Elasticity, Toughening and Damping Enhancement of Polypropylene after Blending with Polysiloxane Elastomer

Huan Yao (Peter) Huang, Balaji Rengarajan, Robert Shanks

School of Applied Sciences, RMIT University, Melbourne, Victoria, 3000, Australia

Polypropylene (PP) is a thermoplastic with moderate modulus, strength and temperature resistance, but poor toughness. Elastomers are known to enhance PP toughness and in this work a polysiloxane (PSil) elastomer has been used to modify PP. PP– PSil blends were formed by extrusion with PSil as a dispersed phase. PSil increased the thermal stability of the PP blends, and increased PP crystallinity causing a slightly increased modulus. The damping factor determined from modulated force thermomechanical analysis was a maximum at 2 %·v/v. PSil increased the activation energy of the glass transition for PP molecules in the blends.

1. Introduction

Polypropylene (PP) is a high performance semicrystalline polyolefin with a relatively high melting temperature (162-167 °C) for homopolymers and a variable glass transition temperature (10-20 °C) that lacks toughness for some applications, particularly at low temperatures. Blending PP with elastomers such as poly(ethylene-co-propylene)-diene (EPDM) is used to enhance the toughness of PP [1]. Improvement of toughness is often accompanied by deterioration of strength and processability of the blends. Thermal stability is increased by combination with higher thermal stability components [2].

Polysiloxanes (PSil) are lubricants with low surface energy and low glass transition temperature that could toughen PP and furthermore modify the flow for ease of processing [3]. Yet blending polysiloxane with PP may deteriorate the strength. PSil are not expected to be miscible with PP, their mixtures will consist of two phases, continuous or matrix phase of PP and a dispersed phase of small droplets or particles of PSil. The dispersed elastomer can modify the mechanical response of PP by absorbing energy by elastic or viscoelastic deformation. Elastomer particles in PP are known to cause increased PP deformation in regions near the interface with the elastomer. This deformation is called shear banding due to its appearance in microscopy.

The aim was to prepare PP–polysiloxane blends by extrusion and characterize the thermal and thermomechanical properties by using different volume fractions of polysiloxane and determine the extent that polysiloxane will modify PP. Analysis and thermal stability of the blends have been performed by thermogravimetry. Mechanical properties were determined using thermomechanometry in tensile dynamic and modulated force modes [4].

2. Experimental

2.1 *Sample preparation*

PP (melt flow index (MFI): 3.5 dg·min^{-1}; density: 0.905 g·cm^{-3}; softening temperature: 152 °C) granules from Bastell and polysiloxane masterbatch (pre-dispersed in PP) granules from Dow Corning (siloxane content: 50 %; density: 0.902 g·cm^{-3}) were tumble mixed before introduction into the single screw extruder with a Gateway screw with a length : diameter ratio of 1:26 (Axon B12). A tape of blends was then extruded with a temperature setting of each zone: 160 °C for feeding zone, 180 °C for melting zone, 180 °C for metering zone, and 160 °C for die-zone, then passed through cold rollers. After cooling the tape at 25 °C, a thermal treatment (annealing) was conducted at 140 °C for 2 h.

2.2 *Thermogravimetry*

Samples of ~7 mg were heated from 50 °C to 800 °C at 10 °C·min^{-1} using a thermogravimetry (TGA) instrument (Perkin-Elmer TGA7) for characterization of the thermal stability and confirmation of composition of each blend. The purging gas (flow rate: 20 mL·min^{-1}) was nitrogen from 50~700 °C, then it was changed to air at 700 °C.

2.3 *Tensile stress-strain characterisation*

A tensile stress-strain test was carried out using dynamic (changing with time) force thermomechanometry (TA Instruments DMA Q800). Rectangular samples of 3 mm x 25 mm were cut from the extruded tapes, and the dynamic force was increased from 3 N to 18 N at 3 N·min^{-1}. The scan was conducted at 25 °C with air purge-gas.

