TEMPERATURE AND STRAIN RATE DEPENDANT MECHANICAL BEHAVIOUR OF ALL-PP COMPOSITES - COMPARISON WITH GMT AND NMT

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ABSTRACT

Polypropylenes reinforced with oriented polypropylene fibres, so-called "all-PP" composites, have specific economic and ecological advantages over composites based on glass fibres since, upon recycling a PP-blend is obtained that can be reused to make all-PP composites or can be used for other PP-based applications. Although static properties of all-PP composites at room temperature can compete with those of traditional composites (i.e. glass-fibre-reinforced PP and natural-fibre-reinforced PP), due to the highly viscoelastic character of PP, their mechanical behaviour will strongly depend on temperature and strain rate. This influence on tensile modulus and strength of all-PP tapes and composites is investigated. For the later, the same influence is investigated on the energy absorption capacity using full penetrating dart-impact tests. Similar trends on the influence of strain rate and temperature are observed of both tapes and composites revealing similarities in the failure mode. For comparison reasons, the mechanical response of these newly developed all-PP composites is compared with that of glass-mat-reinforced thermoplastics and natural-fibre-mat-reinforced thermoplastics, over a wide temperature range. The tensile strength and the impact energy of all-PP composites is superior for the whole range of temperatures tested (-40°C to 140°C), while the stiffness is higher for temperatures as high as 40°C. At higher temperatures glass-fibre-reinforced PP shows higher stiffness while natural-fibre-reinforced PP are inferior for the whole range of tested temperatures.

1. INTRODUCTION

With new EC directives on automotive recyclability coming into play by 2015, an all-polypropylene (all-PP), mono-component, recyclable system would be of considerable commercial gain to this sector where the traditional choice is glass-fibre-reinforced PP (e.g. GMT). A different alternative towards environmentally friendly composite systems in the automotive sector is to use natural fibres like flax, hemp and sisal to reinforce PP. Although these fibres do have some ecological advantages over glass fibres since they are renewable and can be incinerated, natural fibres do not have advantages with respect to mechanical recycling issues. In fact, next to mechanical degradation the poor thermal stability of these ligno-cellulose fibres may lead to severe additional thermal degradation during subsequent recycling/reprocessing steps. Clearly the introduction of any 'foreign' fillers, like talc, chalk or fibres like glass and natural fibres is in conflict with the basic idea behind recycling and mono-material products. Therefore all-PP composites have specific economic and ecological advantages over composites based on glass or natural fibres since, upon recycling, a polypropylene blend is obtained which can be reused to make again all-PP composites, or alternatively, be used for other PP-based applications.

Two main routes have been recently proposed to manufacture such composites. The 'hot compaction' process developed at the University of Leeds [1] is a possible route, which has also been investigated for a range of polymers as well as polypropylene [2-4]. This method is a difficult process to apply industrially since it is accompanied with a very small processing window (2°C) [5]. In order to overcome this problem an alternative route was proposed by Peijs et al. [6-8] based on the 'hot compaction' of co-extruded fibres/tapes. A temperature-processing window of >30°C can be achieved using this method.

Although recyclability is a very important issue nowadays, mechanical performance at a wide range of temperatures remains of key importance for many engineering applications, including automotive industry.

The production of highly oriented, high strength polymer fibres by the careful control of processing routes has been well documented over the past 30 years. High performance polyethylene and polypropylene fibres are good examples of such materials with excellent short-term mechanical properties. It is well established that polymers exhibit viscoelastic behaviour, the extent of which depends on the temperature and the strain rate they are loaded, in addition to parameters such as molecular weight, molecular structure, crystallinity and chain entanglements [9]. Consequently, polymer fibres are expected to show a pronounced time dependent behaviour under continuous static loadings. With respect to durability this implies that the mere fact that polymer composites are loaded well below the critical stress, as determined in a short-term test, will not ensure that they will sustain this load for an infinite period of time. Moreover, mechanisms, which are responsible for the change in long-term behaviour, are generally accelerated when the polymer composites are exposed to higher temperatures, higher stress levels or other, more severe, environmental conditions such as moisture and/or solvent. In contrast to these limiting factors, the viscoelastic character and the relatively high work-to-break of these fibres compared with carbon, aramid and glass fibres renders them eminently suitable for applications where impact resistance and vibrational damping is required.

