filler is < 100 nm in at least one dimension. Significant improvements in various mechanical, physical, functional, barrier and transport properties of polymers are realized with the addition of even low loadings of nano-fillers (<5 wt %) [1, 2]. In general, three major characteristics define and form the basis of performance of polymer nanocomposites:

(i) Nanoscale inorganic constituents and their variation in properties from micron-scale fillers: Distinct differences exist between nano- and micro-scale or bulk material properties. Many studies have reported that conductivity, optical, magnetic, electronic, biological (anti-microbial) and even mechanical properties of several inorganic nanoparticles significantly change as their size is reduced from macro-scale to micro- and nano-levels. In some cases, it has been shown that nanoparticles are more active than their traditional counterparts since they have higher percentages of atoms on their surfaces [3].

(ii) Nanoscopical confinement of matrix polymer chains: This characteristic feature of nano-scale fillers is important for better interfacial interaction between them and the matrix polymer and enhanced nucleation capability. That is, nano-fillers restrict the mobility of the polymer chains in their vicinity and thereby affect the overall matrix rigidity (particularly with rigid fillers).

(iii) Nanoscale arrangement of these constituents and creation of large volume of interfacial polymer: The nano-level dispersion of fillers in the polymer matrix and huge interfacial areas provide an opportunity for fine tuning their surface properties, and thereby a potential to tailor various required properties for different end applications. For example, chemically attaching a small amount of bromine on the ammonium cation of clay layers or modifying clay layers by phosphonium to improve the fire performance of polymer/clay nanocomposites [4].

Full exploitation of these fundamental characteristics of nano-reinforcements in polymers facilitates the achievement of enhanced multi-functional properties. Polymer-clay nanocomposites originated from pioneering research conducted at the Toyota Central Research Laboratories in late 80s and early 90s, where the replacement of inorganic exchange cations in the galleries of native clay was effected using alkylammonium surfactants that compatibilized the surface chemistry of nano-clay and the hydro-phobic polymer matrix. This concept was later expanded to many polymers and enhanced properties obtained. But there are still some issues on toughness, flame retardancy (and thermal stability), and scratch/wear response of the resultant nanocomposites, and/or achieving a balance between different properties, which require in-depth understanding. We have made several efforts [5-15] to clarify and understand certain facets of these critical issues, some of which are outlined below.

2 Deformation and toughening mechanisms

It is generally accepted that the major contribution to toughness of polymers comes from the plastic deformation mechanisms. It is important to note that the material adjacent to the crack-tip is usually under plane-strain condition and is therefore subjected to high plastic constraint. Without a constraint relief mechanism, the material under this triaxial stress tends to brittle failure with a low toughness. In polymer/rubber binary blends, cavitation of rubber particles occurs, releases the high plastic constraint and initiates large scale plastic deformation of the surrounding matrix material. While there are a few studies [16, 17] that show significant increases in the fracture toughness of some binary polymer/clay nanocomposites via initiation and development of a large number of microcracks due to delamination of clay layers and increase of fracture surface areas caused by crack deflections, the majority studies have shown toughness drops. This is particularly true when clay was well exfoliated in the matrix since it is believed that the presence of a stiff nano-filler will hinder the mobility of the surrounding chains, and thus limiting its ability to undergo plastic deformation. To clarify and understand the role of clay layers and their constraint effect on the adjacent polymer matrix, we have investigated the influence of preferentially organized lamellae in the vicinity of clay layers on the toughening processes [7]. It was shown that the crystalline lamellae are aligned normal to the lateral interface (on both sides) of each clay layer and matrix, and closely organized to each other depending on the orientation of clay layers. These preferentially organized layers are around 30-40 nm (including both sides) for each clay layer (Figure 1a) and confirm that nucleation occurs at the silicate surface during crystallization of the polyamide matrix. Hence, as the inter-platelet distance is smaller, the entire lamellae in the region are highly constrained. In the same way as rubber cavitation is a necessary condition for matrix shear yielding to impart high toughness to polymer/rubber blends, full debonding at polymer/clay interfaces is an essential factor for effective toughening in polymer/clay nanocomposites so that shear yielding of large volumes of matrix material may be promoted. However, owing to the strong tethering junctions between individual clay layers (if they are well-dispersed) or the outermost surfaces of clay layers (if intercalated) and matrix, full-scale debonding at the clay-matrix interface is rarely seen in plastically deformed samples indicating that the constraint on the polymer has not been relaxed (Figure 1b). The delamination increased the interlayer distance (due to movements of clay layers), hence dissipating energy in deforming the polymer inside the intra-gallery and the transcrystalline lamellae that are firmly bonded to the outermost surfaces of the clay particle. As the extent of delamination was limited and no debonding of clay layers was observed, which were necessary for creating free volume in the matrix, the material failed in a brittle manner.
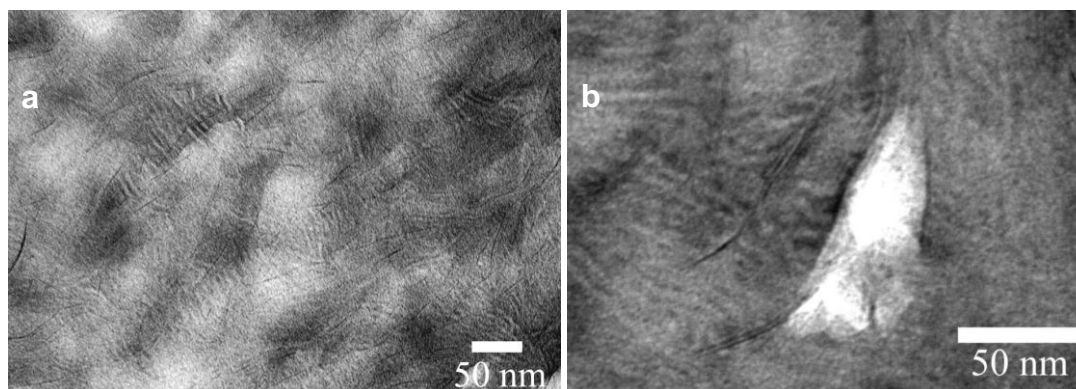