2.4 *Modulated-force thermomechanometry*

Modulated force thermomechanometry (mf_TM, Perkin-Elmer Diamond DMA) was used to characterize the viscoelastic properties. Rectangular samples of 8 mm x 25 mm were cut from the extruded tapes, and a synthetic frequency mode with a combined multi-frequency of 0.5, 1, 2, 5, 10 Hz was selected. Scanning was from –40 °C to 140 °C at 2 °C·min^{-1}. The synthetic frequency mode imparts a composite modulated force that is the sum of each of the five frequencies shown. Fourier analysis was used to deconvolute the response into the component frequencies. A constant deformation of 20 µm was used and the modulated force varied accordingly. Nitrogen purge gas was used at a flow rate of 25 mL·min^{-1} and 100 mN initial static force was used. The resulting complex modulus was separated into the storage modulus (E'), the in-phase component corresponding to elasticity) and the loss modulus (E"), the out-of-phase component corresponding to viscoelasticity), with the damping factor equal to their ratio E"/E'=tan(δ), representing the fraction of energy dissipated relative to that stored elastically.

3.   Results and Discussion

3.1 *Composition and thermal stability*

Figure 1 shows an increase in the temperature of maximum mass loss rate, the peak of the differential thermogravimetry curve, indicative of an increase in thermal stability of the PP– polysiloxane blends with increasing polysiloxane volume fraction. The results are summarised in Table 1. PSil has high temperature resistance and its dispersion in PP binds the PP molecules to the large number of PSil particles. Degradation by chain scission and volatilisation of PP fragments is reduced by the network of PSil particles thereby retarding degradation of PP until higher temperatures..
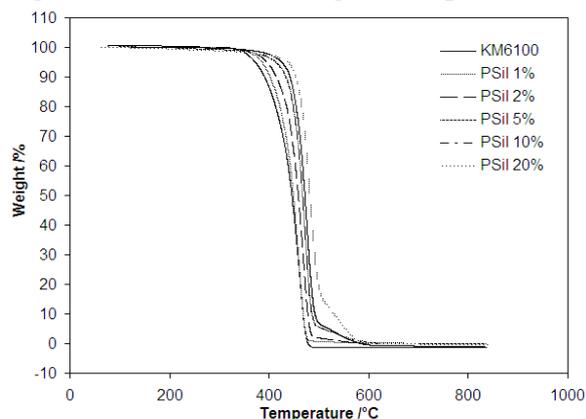

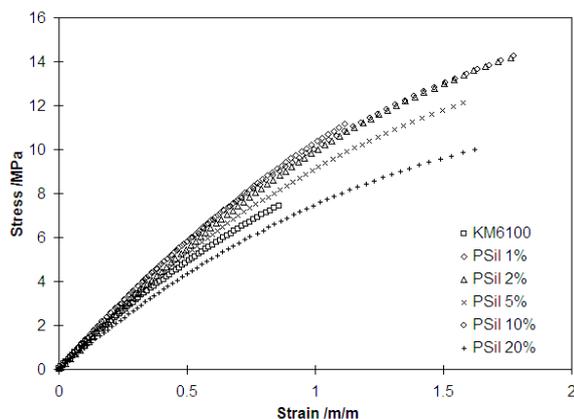Fig. 1. TGA curves for each PP–SPSil

Fig. 2. Tensile stress-strain curves for each PP–PSil

Table 1. PSil content and degradation temperature, tensile modulus, glass transition temperature and activation energy

PSil content (%·w/w)	Degradation temperature (°C)	Tensile modulus (MPa)	T_g $(\tan(\delta)_{max.})$ (°C)	E_{act} for T_g (kJ·mol^{-1})
0	461	1166	0.3	83
1	461	1250	1.3	111
2	472	1149	3.7	139
5	473	1134	2.2	108
10	477	1247	2.8	104
20	482	956	6.3	125

3.2 *Tensile stress-strain test*

The tensile modulus of each PP and PP–PSil was obtained from the initial gradient of the tensile stress-strain data. Figure 2 shows a trend of increasing PSil content decreasing the modulus while increasing elongation at break. Table 1 shows that composites containing 1 %·v/v PSil and 10 %·v/v PSil gave the highest tensile modulus, the modulus of 2 %·v/v and 5 %·v/v PSil were slightly lower. When the composition of PSil in the blends reached a limit (between 10 and 20 %·v/v) the tensile modulus decreased significantly. Other elastomers dispersed in PP show a similar trend where there is an optimum for increased toughness with retention of strength before strength is ultimately decreased by the elastomer. If PP and PSil were miscible there would be a continuous change in properties from those of PP to those of PSil with concentration change.

