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Impact and tensile energies of fracture in polymer–clay nanocomposites

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ABSTRACT

Impact strength and tensile energy absorption of polymer–clay nanocomposites were measured using polymers that are glassy or rubbery at ambient temperatures. The results highlight the apparent contradictions that arise in these tests. Polystyrene, with initially low toughness, suffered a decrease in impact strength of 3% (notched) and 23% (un-notched) but the tensile energy at break increased by 120%. ABS suffered a catastrophic collapse of toughness in all three tests of up to 90%. A suggestion is that the arrangement of comparatively rigid mineral tactoids inhibits the toughening function of the rubbery zones. The use of poly(ε-caprolactone) showed that processing-induced degradation of surfactant did not significantly impair toughness. There is an emerging view that clay reinforcement is more effective with polymers above T_g but these results suggest that the interpretation of impact strength, a property highly rated by industrial users, is less easily explained.

1. Introduction

The ability of smectite clays to improve the stiffness, strength and resistance to permeation of gases and solvents when added at relatively low levels ($\sim$5 wt.%) to thermosetting and thermoplastic polymers has been well documented and reviewed [1–3]. The effect of clay additions on toughness, particularly toughness as measured by impact methods rather than elongation at break in a tensile test, is rather more uncertain, as often found in other materials [4]. High strain rate testing can change a ductile material to brittle [5] which is one of the reasons why impact testing can give quite contrary results to toughness inferred from tensile tests [4].

The early reports of nylon–montmorillonite nanocomposites, which still rank among the highest performance polymer–clay nanocomposites, indicated that impact strength was only slightly reduced compared with nylon unmodified by clay [6]. Later reports show a reduction for un-notched (Charpy) impact tests [7] and a number of other reports suggest that clay additions reduce the impact energy of polymers [8–11] in some cases even when the tensile elongation has been increased [11]. However there are a few reports of clay additions actually increasing the impact energy of epoxies [12–14]. There is a tendency for academic researchers to avoid the use of impact tests, perhaps because of their ambiguities; unstable crack growth, a wide range of energy sinks and ill-defined notch radius. However for industrial applications, impact strength is rated highly in the list of criteria for materials' selection. Indeed, many otherwise satisfactory plastics have a tendency towards brittle fracture under impact loading [4]. The well-documented property advantages that dispersed smectite clays can offer need to be accompanied by retention of impact strength. Table 1 gives a brief summary of some recent literature on impact testing of nylon–clay and epoxy–clay nanocomposites showing that toughness of epoxy composites can significantly increase with clay addition.

In this work we studied the toughness and morphology of polymer–clay nanocomposites focusing on a glassy polymer (polystyrene, PS), a PS-based toughened copolymer (acrylonitrile–butadiene–styrene, ABS) and a rubbery polymer easily processed at low temperatures (poly(ε-caprolactone), PCL). The same organoclay was used in each case. PS and PCL represent brittle and ductile categories while ABS represents one of the most successful attempts to toughen glassy polymers. The choice is made to inform recent claims that clay is effective in influencing toughness only if the matrix polymer is above T_g [15]. The argument is that clay platelets are sufficiently small, comparable in dimensions to the radius of gyration of the polymer chain, and sufficiently well attached to the polymer to be able to rotate and re-orient during deformation in a way that larger scale reinforcements, carbon or glass fibres, for example, cannot [16]. Commercial grades of PS, ABS and PCL were studied.

2. Experimental details

Polystyrene (Styron 634 with melt flow index (MFI) 0.35 g min^{-1} at 200 °C and 5 kg, $T_g = 90$–130 °C; manufacturer's data) and ABS (Magnum 3904 with MFI 0.5 g min^{-1} at 220 °C and 10 kg, $T_g = 90$–130 °C for the acrylonitrile–styrene phase; manufacturer's

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Table 1
Toughness data for nylon–clay and epoxy–clay nanocomposites from the literature

Material[a]	Impact strength (notched)/kJ m^{-2}	Reference
Nylon 6	33.7 J m^{-1}[b]	[8]
NCH5	22.8 J m^{-1}[b]	
Nylon 6	7.1	[9]
NCH10 exfoliated	3.2	
NCH10 intercalated	4.3	
Nylon 6	6.1	[10]
NCH4	3.4	
Epoxy	5.5	[12]
ECN0.5-Na	9.5	
ECN1-Na	7.2	
ECN0.5-30B	13.0	
ECN1-30B	10.5	
Epoxy	5.8	[13]
ECN1	9.6	
ECN3	9.1	
ECN5	7.2	
Epoxy	6.5	[14]
ECN7.7-exfoliated	7.2	
ECN15.5	7.3	