One of the most important factors determining the failure behaviour of glassy polymers is yielding, and, after the onset of yielding, the limit of plastic deformation, determined by maximum plastic strain. With decreasing strain rate, or equivalently, increasing temperature, the yield stress will drop [10,11]. However, at low temperatures and/or high strain rates, the yield stress exceeds the tensile strength and the fibre will fracture before reaching the yield point. Since both the tensile strength [12] and the yield stress [12,13] depend strongly on temperature and strain rate, the failure mode is likely to change from brittle fracture to yielding with increasing temperature or decreasing strain rate [12]. Experimental observations of this change in the failure mode further referred to as the brittle-to ductile transition, have been reported on the example of PE fibres [12,13].

Since the deformation as well as the failure behaviour of polymers is strongly influence by the time-scale and the temperature of the experiment [10], it is important to consider such parameters when designing with these materials. The aforementioned influence will be more pronounced when both the matrix and the fibres in the composite are made out of polymer, as in case of all-polymer composites. In traditional polymer composites, the time-scale will have a large influence mainly in off-axis loading situation where the properties are strongly governed by the viscoelastic polymer matrix.

In polymers time-dependent viscoelastic behaviour shows itself in a number of ways, such as creep and stress relaxation experiments, mechanical characterisation tests at different temperatures and strain rates, as well as dynamic, cyclic loading tests, such as dynamical thermal analysis (DMTA) tests. In this study we will focus on the effect of temperature and strain rate on the mechanical properties of all-PP tapes and composites. The influence of both parameters will be considered on the tensile and impact properties of this material. Many of the applications under consideration for deployment of this material are in the automotive industry, wherein component life expectancies exceed 10 years. Therefore superposition principles will be employed to predict the long-term durability of these materials.

In earlier studies the mechanical properties of all-PP [14] and that of natural fibre reinforced PP (e.g. NMT (natural mat PP)) [15] were investigated at room temperature. It was concluded that mechanical properties of these novel all-PP materials are quite high, and if the specific properties (density related) are considered, all-PP composites directly compete GMT and NMT. In some cases all-PP composites present even superior performance compared to GMT and NMT (i.e impact related properties). Nevertheless, unlike glass fibres, which show basically linear elastic behaviour, PP fibres are viscoelastic and their properties are highly time- and temperature- dependent. Beside that, alike natural fibres, they will present thermal degradation in their properties at elevated temperatures, due to their thermal instability.

Consequently all-PP and natural fibre reinforced composites may not have similar advantages as glass-fibre-reinforced PP with regard to high temperature behaviour. Therefore, a final aim of this study is to compare the mechanical performance of all-PP with GMT and NMT composites at a wide range of temperatures.

2. EXPERIMENTAL

Material Manufacturing

The tapes throughout this investigation are co-extruded three layer tapes, with a A:B:A (copolymer:homopolymer:copolymer) structure, and are supplied by Lankhorst Indutech BV in the Netherlands. The tape is 2.2mm wide 0.065mm thick. Layer A (5%~ 3μm) is an i-PP copolymer and B is an i-PP homopolymer. Compacted sheets are obtained by compacting several layers of all-PP fabric. Six-seven layers of fabric are necessary to get a 1 mm thick sheet due to the low nominal weight of the fabric (105g/m^2). All-PP fabrics have to be heated and cooled under constant pressure in order to get optimal properties and compaction. If a standard hot-press were used, cycle times would be too long for any realistic applications. But a continuous process such as belt-press technology is suitable to produce sheets from all-PP fabric rolls in spite of a high-investment cost. Isobaric belt-presses usually develop 20-40bar through heating and cooling. The output speed is in the order of several meters per minute. A compaction temperature of 145ºC was found appropriate to get a full compaction.