Figure 1. TEM micrographs taken in the core region of injection-molded polyamide 6/organoclay nanocomposite (90/10) along a plane normal to flow direction **a** showing preferential organization of lamellae in the vicinity of clay layers; and **b** subjected to a tensile extension of 60% indicating the existence of transcrystalline layers even after delamination.

To tackle this problem, ternary nanocomposites have been developed by adding a soft elastomeric dispersed phase to polymer/clay systems. Although several studies were reported based on this approach, e.g. [18, 19], only one mixing sequence was employed to melt-compound the ternary nano-composites. Recently, we have prepared polyamide 66/organoclay/maleic anhydride grafted styrene-ethylene/butylene-styrene triblock copolymer (SEBS-g-MA) (80/5/15) ternary nanocomposites using four different blending routes [5, 6]. Distinct differences in microstructures were observed depending on the processing sequence, which in turn controlled their mechanical properties, particularly, modulus and fracture toughness. More significantly, depending on the blending sequence, as polyamide 66 is

more polar than SEBS-g-MA, silicate layers were well dispersed in the former, whereas thick platelets of clay were evident in the latter. Nevertheless, if binary nanocomposite was prepared first and then blended with rubber, most of the clay would be present in polyamide matrix with good dispersion and distribution. In brief, based on the fracture mechanisms and mechanical properties it was shown that the presence of organoclay in SEBS-g-MA phase and the two-time extrusion of SEBS-g-MA made the latter more rigid and reduced its ability to cavitate, ultimately lowering the toughening efficiency. The presence of maximum percentage of exfoliated clay in the continuous matrix improved the stiffness of the nanocomposite. But it has a negative influence in significantly improving the fracture toughness as it constrains the matrix mobility and restricts the yielding. To address this issue and to obtain superior toughness and minimum reduction in stiffness/strength, polyamide 6/organoclay nanocomposites were prepared by incorporating polyethylene-octene elastomer grafted with maleic anhydride (POE-g-MA) as a toughening agent [9]. When organoclay and POE-g-MA particles are added to polyamide matrix by simultaneous (or two-step) blending, both organoclay layers (intercalated) and POE-g-MA particles are dispersed separately in the matrix and there is no evidence of organoclay layers present in the POE-g-MA particles. The results (Figure 2a) reveal significant improvements in fracture toughness of the ternary nanocomposites with increase in POE-g-MA content. G_C values are for neat polyamide 6 and polyamide 6/organoclay binary nanocomposite. The latter satisfies the specimen thickness requirement for valid G_{IC}. J_C values for polyamide 6/POE-g-MA binary blends; and polyamide 6/POE-g-MA/organoclay ternary