[a] NCH and ECN: nanocomposites, the number refers to the inorganic content in wt.% in the nanocomposite. Codes after the dash represent different clays.
[b] ASTM D256 used and thickness of sample not given.

data, −65 °C for butadiene) were obtained from Dow Chemicals (via Resin Express Ltd, High Wycombe, UK). Quaternary ammonium-treated montmorillonite clay (Bentone® 111, surfactant: benzyl dimethyl hydrogenated tallow ammonium halide [17]) was generously supplied by Elementis Specialities (Hightstown, USA). Natural sodium montmorillonite (type: BH natural) was kindly supplied by Blackhill Bentonite LLC (Wyoming, USA). Its composition includes 71.71% SiO_2, 17.13% Al_2O_3, 3.54% Fe_2O_3, 1.57% MgO, 2.31% CaO, 0.49% K_2O, 2.58% Na_2O, 0.15% TiO_2 and 0.52% others [18]. PCL ($\overline{M}_n = 80,000\ \text{g mol}^{-1}$ and $T_g = -50\ °\text{C}$ [19]) was from Sigma–Aldrich Chemicals, and poly(ethylene glycol) (PEG) ($M_w = 10,000\ \text{g mol}^{-1}$ and $T_g = -40$ to $-20\ °\text{C}$) was from VWR International. All the materials were used without further modification.

PS and ABS were mixed separately with the organoclay on a heated twin toll mill (Carter International, Rochdale, UK) to give an inorganic content of 4 wt.% in the nanocomposites, which is within the typical clay loading range for reinforcement in polymer nanocomposites, i.e. 1–5 wt.%. The mixture was stripped from the rolls and re-fed at least five times to ensure lateral mixing. The average processing temperatures were 170 °C and 190 °C for PS and ABS respectively. PCL–organoclay and PEG–natural clay nanocomposites with inorganic contents of 4 wt.% and 8 wt.% were prepared in the same way as above except their average processing temperatures were 110 °C and 90 °C respectively. These two clay loadings were chosen to prepare nanocomposites with (a) the same inorganic content as in PS–clay and ABS–clay composites and (b) a higher inorganic content to see if a regime of reduced impact energy could be found for higher clay additions. Some PCL and PCL–clay nanocomposites were annealed in an oven at 200 °C for 30 min to give the organoclay similar heat treatment to that experienced in styrene polymer processing. The amounts of organoclay and natural clay added to polymer melt during processing to give the specified inorganic contents were determined by the inorganic content in the nanocomposite divided by the inorganic content in the clay. The inorganic contents in the clay are 77.8 wt.% and 93.8 wt.% for Benton® 111 and the natural clay respectively from loss on ignition at 600 °C [20].

A Siemens D5000 X-ray diffractometer (40 kV, 40 mA) equipped with a graphite monochromator and with Cu$K\alpha_1$ radiation ($\lambda = 0.15406$ nm) was used for X-ray diffraction (XRD) of the composites. The scanning step was 0.02° with a scan time of 2.5 s per step.

Impact testing was carried out on a Zwick 5102 pendulum impact testing machine using a 0.5 J hammer or on a Zwick 5110 Charpy impact testing machine using a 2.7 J hammer for higher impact strength materials, and a 10.8 J hammer for un-notched ABS samples. The tests were conducted according to ISO 179, the blow direction of the hammer was edgewise. Test specimens with dimensions of 80 mm × 10 mm × 4 mm were prepared using an injection moulding machine (Ray-Ran Test Equipment Ltd, Nuneaton, UK) operated at 0.7 MPa. The barrel temperatures for PS, ABS, PCL and PEG were set at 200 °C, 220 °C, 110 °C and 90 °C respectively. In the case of notched samples, 2 mm-depth notches were prepared using a 45° cutter (Ray-Ran Test Equipment Ltd) at low speed on a milling machine. Seven specimens were tested for each condition.