In addition to PP tapes and all-PP composites, two types of reinforced PP are used for comparison. The first is Symalit®, (hereafter referred to as GMT) and is a random glass reinforced PP with a fibre weight fraction of 23% while the second is a random natural reinforced PP (hereafter referred to as NMT) with a fibre weight fraction of 30%, both manufactured by Quadrant Composites. GMT and NMT have a thickness of 2mm and 4mm, respectively.

Testing procedure

All-PP tapes are tested statically on an Instron Tensile Testing Machine, with a 500N load cell and data acquisition computer. Woven all-PP specimens (300x150x1.3) were tested in a MTS 831 with a 10kN load cell and data acquisition computer. For the tape, fibre clamps were used to minimise failure within, or very close to the gripping region. Self-adjustable clamps were used for the woven specimens in order to avoid slipping of the specimens. Tensile tests were performed at different strain rates (0.1 - 0.001s^{-1}) and different temperatures (-40 - 80°C) with a small preload (~1N). The distance between the clamps was set to 250mm. An environmental chamber was attached to the testing machines in order to adjust the testing temperature. PT 100 thermometer temperature probes were placed inside the chamber in order to check the absolute temperature. The temperature was held for 5 minutes to allow uniform temperature within the specimen, and then tensile testing was commenced. At least three measurements were done for each strain rate and temperature. In case of large deviations between the measurements, additional tests were contacted. The stiffness of the tape and that of the woven specimens was calculated at a strain range of 0.05% - 0.2%; in all cases this proved to be a linear and reproducible region of the stress-strain curve. GMT and NMT specimens were tested statically, at different temperatures (-40 – 140°C) while a constant strain rate (0.001s^{-1}) was employed.

Impact tests were performed on all-PP woven specimens and on GMT specimens using a Zwick Rel tensile testing machine fitted with an environmental chamber and an impact striker with a diameter of 10mm and a specimen holder aperture of 20mm containing a force transducer. The tests were performed at impact speeds of 10, 4.3, 1 and 0.1m.s^{-1} to determine the effect of impact speed on the impact strength in case of all-PP specimens while GMT was tested only at 1m.s^{-1}. The chamber temperature was heated by a circulating air oven and cooled by liquid nitrogen. As before, the specimens were placed in the chamber at room temperature and then the chamber was heated/cooled to achieve testing desired temperature.

The specimen was allowed to stabilise for 10 minutes at the test temperature before testing. The temperature of the specimen was monitored externally using a thermocouple mounted in the specimen holder; this is important since unlike tensile tests there is a large contact area between impact specimen and holder. The impact striker, mounted on the crosshead, is pushed through the specimen and the force recorded. The tensile penetration energy is defined as the total energy absorbed by impact, which is the integral of the force time curve during penetration.

3. RESULTS & DISCUSSION

Viscoelastic response of all-PP tapes and composites

As mentioned in the previous paragraphs, all-PP tapes and composites are expected to show a pronounced time and temperature effect on their mechanical response. This effect on the tensile stiffness and strength of the tape is illustrated in Fig. 1a and 1b, respectively. Fig. 2a and 2b present the same effect in case of woven laminated specimens.
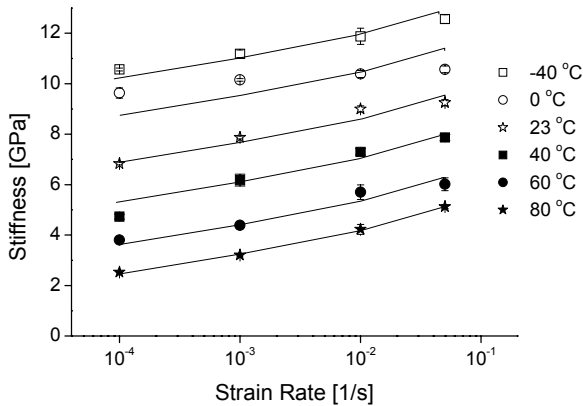