nanocomposites are not J_{IC} values since the specimen thickness requirement given in the ASTM standard is not met. TEM analyses of the deformation features from single-edge-double-notch four-point-bend (SEDN-4PB) specimens revealed the internal cavitation of POE-g-MA particles along with craze-like damages consisting of line arrays of expanded voids in both the un-reinforced and organoclay reinforced polyamide 6/POE-g-MA blends, followed by severe matrix plastic deformation at the crack-tip region. A schematic of these processes in the sub-critical damage zone around the crack-tip is shown Figure 2b. It is this plastic work that mainly contributed to the drastic enhancement of fracture toughness of the ternary nanocomposites, besides the energies absorbed in cavitation and stretching of rubber particles, and the delamination of clay layers.
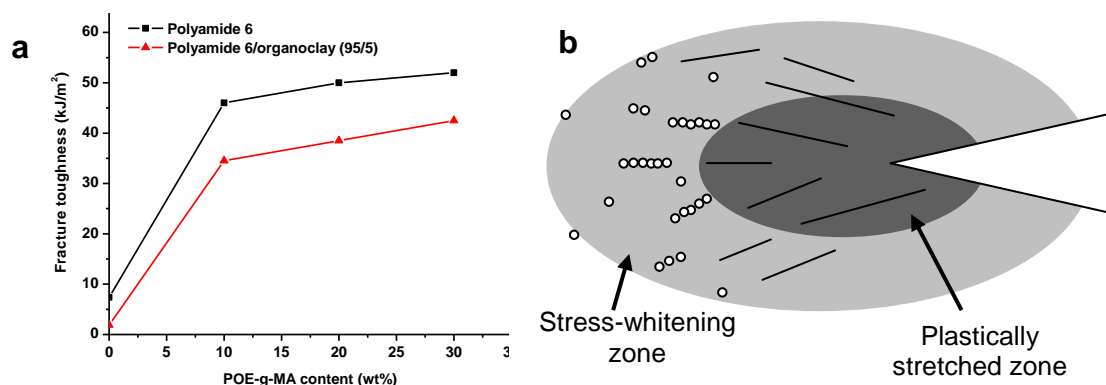

Figure 2. *a* Effect of POE-g-MA loading on quasi-static fracture toughness of nylon 6 blends and nanocomposites; and *b* schematic of the deformation processes in a ternary nanocomposite showing arrays of voids (croids) and plastic zone around the crack-tip region.

Based on our studies, it is found that the level of toughness enhancement of ternary nanocomposites depends on: (a) the location and extent of dispersion of organoclay, and (ii) the internal cavitation of rubber particles leading to effective relief of crack-tip tri-axial constraint and thus activating the matrix plastic deformation.

3 Time-temperature yielding behavior

Polymers are viscoelastic, and hence their tensile stress-strain behaviors are temperature and strain rate dependent. The tensile stress-strain responses and corresponding deformation mechanisms are even more complicated when another component is incorporated. Despite the requirement of thorough knowledge on their time-temperature yielding behavior, unfortunately, there is little information available on this topic of polymer nanocomposites. Thus, to gain an understanding of the tensile yield deformation behavior of polymer nanocomposites, we have conducted tensile tests on polyamide 6/ organoclay nanocomposites, with and without POE-g-MA rubber particles, over a temperature range below the glass transition and at strain rates of 10^{-4} to 10^{-1} s^{-1}. It was shown that the yield strength

varied with temperature and strain rate which could be described by Eyring's equation thus providing results on activation energy and activation volume for the physical mechanisms involved in these processes. Below the glass transition, the incorporation of organoclay layers drastically reduced the activation parameters of polyamide 6 from 1.70 nm^3 to 1.15 nm^3, hence providing further affirmation of the constraint effect of nano-reinforcement in the matrix. With the addition of 20 wt% POE-g-MA in the binary nanocomposite, the molecular mobility hindrance induced by organoclay layers was offset and the activation parameters were restored.