Tensile tests were conducted on an Instron 5564 using a 1 kN load cell according to ASTM D 638M. An extensometer was fitted at low strains to obtain tensile moduli. The specimens were dog bone shaped with dimensions of Type III (60 mm × 10 mm × 4 mm). The rate of cross-head motion was $1\ \text{mm min}^{-1}$ (initial strain rate $1.4 \times 10^{-3}\ \text{s}^{-1}$) with the extensometer fitted, and $5\ \text{mm min}^{-1}$ ($6.9 \times 10^{-3}\ \text{s}^{-1}$) thereafter in the case of ductile specimens. All test specimens were moulded in the same way as for impact testing specimens. Six specimens were tested for each sample.

Field emission scanning electron microscopy (FE-SEM) on fracture surfaces was performed on a JEOL JSM6300F with an operating voltage at 10 kV. All the specimens were sputter-coated with gold.

Transmission electron microscopy (TEM) was conducted on a JEOL JEM 2010 electron microscope, operating at 200 kV. TEM specimens were prepared by ultramicrotoming pre-trimmed nanocomposite blocks with a diamond knife on a Reichert Om U2 microtome (Reichert Ophthalmic Instruments, New York) at room temperature to give sections with thickness less than 70 nm. The sections were transferred from water to 400-mesh copper grids.

3. Results and discussion

The PS–clay and ABS–clay nanocomposites were characterised using XRD and TEM, which gave confirmatory information about the nanostructure. Fig. 1 shows XRD traces of clay and its nanocomposites with PS and ABS. It is seen that 2θ of the (001) peak of the organoclay shifts to lower angles in both cases: from 4.5° to 2.6° and 2.9° for PS and ABS respectively. This corresponds to the increases of basal plane spacing d_{001} from 2.0 nm to 3.4 nm and 3.1 nm respectively, suggesting both PS and ABS form intercalated nanocomposites with the clay to some extent but, as explained

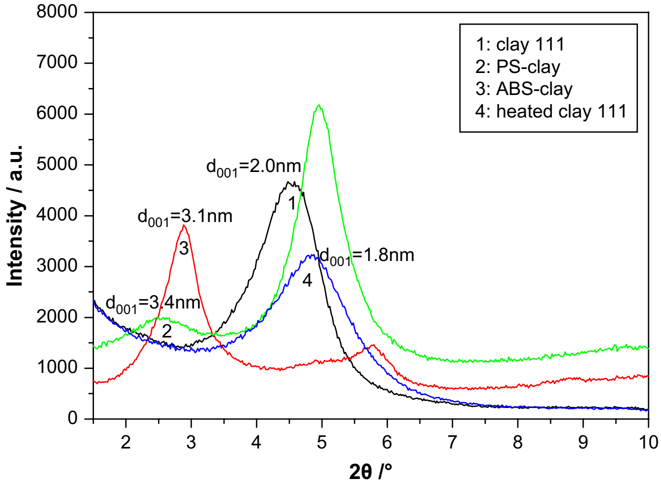

Fig. 1. XRD traces of clay 111, PS–clay and ABS–clay nanocomposites.

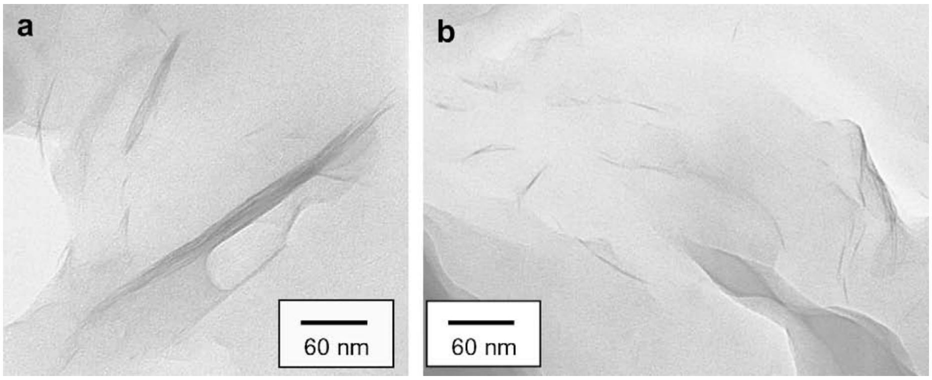

Fig. 2. TEM images of (a) PS–clay and (b) ABS–clay nanocomposite.

below, the PS nanocomposite contains undispersed clay while the ABS composite has exfoliated material not detected by XRD. Thus the large peak at 5° of 2θ in the PS material coincidently corresponds to the second order (002) reflection of the intercalated clay but in fact represents undispersed organoclay without polymer in the galleries that has been modified during processing causing relaxation of the intercalated surfactant. Heat treatment of the clay in the absence of polymer for the corresponding thermal cycle indeed produced a (001) peak at a lower 2θ at 5°, suggesting the sharp peak at 5° is mostly for the clay and some of the clay remains un-intercalated with the polymer.