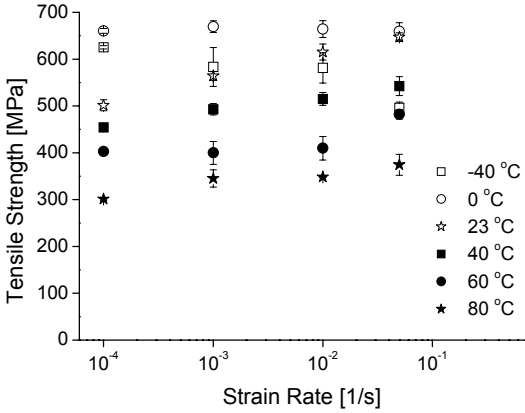**Fig. 1a.** The tensile stiffness of all-PP tape vs. strain rate for a range of temperatures

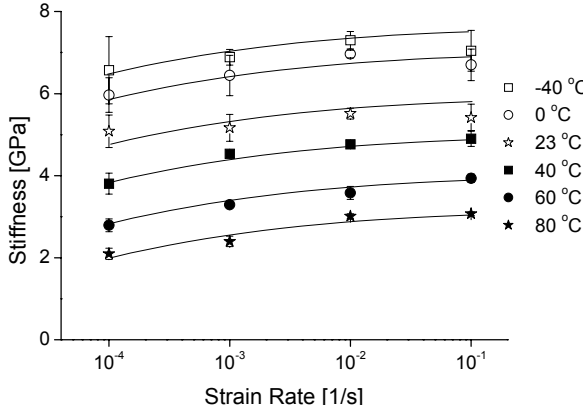**Fig. 1b.** The tensile strength of all-PP tape vs. strain rate for a range of temperatures

Fig. 2a. The tensile stiffness of all-PP composites vs. strain rate for a range of temperatures
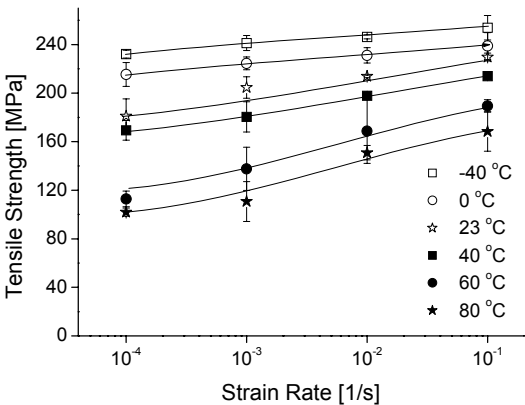

Fig. 2b. The tensile strength of all-PP strength vs. strain rate for a range of temperatures

The trend in both cases is that as the strain rate is increasing, the stiffness and strength of the tape and that of the woven composite are also increasing. Temperature has an opposite influence on the response of tapes and composite. An increase of the testing temperature leads to a decrease of both stiffness and strength. These observations are in agreement with

previous observations [10,11]. The brittle to yielding transition mentioned earlier [12,13] is not obvious here at a first approximation. A reason for that could be the fact that the range of strain rates or temperatures used here was not broad enough for such transition. The variation of the tensile strength of the tape with temperature (Fig. 1b) shows some discrepancies, especially below room temperature (RT). The strength of the tape at –40°C seems to be lower than that at 0°C. Discrepancies are also observed on the effect of strain rate for those temperatures. One could attribute these differences to the T_g of the all-PP tape, which is around 0°C. Nevertheless, due to the high degree of orientation of these tapes, the amorphous phase of the material is very small and its effect is expected to be negligible. The aforementioned differences are considered to be a result of failure of the tape close to the grips at low temperatures.

Using the principle of time temperature superposition, these data can be adapted to provide the master-curves at a wider range of strain rates. The principle of time temperature superposition states that it is possible to provide information on strain rates outside the range experimentally available by shifting data obtained at higher or lower temperatures, by a shift factor, a_T in the time scale. This shift factor can be modelled using WLF (Williams-Landel-Ferry) or Arrhenius equations. The WLF equation is very successful for describing the behaviour of amorphous polymers above T_g. For semi-crystalline polymers like PP the shift factor seems to be better calculated using the Arrhenius equation [16-20]. The result is a 'master-curve' of data which provides a much wider range of information than experimentally possible for a given reference temperature, T_{ref}. This method oversimplifies the complex behaviour seen in semi-crystalline polymers and is only valid for processes, which show constant activation energy, E_a (see eq.1).