In addition, tensile dilatometry technique was employed to characterize their tensile deformation mechanisms in order to differentiate the dilatational processes (voiding/debonding due to organoclay and rubber particles or matrix "croids") and shear yielding (due to matrix with zero volume change). Dilatometric response indicated that neat polyamide 6 yielded by shear in tension as there was no increase in volume strain measured (Figure 3). The presence of organoclay layers changed the tensile yield deformation behavior of polyamide 6 matrix from deviatoric-dominant to dilatational-dominant plasticity. In polyamide 6/organoclay/POE-g-MA ternary nanocomposite, the volume strain response indicated that shear deformation was the predominant mechanism at yield and subsequently extensive dilatation took place in the post-yield region leading to stress-whitening and uniform extension of the specimen without any localized necking, which was a characteristic of neat polymer.
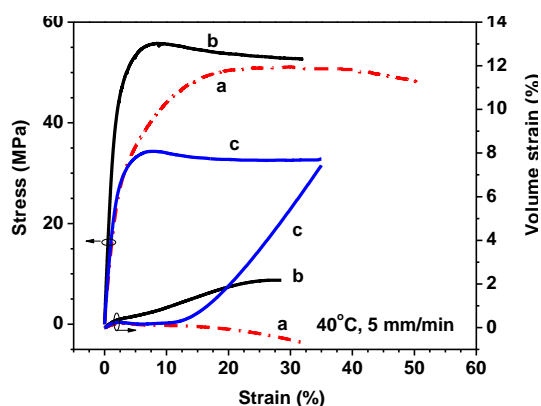

Figure 3. Stress-strain curves of neat polyamide 6, its binary and ternary nanocomposites plotted along with their volume strain responses at 40°C and 5 mm/min (**a**: neat polyamide 6, **b**: binary, and **c**: ternary nanocomposite).

TEM analyses revealed the formation of submicron and nano-voids at some locations in-between the stacked organoclay layers due to the weak interaction between the stacked clay layers in the binary nanocomposite. This phenomenon was attributed to the increase in volume strain measured from the tensile dilatometry test. While in the ternary nanocomposite, cavitations of POE-g-MA particles in line arrays (resembling the craze-like deformation structure) was noted to be the predominant dilatational deformation mechanism which contributed to the volume increase.

4 Flame retardancy

The use of polymers in various fields is always associated with fire hazards that are detrimental to the environment and human life. Even though complete protection against fire by the use of polymers for indefinite periods is impossible, the use of fire-retardant materials can delay the fire spread or keep a structure intact against fire, thus allowing sufficient time for safety measures to be taken. To improve the fire properties of a polymer, the most common approach is to add phosphorous and halogen-based flame retarding agents. These compounds, depending on their nature, act chemically and/or physically in the solid, liquid, or gas phase and interfere with combustion during different stages of the process. These conventional flame retarding agents, despite their beneficial performance, generate corrosive and toxic combustion products, like dioxins and furans. Hence, much attention was diverted on using layered silicates as flame retarding agents in different polymers. Even at low loadings of silicate, with no additional flame retardants in the system, the heat release and mass loss rates were greatly reduced in addition to the huge delay in burning compared to corresponding neat polymers, for example, see [20]. The reduction in peak HRR is an important parameter signifying fire safety, as it represents the point in a fire where heat is likely to propagate further (flame spread) or ignite adjacent objects. It was shown that the structure of the nanocomposite collapsed during combustion and a

multilayered carbonaceous-silicate structure was formed on the polymer surface that insulated the underlying material from the heat flux of the flame and also acted as a mass transport protective barrier by reducing the mass transfer between gaseous and condensed phases. Other mechanisms which lowered the peak heat release rate of polymer in the presence of clay were also reported and included: (a) radical trapping effect by paramagnetic iron within the clay, (b) chemical cross-linking of decomposing polymer induced by clay due to long residence times for polymer radicals and some catalytic capability of clays to aromatize hydrocarbons, and (c) at higher temperature, the inorganic additive's ability to act as a radical scavenger due to adsorption to Lewis acid sites. This may interrupt the burning cycle as radical species are needed to break down the polymer chains into fuel fragments. Nevertheless, the total heat released was almost similar to the neat polymers as the nanocomposites did not self-extinguish until most of the fuel was burnt, i.e., they burnt slowly but completely. It was also shown that in almost all studies on polymer/clay nanocomposites, the clay layers tended to develop large lateral surface cracks in which vigorous bubbling still occurred. This is a plausible reason why these materials by themselves are unable to meet the existing requirements of the ignition resistance tests (e.g., vertical burning UL94) and hence, many researchers have included additional conventional flame retardants, like phosphorous or bromine in their systems. Therefore, the original concerns of eco-friendliness recur. It is hence necessary to obtain a better physical understanding of the formation and stability of protective barriers under fire conditions so as to develop environmentally benign and superior flame retardant polymer/layered silicate nanocomposites. It is also necessary to understand whether elimination of major cracks in the char is enough to improve the fire performance or if other mechanisms need to be operative or if additional conventional flame retarding agents must be added?