XRD is not able to detect exfoliation of clay platelets without the use of internal standards and an assurance of isotropy [21] while TEM shows the morphology of nanocomposites more directly although the extent of sampling is small and many image areas are needed to guarantee representation. Representative TEM images of PS–clay and ABS–clay nanocomposites are shown in Fig. 2. Most of the clay platelets appear as intercalated stacks with a few exfoliated single platelets in the structure of the PS–clay nanocomposite, as seen in Fig. 2a. In contrast, the image for the ABS–clay nanocomposite (Fig. 2b), indicates a large number of exfoliated clay platelets with a minor proportion of intercalated clay stacks. The average number of clay platelets per stack, n, taking $n = 1$ for exfoliation, for ABS–clay nanocomposite is smaller than that for the PS nanocomposite, being approximately 2 versus 5, indicating a better dispersion for the former (note that a greater d_{001} does not necessarily imply better dispersion). From the heat treatment results, the 5° peak corresponds to regions of clay that have not been intercalated in polystyrene and the polystyrene system is a mixture of conventional, intercalated and exfoliated composites.

The values of notched impact strength are shown in Fig. 3 giving a comparison with pristine polymers. The incorporation of organoclay has a negligible effect (3% decrease) on the impact strength of PS while it dramatically lowered the value for ABS by up to 90%. The fractured halves of neat ABS specimens did not separate after impact unlike those of clay-reinforced samples. The toughness of ABS under impact testing is seriously reduced by clay additions and this is discussed further below. Indeed adding hard filler can change the mode of failure [5]. Fornes and Paul [22] who studied the impact strength of several nylon–clay nanocomposites showed that the nylon with the greatest impact strength had the largest decrease due to clay addition. The drop in impact strength of ABS compared with PS represents a similar trend.

In the classic example held up as a paradigm for polymer–clay nanocomposites, namely nylon 6–montmorillonite, the Charpy impact strength of nylon 6 is essentially unchanged being 6.2 kJ m^{-2} compared to 6.1 kJ m^{-2} for the composite. For a natural clay which forms a conventional composite with nylon, it decreases to 5.9 kJ m^{-2} [6], only a 5% decrease, which again is within experimental error. In the nylon systems, impact strength appears to be relatively insensitive to the state of dispersion of the filler or indeed whether the filler produces a conventional powder-filled composite or a nanocomposite. It is not clear from the literature whether intercalated or exfoliated systems give better toughness; some intercalated nanocomposites give higher toughness than exfoliated [9], while in other cases the results are reversed [12,23].

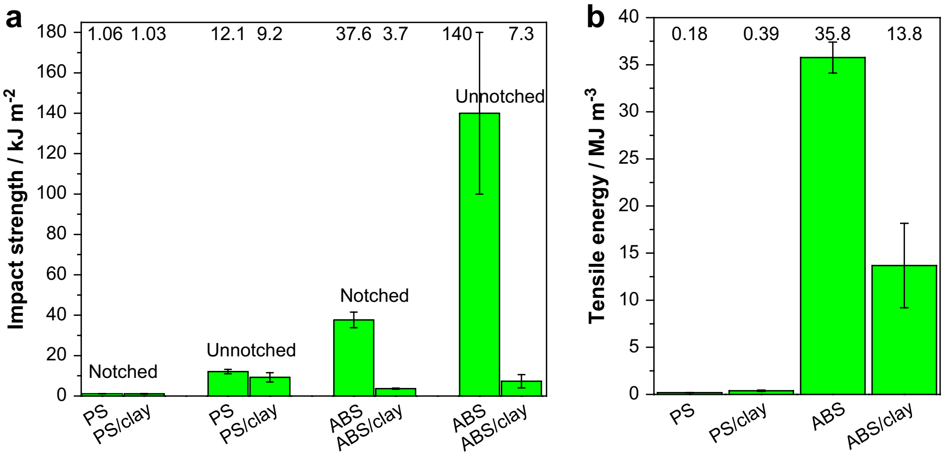

Fig. 3. (a) Charpy impact strengths and (b) tensile energies at break of PS, ABS and their clay nanocomposites containing 4 wt.% inorganic content (mean values are given at top of chart. Error bars represent standard deviations from 7 and 6 measurements for impact and tensile tests, respectively).