$$\log a_T = \frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \qquad (1)$$

Where,
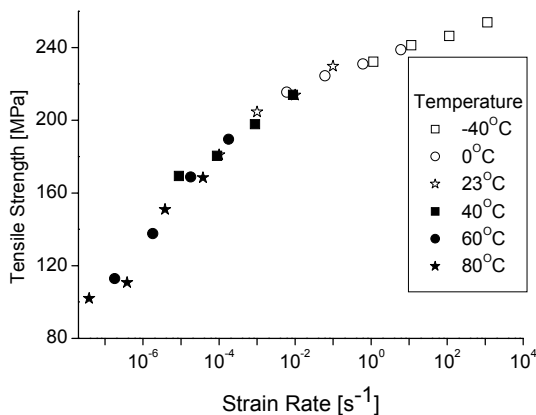|		
a_T	=	shift factor
E_a	=	activation energy for the change in property
R	=	Universal gas constant [8.314 J.mol^{-1}.K^{-1}]
T	=	Temperature of data to be shifted [K]
T_{ref}	=	Reference temperature of data [K]

Fig. 3a. Tensile strength master-curve of all-PP composites for a reference temperature of 23°C
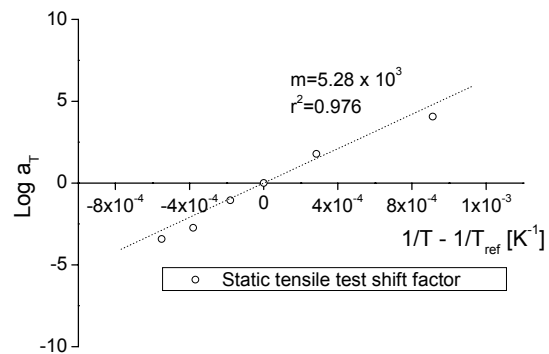
Fig. 3b. Determination of activation energy for time temperature superposition of tensile strength

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The use of these techniques assumes time and temperature equivalence and does not include any allowance for degradation or aging of the polymer due to environmental effects, such as oxidation. Using a horizontal shift factor, a_T, these results can be shifted to create a master-curve at a reference temperature of 20°C. The time-temperature equivalence is applied on the experimental data presented in Fig. 2b. Shifting of these date will provide us with a strength master-curve, which is shown in Fig. 3a. The shift factor used in Fig. 3a is shown in Fig. 3b. The activation energy, E_A, can be determined from eq. 2, based on eq. 1.

$$E_A = m(2.303R) \tag{2}$$

Where m =   Gradient of fit line in Fig. 3b

R =   Universal gas constant

This shift factor shows approximately constant value (as indicated by the r^2 fit parameter) with an activation energy of ~100kJ.mol^{-1}. The calculated activation energy is of the same order as previously reported using the same simple Arrhenius shifting of oriented PP: 210kJ.mol^{-1} [16], and 364kJ.mol^{-1} [17] and those used in more complex models of oriented PP, typically 50kJ.mol^{-1} [18-19]. This more complex model of Wortmann and Schulz considers the contribution of amorphous and crystalline phases separately, with different mechanical properties. It is likely that in highly oriented PP, such as that considered here, the high degree of orientation of the amorphous phase leads to the moduli of crystalline and amorphous phases being considerably closer than in is seen in unoriented PP. This may explain the apparent validity of this simple Arrhenius shifting. It has been reported that using a simple Arrhenius shift can yield unrealistically high activation energies [20]. Since a single activation energy leads to a good fit of the data, it is likely that the same mechanisms are occurring in all the specimens, which is likely since the temperature range here is quite small. This master-curve provides useful information predicting the modulus of loading from 10^{-9} to 10^9 seconds. These are presented as more familiar time equivalents in table 1.