To address these specific questions, we have prepared highly filled nanoclay (10, 20 and 30 wt%)/ polyamide 6 composites and characterized their thermal and flammability properties to identify a critical composition that is needed to form a stable char with no apertures or cracks and to understand the physical flame retarding mechanisms [11]. TEM observations indicated that the clay layers at all loadings are well dispersed, finely distributed, and oriented with their planar dimensions along the injection molding direction. It is noted that in all reported studies on flame retardancy of polymer/clay nanocomposites, analysis of combustion chars from XRD revealed that the interlayer spacing was 1.3 nm for all matrices (thermoplastics or thermosets) and nanostructures of the original nanocomposites (exfoliated or intercalated), inferring the same nature of the residue. Nevertheless, the fine dispersion of clay layers in a polymer matrix is important for improvements in many physical and mechanical properties and is possible by modification with organic surfactants. The main disadvantage of this process is that these low molecular weight alkyl ammonium surfactants are thermally unstable and decompose usually from ~200 ^{o}C which is lower than the processing temperature of most engineering polymers and thus adversely affects the thermal stability. This was clearly observed in our study; the dispersion of clay layers or its loading in polyamide 6 did not have any positive effects on the thermal stability of polyamide 6 implying that the barrier properties of delaminated clay layers are not the primary determining factors of thermal stability. Instead, organoclay containing materials decomposed earlier than neat polymers. The continuing effect of this was reflected on the ignition times during fire (cone calorimetry) testing where the ignition of nanocomposites (~57, 55 and 51 s for 10, 20 and 30 wt% organoclay loadings, respectively) occurred earlier than neat polyamide 6 (~66 s). This seems to the first drawback of flame performance of polymer/organoclay nanocomposites. Despite the early ignition, nanocomposites showed significantly reduced heat release rates (and peak HRR) compared to neat polyamide 6 and among the nanocomposites there seems a slight reduction of heat release rates with increasing organoclay loading, but the differences are not significant. However, the total heat released per unit area is somewhat higher (due to the presence of organic surfactant) than the neat polymer. This clearly suggests that the nanocomposites does not self-extinguish even after a protective char is formed (see below) until most of the fuel has been burnt out. The mass loss rate curves of all the samples are also proportional to the heat release rate curves.

As expected, the neat polymer completely melted and no residue was left behind at the end of the test. In the presence of organoclay, at low loadings, many discrete island-like structures (with many large cracks) were observed (Figure 4a). In contrast, at higher loadings, the residues appeared to be solid-like and continuous (Figures 4b and 4c). Also, as mentioned before, wide-angle XRD analyses on the collected residues of nanocomposites revealed that the delaminated/exfoliated nanostructures of clay present prior to burning collapsed in all cases irrespective of the loading giving an interlayer spacing ~1.3 nm suggesting that this spacing is a thermodynamically stable form of the clay-carbon

material (0.7 nm being the thickness of an individual clay layer and 0.6 nm corresponding to the carbonaceous layer intercalated within the clay layers) produced by thermal degradation.

Figure 4. Photographs of combustion residues for **a** 10; **b** 20; and **c** 30 wt% organoclay in polyamide 6 matrix.

TEM examinations (on cross-sections beneath the surfaces of residues) indicated that in all the materials, large empty spaces below the surface of multi-layered structured barrier are seen (Figure 5). This is attributed to the carbonaceous matter left behind the degradation products, which also suggests that the silicate layers after exposing to flame are not reinforcing the whole char (except for some regions). At 10 wt.% of the rigid phase, although the prevalence of a protective-silicate char at the surface is seen, it is very thin ($\sim$0.2-0.4 μm), non-uniform, and broken. This clearly implies that the migration of all the clay layers from within the sample to the burning surface has not taken place or the rising bubbles may have pushed most of the silicate layers out of the sample. At 20 and 30 wt% organoclay loadings, the thickness of the protective barriers increased ($\sim$1-1.3 μm and 1.8-2.0 μm, respectively). However, the packing of layers is not perfect and openings are seen at 20 wt% of loading; while at 30 wt% organoclay, the protective silicate-rich layer was heavily packed, continuous and uniform. In addition, high magnification TEM micrographs of the protective barrier clearly revealed the well-ordered multi-layered arrays of silicate-carbonaceous structure formed after combustion. Despite the uniformity, thickness and stability of the protective layer at 30 wt% organoclay, there was no stage during the experiment where the fire completely extinguished until most of the fuel was burnt. This indicates uninterrupted supply of oxygen to the burning substances underneath the protective char; it also means uninterrupted diffusion of decomposition products to the ambient. Thus, the results suggest that we do not need higher percentages of clay and even smaller loadings of clay (<10 wt%) should be enough to achieve significantly delayed heat release and mass loss rates. Factors such as incoherency, poor stability, and non-uniformity of the char or presence of large cracks are insignificant in slowing down the heat release and mass loss rates. Ideally, for most effective flame retardancy performance, it is beneficial to have a situation where most of the high aspect ratio clay layers quickly migrate to the burning surface of the polymer from inside, with effective coupling between adjacent layers, and not having any apertures (not even finer ones) to fully shield/protect the polymer melt. Also, the protective layer should be densely packed so that it has sufficient physical strength not to be broken or disturbed by bubbling.