The nylon–montmorillonite results go further by suggesting that conventional composites of similar composition can compete in fracture toughness.

In a recent review [7], the Toyota authors complemented the results for notched samples with values of un-notched Charpy impact strength. These were above 150 kJ m^{-2} for nylon 6 and 52.5 kJ m^{-2} for NCH5 which is the nanocomposite containing 5 wt.% organoclay, representing a decrease of over 60%. It is important to recognise that impact tests on different geometries often rank materials differently because impact strength consists of energy terms arising from various stages of the failure process, i.e. initial impact, local plastic yielding before fracture and finally deformation of the material around the tip of the propagating crack [4]. Tests on notched specimens tend to measure resistance to crack propagation [4]. In contrast, tests on un-notched specimens place a greater emphasis upon ductility prior to crack initiation [4], and can be used to detect the presence of agglomerates in the specimens [5].

Un-notched impact tests were also conducted in this work and the results are given in Fig. 3. As with notched tests, the impact strength of PS underwent a slight decrease and ABS showed a significant decrease, confirming the decrease in toughness under high speed tests due to addition of clay. Compared to notched results, the decreases were greater, suggesting the presence of agglomerates in these nanocomposites. Agglomeration or large particles could be detected in fracture faces but only below about 1 μm.

Interpretation of fracture surfaces involves an element of subjectivity and inference of energy absorption from surface topography is fraught with difficulties. FE-SEM images of the impact fracture surfaces of PS and PS–clay composites (Fig. 4a–d) suggest that there is a rougher fracture surface at a fine scale on the nanocomposite, which is often judged to indicate that more energy was absorbed during fracture. This appearance should be contrasted with the impact test results discussed above. Small clay particles with a typical size of under 0.6 μm could be seen at higher magnification, supporting previous XRD results that the PS–clay composite is a mixture of conventional composite and nanocomposite. These particles are small, and hence should not cause the toughness to deteriorate substantially. The impact fracture surfaces of ABS and ABS–clay nanocomposite are shown in Fig. 4e and f. There are fewer drawn fibrils on the ABS–clay nanocomposite surface compared to that for ABS, which is consistent with the impact test results. Cryogenic fracture surfaces on these four samples were also observed using FE-SEM but clay particles were not identifiable in the ABS–clay nanocomposite.

Since the results for impact strength and fractography of PS and PS–clay nanocomposite were contradictory, low speed tensile testing was carried out to determine the energy at break under the stress–strain curves, and the results are given in Fig. 3b. The energy absorbed by PS was increased from 180 kJ m^{-3} to 390 kJ m^{-3}, i.e. up by 120%. Thus if the tensile curve or the impact fracture surface was the only evidence available, one would conclude that the clay had increased the toughness of PS. This again raises the importance of conducting impact tests in materials selection in engineering and other applications. On the other hand the tensile energy at break for ABS was significantly decreased by clay addition, consistent with the impact test results.