Table 1 Equivalent time units

Time [s]	Equivalent
1.58×10^8	5 years
3.15×10^7	1 year
2.68×10^6	1 month
8.64×10^4	1 day
3.60×10^3	1 hour

Comparison of all-PP composites with GMT and NMT
As mentioned in the introduction section, one of the possible application sectors of all-PP composites is the automotive industry. In order to investigate the potential of all-PP composites in this sector direct comparison of the mechanical response of all-PP composites with that of GMT and NMT is made and presented in this paragraph. In Fig. 4 this comparison can be seen in respect to the tensile response (stiffness (4a) and strength (4b), respectively) along the 0°/90° tape direction at a wide range of testing temperatures (-40 and 140°C). Both stiffness and strength decrease with an increase of the testing temperature for all three materials. All-PP composites show higher values of tensile stiffness compared with that of NMT composites for the whole range of tested temperatures, while GMT shows higher properties above ~ 40°C. The stiffness of GMT is much less temperature dependent than that of all-PP and NMT since it contains 'elastic' glass fibres instead of highly viscoelastic PP

fibres or thermally unstable natural fibres, respectively. However, in terms of absolute values, even at 140°C the all-PP composite still possesses a modulus similar to that of GMT.

Fig. 4b shows that all-PP composites have superior tensile strength compared with that of GMT and NMT for the whole range of testing temperatures. All three composites present a decrease of their strength as the temperature is increasing, nevertheless, even at 140°C all-PP composites show strength values twice as high as those of GMT and NMT. The strength of the all-PP composites can be seen to decrease in two linear regions, with a transition at ~90°C. Semi-crystalline polymers often show a second transition, α^*, between T_g and T_m. This is due to movement of crystalline regions past one another in the relatively mobile amorphous phase at temperatures between T_g and T_m. This transition coincides with T_α^*. Thus, increased crystal mobility will allow greater viscous flow and reduce the strength of the composites. The effect of this transition will be more pronounced in case of all-PP composites and will be diminished in case of GMT and NMT due to the existence of glass and natural fibre, respectively.
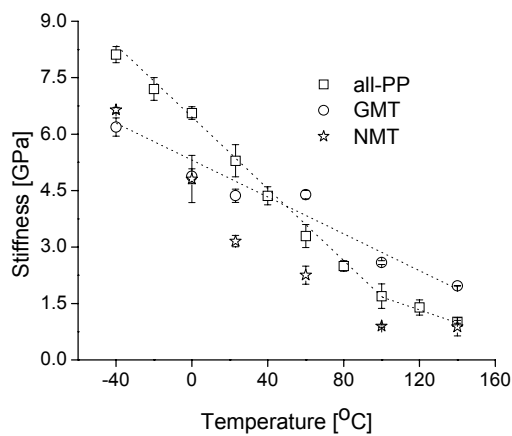

Fig. 4a. The tensile stiffness of all-PP, GMT and NMT composites vs. temperature
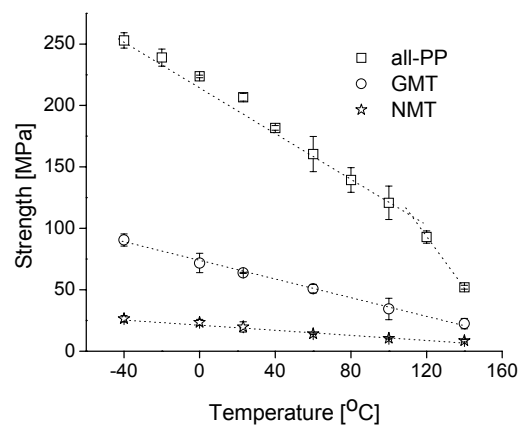
Fig. 4b. The tensile strength of all-PP, GMT and NMT composites vs. temperature