Figure 5. Low magnification TEM micrographs of cross-sections beneath the top surfaces of combustion residues of polyamide 6 nanocomposites with **a** 10; **b** 20; and **c** 30 wt% organoclay.

So, to realize superior flame retardancy performance of polymer/clay nanocomposites, efforts should be made towards:
(a) replacing conventional alkyl ammonium surfactants - several efforts were directed towards this aspect and included using thermally stable (like aromatic compounds) surfactants or nitrogen-based compounds and water-assisted approach. Thermally stable surfactants decompose at higher temperatures than conventional alkyl ammonium surfactants and improve fire performance of polymer/

clay nanocomposites. Nitrogen-based compounds, in contrast, produce nitrogen gas during thermal decomposition and improve the self-extinguishing properties of nanocomposites; the idea is to stop a fire by blocking oxygen intake, i.e., replacing air by nitrogen and creating an almost inert atmosphere, where the fire would inevitably extinguish. In water-assisted approach, as the name suggests, water is used as a substitute to organic agents. The underlying concept is that water is both a powerful swelling agent for pristine clay and a natural plasticizer of polyamide and hence, would assist the intercalation/exfoliation of clay layers in the polyamide matrix and improving its thermal stability. Based on this concept, we have prepared polyamide 6/clay nanocomposites where the clay layers were finely dispersed even without using any organic surfactants [10]. The degradation temperature of the final nanocomposite is higher than conventionally prepared organoclay nanocomposite (Figure 6) proving the advantage of nanocomposites based on clay which does not contain alkyl ammonium surfactants.
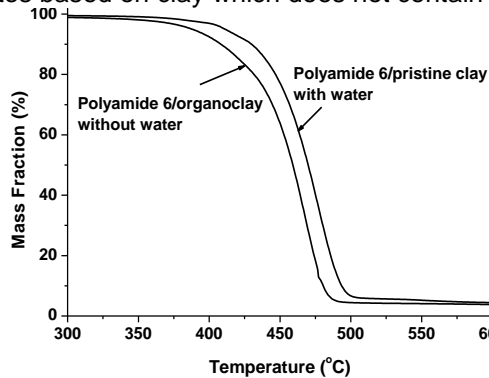

Figure 6. Thermogravimetric analysis (TGA) curves for polyamide 6/clay nanocomposites (95/5) prepared conventionally and with the aid of water.

(b) improving the coupling of silicate layers upon fire;
(c) having a second layer of defense with another additive apart from silicate layers; and
(d) improving the migration of clay layers to the burning surface upon fire.

5 Wear/scratch characteristics and mechanisms

Apart from the above-mentioned characteristics of polymer nanocomposites, it is a 'must' that a material irrespective of where and under what conditions of usage should be resistant to scratch/wear damage, which can occur due to airborne particles, road gravel, and during cleaning operations or handling. For efficient and effective functioning of materials, it is thus necessary to reduce material damage and material removal; and in some cases of precision engineering, to have control on the extent of material removal. However, as polymers are highly sensitive to scratch/wear damage, they exhibit various modes of deformation even within a narrow range of contact variables (slider geometry, applied normal load, slider velocity, interfacial lubrication, and testing temperature). Besides, there is always an overlap of different mechanisms in any particular contact process and any combination of the different mechanisms may represent the actual situation. This in turn confirms the complexity of wear/scratch damage in polymers and limits their applications.

In the past decade, many studies were reported on wear/scratch damage in polymers filled with different nanoparticles and in most cases, improved wear/scratch properties were achieved and attributed to the presence of nanoparticles themselves or to the improved mechanical properties like modulus and hardness or to the formation of transfer films on the slider contact surface. Despite these positive effects, there are still some critical questions that are yet unanswered in relation to the scratch /wear response of polymer nanocomposites. These include, what are the relations between residual depths (or wear rate), material deformation and wear damage? Is modulus/hardness the primary parameter in determining scratch depth or wear rate? Does the presence of dispersed nanoparticles by themselves result in enhanced tribological properties? In addition, few efforts have been made to model stress fields induced by different slider geometries and hence, no explicit correlations between material parameters and wear/scratch damage for polymer nanocomposites are available to date. We have made several efforts to clarify and understand several aspects of these issues, some of which are briefly described here.