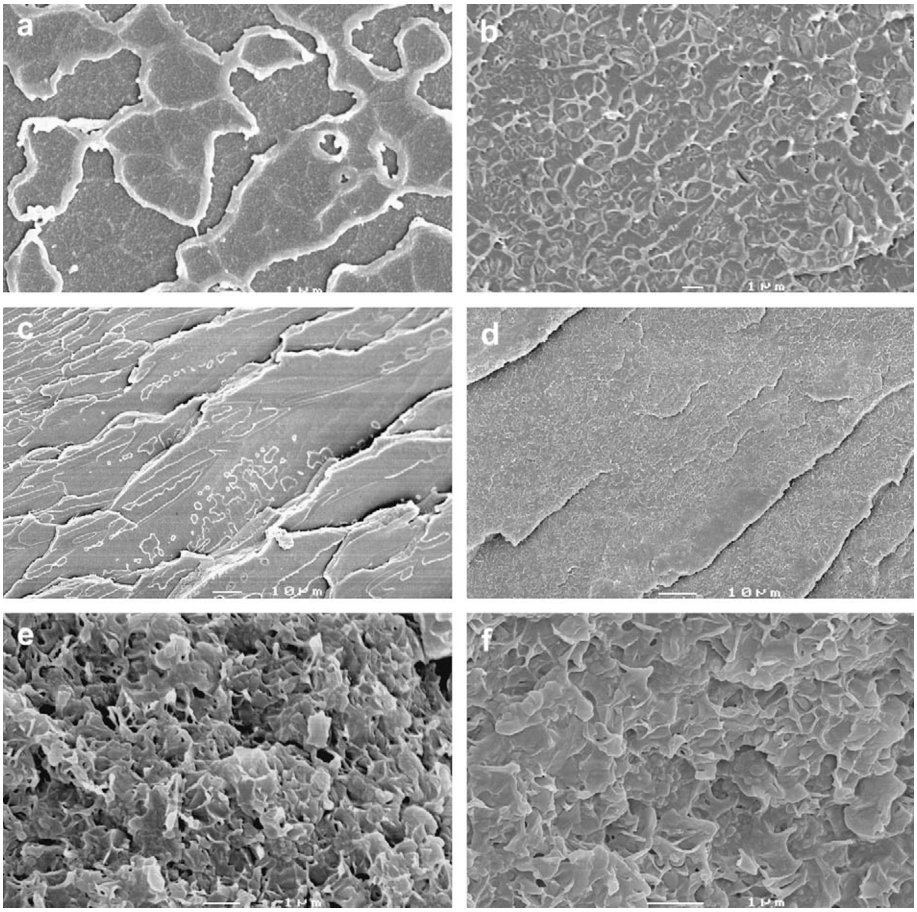

Fig. 4. Field Emission SEM images of the impact fracture surface of (a) PS, (b) PS–clay nanocomposite, (c) PS at a lower magnification, (d) PS–clay nanocomposite at a lower magnification, (e) ABS and (f) ABS–clay nanocomposite.

Lower speed tensile testing may allow clay platelets, more appropriately, the clay and its local environment of adsorbed and partially immobilised polymer, to change structure under external stress to resist fracture. Enhancement in the energy absorbed in tensile testing of PS could be attributed to microvoid formation due to delamination of clay tactoids as proposed by Dasari et al. [9] and Jiang et al. [24]. These microvoids can release strain constraints and induce local shear deformation in polymer ligaments [24]. The increased tensile energy in the PS–clay composite with little exfoliation as opposed to the decreased energy in the ABS–clay composite with more exfoliation, agrees with the results from Dasari et al. [9] who found that the intercalated nanocomposite structure is more prone to form microvoids than the exfoliated structure; so one explanation of these differences could rest with nanostructure of the composite.

A simple explanation for loss of toughness could be that all the polymers described above and their nanocomposites were processed at around 200 °C, the temperature at which most organoclays start to degrade [25]. It can therefore be conjectured that the fall in impact strength is due to the degradation of organoclay during melt processing. Therefore another nanocomposite system which can be processed at much lower temperatures at which the degradation of the surfactant cannot be held responsible was tested using the same organoclay. In this way, samples could be made at low temperature and annealed at high temperature to simulate the heat treatment of the PS and ABS. PCL–organoclay nanocomposites were prepared at 110 °C, and some were annealed at 200 °C for 30 min. Table 2 shows that the fall in toughness of annealed 4 wt.% clay–PCL (21%) is similar to the loss of toughness of the unfilled polymer (24%) and the 8 wt.% clay–PCL retains it toughness. We conclude that slight degradation of this organoclay, if it occurred during processing, was not the main cause of decrease in impact strength.

The PCL based nanocomposites retained substantial impact strength and again there was a contradiction with the energy absorbed in tensile testing. Impact strength fell slightly with clay addition but the average 'toughness' of the pristine PCL determined by tensile testing was dramatically increased from 21.7 MJ m^{-3} to 108 MJ m^{-3} and 116 MJ m^{-3} after addition of 4 wt.% and 8 wt.% clays respectively, corresponding to increases of 400% and 430%. XRD and TEM of PCL–clay nanocomposites containing the same clay were available in our previous work [20], which shows that the nanocomposites are partially intercalated and partially exfoliated, and d_{001} was increased from 2.0 nm to 2.8 nm.