The penetrative impact energy of woven tape all-PP composites was also investigated. The (thickness) normalised penetration energy for a range of temperatures and speeds (strain rates) is shown in Fig. 5. In Fig. 5a it is demonstrated that all-PP composites have impact strength in excess of that of GMT. Nevertheless, GMT is almost stable in respect to temperature due to the thermal stability instilled by the glass phase. The effect of impact temperature is clearly quite small. Since the temperature range passes through the glass transition temperature of polypropylene (~ -10°C), a large difference would be expected in impact performance, since below T_g, semi-crystalline polymers have a much lower strain to failure and hence a lower resistance to crack propagation. This is characterised by low penetrative impact energy. However, since all-PP tapes are highly oriented, it is expected that there is no significant glass transition, due to the absence of the amorphous phase. Therefore, there is a slight increase in penetrative impact energy for composites at -40°C, and not the large decrease that would be associated with the impact performance of a semi-crystalline polymer below T_g. Decreasing temperature leads to increased impact energy, as does an increase in impact speed (see Fig. 5b), but the effect due to increasing the impact speed is much greater. An increase in strain rate of two decades leads to a 10% increase in tensile strength (see Fig. 3b), but this alone cannot explain the mechanism behind the large increase in penetrative impact energy absorbed at impact speeds of 10m.s^{-1}. During penetrative impact of all-PP composites, numerous failure modes operate. On initial impact the composite is deformed in bending, this

causes a tensile deformation in the constituent tapes, and tape debonding. These tapes ultimately fail in tension. The stiffness and strength of the tapes has been considered here, but not the debonding processes.
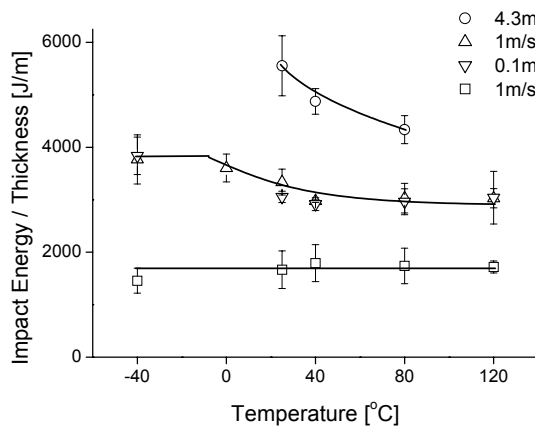

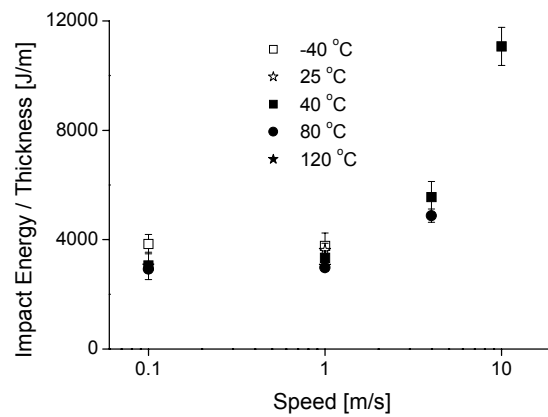**Fig. 5a.** Penetrative impact energy vs. impact temperature of all-PP and GMT composites

Fig. 5b. Penetrative impact energy vs. impact speed for a range of impact temperatures

4. CONCLUSIONS

The strain rate and temperature dependant behaviour of all-PP tapes and composites was measured in respect to the mechanical response of these materials. The results revealed viscoelastic behaviour of the material, mainly when the tensile properties were considered. As the testing temperature is increasing or the stain rate is decreasing, a decrease in both tensile stiffness and strength is observed. The absorption of energy during penetrative impact does not directly follow the expected trends. This is attributed to changes in the failure mechanisms at low temperatures. It was nevertheless shown, that the orientation of the amorphous phase in semi-crystalline polypropylene had as consequence a reduction of the dramatic decrease in stiffness normally seen at T_g. By doing so the stability of the mechanical properties can be greatly improved in the region between -40°C and 120°C.

Despite the wholly thermoplastic nature of all-PP composites, the strength and modulus compare well to GMT and NMT. The tensile strength exceeded that of GMT and NMT at all temperatures investigated, while the tensile stiffness possessed a higher modulus at low temperatures, but a slightly lower modulus at high temperatures.

A master-curve in case of tensile strength was successfully produced using an Arrhenius equation to shift data in the time scale. This master-curve can be used to predict the behaviour of the material outside the time scales experimentally feasible.

References
1. **Hine, P.J., Ward, I.M., Olley, R.H., Bassett, D.C.,** "The hot compaction of high modulus melt-spun polyethylene fibres", *Journal of Materials Science*, *28* (1993), 316-324.