As mentioned in the previous section, exfoliated polyamide 6/clay nanocomposite prepared with the aid of water has good thermal stability compared to conventional organoclay nanocomposites. But it

exhibits relatively poor wear resistance [13]. It was shown that exfoliation or homogeneous dispersion of nanoparticles with improved elastic modulus and hardness are not enough for improvement in wear resistance; interfacial interaction of clay layers to matrix and other material characteristics are crucial. This is necessary as the load applied on the composites is mainly transferred to the fillers via the interface. Also, exfoliated clay morphology is preferred to aggregate morphology as inhomogeneous distribution and dispersion of particles resulted in extensive material loss due to disintegration/ crumbling of the particle agglomerates. Subsurface TEM analyses beneath the wear track showed that voids were initiated either from within the intra-galleries or due to interfacial debonding at weak interfaces and also from inside large clay aggregates where delamination occurred. It was believed that this subsurface damage will extend and detach to form wear debris caused by repeated sliding of the hard counterface asperities on the soft composite surface resulting in abrasive damage in the form of intense plowing on the wear tracks. Thus, it is important to understand the effects of microstructural homogeneity and/or interfacial interactions in polymer nanocomposites for better understanding of the tribological properties. Further, our studies of wear damage in epoxy/silica and polypropylene/calcium carbonate nanocomposites have revealed the importance of understanding the effects of organic surfactants used to modify the nanoparticles during the wear processes, and the formation and role of transfer films in reducing wear damage [15]. These studies have shown that it is not always valid to assume that nano-fillers or the improved mechanical properties irrevocably improve wear (and friction) properties.

Even the nanoscratching results of polyamide 66-based ternary nanocomposites (whose fracture mechanisms are outlined in Section 2) have revealed that modulus and hardness or scratch depth are not the only factors that should be considered [14]. Instead several aspects of wear/scratch processes like the morphology of the surface and subsurface materials in the wake of the moving indenter require thorough understanding to assess the parameters that control surface integrity and material removal from the polymer nanocomposites. It was shown that the presence of exfoliated clay in polyamide matrix was important in resisting the scratch depth during nanoscratching (normal load ~1 mN, sliding speed ~1 μm/s, Berkovich indenter); however, the results also explained the preferred usage of ternary nanocomposites compared to binary polyamide 66/exfoliated clay nanocomposite and polyamide 66/SEBS-g-MA blend. Enhanced plastic flow and deep grooves (~390 $\pm$ 19 nm) were associated with the nanoscratch in the soft SEBS-g-MA/polyamide 66 blend (Figure 7a). In contrast, brittle cracks occurred in polyamide 66/clay nanocomposite (Figure 7b) even though the residual depth was smaller (~240 $\pm$ 8 nm). In the ternary nanocomposites, though no cracks were observed on the scratch tracks, if clay was least present in the rubber particles, TEM observations beneath the scratch track revealed that those rubber particles close to the scratch track experiences severe stretching, leading to rubber/matrix debonding or rubber cavitation. But the exfoliated clay in the polyamide matrix enhanced its resistance to scratch depth. Conversely, the absence of clay in the matrix made it easier to deform plastically under the indenter with the largest scratch depth. The rubber particles being stiffened by the clay were less able to deform or cavitate.
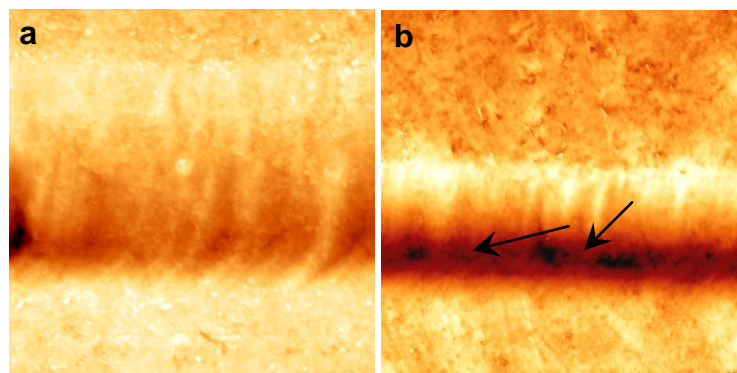

Figure 7. 2D AFM micrographs showing differences in nanoscratch behavior of binary *a* polyamide 66/SEBS-g-MA blend and *b* polyamide 66/organoclay nanocomposite at a field-of-view of 20 μm x 20 μm. The arrows indicate brittle cracks in the polyamide/clay system.