Polyethylene glycol–natural clay nanocomposites provide another interesting comparison. There is no organic surfactant addition to the clay, they are processed at only 90 °C (PEG has $T_g = -20–40$ °C). These nanocomposites are mainly intercalated systems as determined by TEM, and XRD on PEG nanocomposites containing various clay contents [21]. XRD showed d_{001} of the natural clay increased from 1.2 nm to 1.8 nm [21].

Table 2 shows a slight but insignificant decrease (7%) in impact strength when the unfilled PEG was reinforced with clay addition indicating that impact strength can be retained in a predominantly intercalating system.

According to the energy dissipation mechanism proposed by Gersappe [26], clay platelets are sufficiently small to be able to orient along the direction of stress, thus increasing energy dissipation and improving toughness provided the system is above T_g. There is some evidence that impact strength of polymer–clay nanocomposites increases as they are heated through T_g [27–29]. However both PS and the copolymer in ABS have a T_g greater than ambient temperature, apparently making this mechanism inoperable. In contrast, PCL has T_g well below ambient temperature (−50 °C), so mobility of clay platelets could contribute to the enhancement of tensile energy. It should be noted that mobility of clay platelets or tactoids may be limited by three-dimensional networks formed between bridging macromolecules and clays as demonstrated by previous studies (e.g. [30,31]). The "networks" along with interfacial interactions between clay and polymer (see below) may lead to increases in T_g of polymers, similar to the cases in additions of nanotubes or other nanoparticles into polymers [32,33]. Change of crystallinity and crystalline structure in the case of semicrystalline polymers by clay addition may also affect the toughness [15,28,29,34,35]. In the case of PCL, the crystallinity only changes slightly [20], so it is not a primary reason for the increase in toughness. However the crystalline phase and crystallite size may be changed and this has been found in several cases (e.g. [28,29,34]).

Table 2
Notched impact strength of polymers with a T_g lower than ambient temperature with and without clay

Sample	PCL	PCL–clay		A-PCL[a]	A-PCL–clay[a]		PEG	PEG–clay	
		4 wt.%	8 wt.%		4 wt.%	8 wt.%		4 wt.%	8 wt.%
Average/kJ m^{-2}	43.9	34.6	33.2	33.5	27.3	33.1	1.4	1.3	1.3
S.D/kJ m^{-2}	5.1	0.7	2.8	4.0	0.4	0.5	0.2	0.1	0.2

[a] A refers to annealed at 200 °C for 30 min. S.D refers to standard deviation.

Since addition of clay to PS gives a comparable effect on toughness to that in PCL, it is rather difficult to identify the relationship between T_g of polymer and the test temperature as the deciding factor in affecting toughness. This is supported by the findings from Irisk et al. [13] and Park and Jana [14] who demonstrated increases in toughness for epoxies with T_g *greater* than ambient temperature, i.e. approximately 70 °C. Other factors, such as nanostructure as discussed previously, should also be considered. In comparison with intercalation, exfoliated structures provide more extensive interfacial interaction which could lead to greater changes in T_g, chemical bonding and in the case of semicrystalline polymers, in spherulite size and crystallinity, and hence macroscopic properties [28]. Indeed exfoliated nanocomposites do sometimes give higher toughness than intercalated structures [12,23] despite the suggestion that an intercalated structure is preferred for microvoid formation.

Now that the effect of slight degradation of organoclay on decreasing toughness is excluded, there is another possible reason for the loss of impact strength in ABS. It was found that the impact strength of polypropylene copolymer or impact-modified polypropylene was lowered significantly by hard particulate fillers and the reason given for that is that the filler interacts with the soft or rubbery component and nullifies its ability to absorb energy during impact [5]. It is less easy to apply this explanation to the case of ABS–clay nanocomposites because the rubbery phase of ABS, i.e. butadiene, is non-polar and does not interact with clay strongly; indeed it is the least favourite one for clay to interact with among the three components because both acrylonitrile and styrene chain segments can intercalate into organoclay due to their polarity despite the latter contributing only very low polarity.