2. **Rasburn, J., Hine, P.J., Ward, I.M., Olley, R.H., Bassett, D.C., Kabeel, M.A.,** "The hot compaction of polyethylene terephthalate", *Journal of Materials Science*, **30** (1995), 615-622.
3. **Yan, R.J., Hine, P.J., Ward, I.M., Olley, R.H., Bassett, D.C., Bassett, D.C.,** "The hot compaction of SPECTRA gel-spun polyethylene fibre", *Journal of Materials Science*, **32** (1997), 4821-4831.
4. **Jordan, N.D., Olley, R.H., Bassett, D.C., Hine, P.J., Ward, I.M.,** "The development of morphology during hot compaction of Tensylon high-modulus polyethylene tapes and woven cloths", *Polymer*, **43** (1995), 615-622.
5. **Hine, P.J., Bonner, M., Brew, B., Ward, I.M.,** "Hot compacted polypropylene sheet", *Plastic, Rubber and Composites Processing and Applications*, *27/4* (1998), 167-171.
6. **Alcock, B., Cabrera, N., Peijs, T., Schimanski, T., Loos, J.,** "All-polypropylene composites for ultimate recyclability", *Proceeding of ECCM10,* (2002), Brugge, Belgium, June 3-7.
7. **Alcock, B., Cabrera, N., Barkoula, N.-M., Peijs, T.,** "Interfacial properties of all-polypropylene composites", *Proceeding of ICCM14,* (2003), San Diego, CA, USA, July 14-18.
8. **Peijs, T.,** "Composites for recyclability", *Materials Today,* **6** (2003), 30-35.
9. **Galeski, A.,** "Strength and toughness of crystalline polymer systems", *Progress in polymer science,* **28** (2003), 1643-1699.
10. **Brown, N.,** "Yield behaviour of polymers", *In: Browstow, W., Corneliussen, RD., ed. Failure of plastics,* New York: Hanser, (1986), 98-118.
11. **Ward, IM.,** "Mechanical properties of solid polymers", 2nd ed.*,* New York: Wiley, (1983), 377-384.
12. **Cansfield, D.L.M., Ward, I.M., Woods, D.W., Buckley, A., Pierce, J.M., Wesley, J.L.,** "Tensile-strength of ultra high modulus linear polyethylene filaments", *Polymer Communications*, **24** (1983), 130-131.
13. **Covaert, L.E., Bastriaansen, C.W.M., Leblans, P.J.R.,** "Stress-strain analysis of oriented polyethylene", *Polymer*, **34** (1993), 534-540.
14. **Cabrera, N., Alcock, B., Barkoula, N.-M., Peijs, T.,** "Processing of recyclable all-PP composites", *Proceeding of ICCM14,* (2003), San Diego, CA, USA, July 14-18.
15. **Wambua, P., Ivens, J., Verpoest, I.,** "Natural fibres: can they replace glass in fibre reinforced plastics?", *Composites Science and Technology*, **63** (2003), 1259-1264.
16. **Faucher, J. A.,** "Viscoelastic Behavior of Polyethylene and Polypropylene", *Journal of Rheology,* (1959), 3 81-393.
17. **Amash, A., Zugenmaier, P.,** "Thermal and Dynamic Mechanical Investigations on Fiber-Reinforced Polypropylene Composites", *Journal of Applied Polymer Science*, **63** (1996), 1143-1154.
18. **Fytas, G., Ngai, K. L.,** "Study of Viscoelastic Relaxation in Amorphous Polypropylene Near Tg by Dynamic Light Scattering and Shear Creep", *Macromolecules*, **21** (1988), 804-811.
19. **Wortmann, F.-J., Schulz, K. V.,** "Stress Relaxation and Time/Temperature Superposition of Polypropylene Fibres", *Polymer,* **36 (2)** (1995), 315-321.
20. **Wortmann, F.-J., Schulz., K. V.,** "Thermomechanics of Isotactic Polypropylene between -67 and +140C: Investigation of the Relaxation Behaviour Based on Literature Data", *Polymer*, **37 (5)** (1996), 819-824.