In addition to these results, in our most recent study on polyamide 6/organoclay nanocomposites, it was concluded that orientation and extent of exfoliation of clay layers are also important parameters influencing the extent of scratch damage [21]. Residual depths are lower for scratches performed on the cross-sections (normal to the flow direction) of the nanocomposites when compared to those on

the surface (parallel to the flow direction). This suggests the importance of proper physical and spatial characterization of nanocomposites, that is, while orientation and dispersion of clay layers are independent structural features, they must be simultaneously considered in determining the effective structural reinforcement in polymer/clay nanocomposites; otherwise, the results can be misleading if only dispersion or orientation of the structures is considered. TEM images taken from the cross-section beneath the scratch track also revealed the formation of sub-micron to nano-cracks that are associated with the clay layers (Figure 8b). Cracks initiated and grew downwards from the contact edges. The shear-stress dominant region of the scratch subsurface generated by internal sliding friction can easily result in debonding between phases or cracking. Owing to the weak electrostatic interactions between clay interlayers, intra-gallery delaminations of clay platelets occur wherever more than one platelet is stacked under the prevalent stress conditions. More interestingly, under large normal loads of 60 mN clay layers are reoriented from nearly parallel to the sliding direction before scratching (Figure 8a) to an angle with the contact zone (Figure 8b). This is possible under large loads as the scratch grooves are formed beneath the indenter and so the clay platelets must also rotate with the plastically deformed matrix polymer. This is unlike in micro-composites like carbon fiber/polymer, where extensive cracking of fibers is observed and with no rotation of fibers in the subsurface [22]. But the rotation of nanoclay layers suggests that they are able to actively participate in the mechanical response of the matrix polymer under an applied stress field.
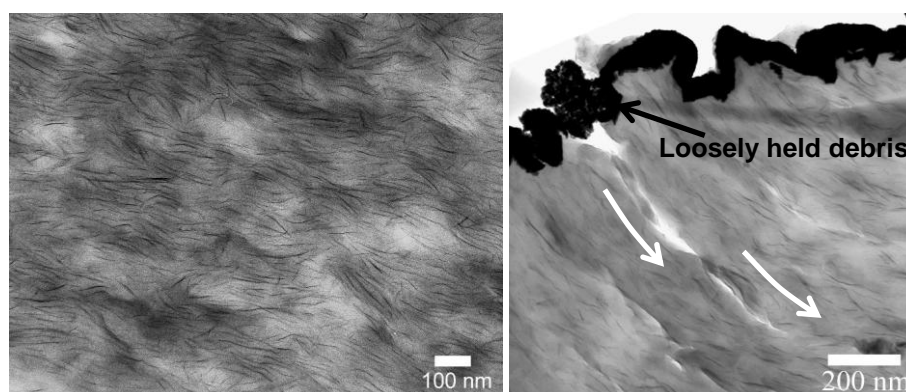

Figure 8. TEM micrographs showing orientation of clay layers in polyamide 6/organoclay nanocomposite (90/10) *a* before and *b* after scratch damage (60 mN of normal load).

It brief, it is important to have a good knowledge of the role of nanoscale additives in different polymers to avoid trade-offs amongst different physical and mechanical properties that are required for the intended applications. Especially, (a) the chemistry and chemical reactions that may occur between the two mating surfaces, (b) the influence of the by-products that may result from these reactions or during the wearing process, (c) the role of these reactions in promoting/stabilizing the film on the counterface, and (e) quantitative understanding of nanoparticle dispersion and orientation, filler/matrix interface interactions, and transfer film properties.

6 Summary

It is evident that polymer/clay nanocomposites have the potential to achieve significantly improved mechanical/physical properties, or any combination thereof, despite several critical issues identified here if the fundamental characteristics of nano-clay (high aspect ratio, large specific surface area, and substantial cation exchange capacity) in polymers can be fully exploited. Hence, their basic structure-property relationships must be thoroughly studied. Poor characterizations of polymer nanocomposites and lack of quantitative descriptions of observed phenomena will often lead to apparent contradictions and misleading impressions on the material systems.

7 Acknowledgements

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