There was no significant change in tensile yield stress in either PS or ABS with addition of 4 wt.% clay platelets (Fig. 5). Young's modulus measured in tensile testing increased in both polymers due to clay but the error bars in the case of ABS make the smaller increase less significant. Crazing and shear yielding, reflected as stress-whitening and necking, proceeded simultaneously during tensile fracture of ABS [4]. Loss of compliance and increased stress in the neck region may restrict formation of crazing and shear yielding. Bucknall [4] found that ABS broke at a lower strain than a comparable high impact PS because the stress is increased in the neck region. Clay tactoids may prevent the rubbery phase from forming crazes and hence toughening, leading to a large reduction in toughness in ABS–clay nanocomposite. Indeed the studies from

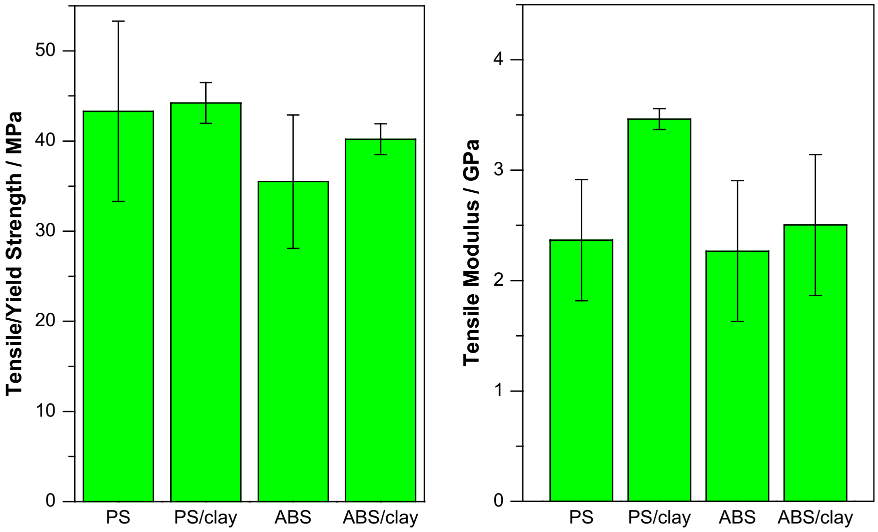

Fig. 5. Tensile properties of PS and ABS with and without addition of clay (the inorganic content in the nanocomposites is 4 wt.%).

He et al. showed craze formation of nylon 6 was suppressed when clay content was greater than 2.5 wt.% [34].

4. Conclusions

Toughness in polymer–clay nanocomposites was studied using brittle and ductile polymers, and polymers with T_g above and below the ambient temperature. High speed impact tests on notched and un-notched samples combined with low rate tensile tests were carried out to study the effect of clay on polymer toughness. High speed tests show that PS, for which the impact strength is initially low, undergoes a slight decrease in impact strength whereas fractography of impact sample surfaces would suggest that the toughness should increase. Lower strain rate tensile tests show a substantial increase in tensile energy at break. This composite includes conventional, intercalated and minor amounts of exfoliated reinforcement as deduced by XRD and TEM. Increase in the energy at break of a glassy polymer–clay nanocomposite such as the PS system during low rate testing may result, as often claimed, from microvoid formation due to delamination of intercalated clay tactoids [9,24].

In the case of ABS, with an intercalated and exfoliated structure, the results from all three assessment methods demonstrate an unequivocal and dramatic decrease in toughness after addition of clay, which is supported by FE-SEM image on the impact fracture surfaces. This large reduction of toughness in ABS is likely to be because the dispersed clay resists microscopic deformation, preventing the rubbery zones from fulfilling their role in absorbing energy in the crack propagation zone in notched tests, and prior to crack initiation in un-notched tests.

Parallel experiments with the same organoclay added to PCL, which can be processed at low temperatures, indicate that the slight degradation of organoclay that may occur during processing of PS and ABS at 200 °C does not significantly contribute to the decrease in impact strength. The PCL–organoclay composite is partially exfoliated and partially intercalated. Impact strength of PCL decreased slightly with clay addition but energy absorbed in tensile testing increased by a factor of four. In another system, PEG–natural clay, without surfactant and with a predominantly intercalated structure, toughness is retained.

A wider consequence of these results is that increased energy absorption in a tensile test cannot be used to infer increased toughness at impact strain rates. There is insufficient evidence from these results to support the emerging view that nanoclay additions to polymers are effective in maintaining toughness only if the polymer is above T_g and neither is there a correlation between the extent of dispersion as deduced from XRD and TEM and the retention of toughness given that the ABS–clay nanocomposite with better dispersion than PS–clay suffered more reduction in impact strength.

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