3.3 *Modulated force thermomechanometry*

The glass transition temperature, T_g, was characterized by the maximum of the $\tan(\delta)$ curves, rather than the E" curves, due to the sharper maxima. Figure 3 illustrates E', E" and $\tan(\delta)$ data for a blend under a single frequency (1 Hz), the peak of tan(™) was selected as T_g under that frequency. Figure 4 and Table 1 show that T_g of the blends increased with increasing PSil content. Figure 5 shows that T_g shifted to higher temperature with increasing frequency. The activation energy (E_{act}) was calculated using the Arrhenius equation where the change in ln(frequency) was plotted against 1/T (1/K) and the slope equal to $-E_{act}/RT$ where R is the gas constant (Figure 6). Table 1 shows the E_{act} value of PP and each PP–PSil.
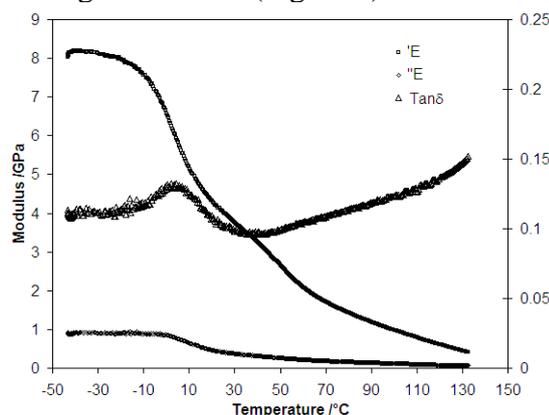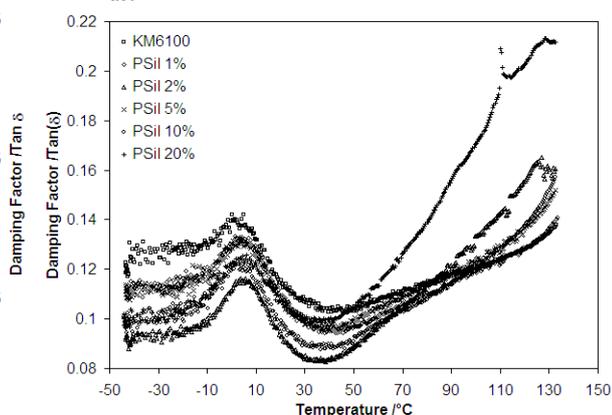

Fig. 3. PP–PSil (5 %·v/v) mf-TM at 1 Hz.
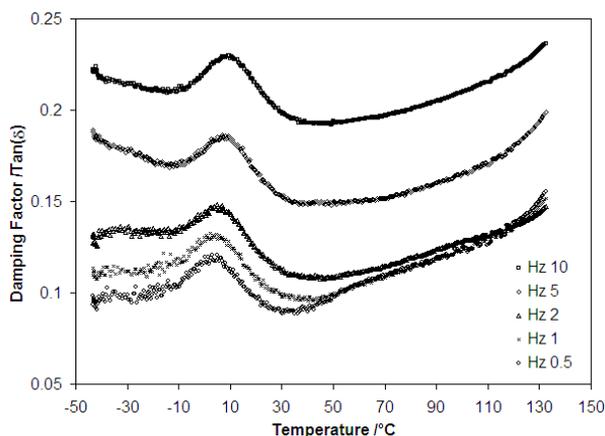

Fig. 4. PP–PSil mf-TM tan(δ) and PSil content
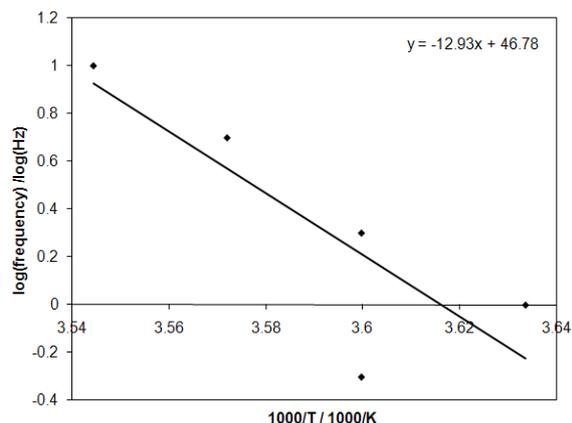
Fig. 5. PP–PSil (5 %·v/v) mf-TM with frequency

Fig. 6. Example Arrhenius plot for activation energy

4. Conclusions

Increased polysiloxane content in the polypropylene-polysiloxane blends increased the mobility of polypropylene during processing and enhanced the thermal stability. The tensile modulus increased slightly when the level of polysiloxane was less than 10 %·v/v, indicative of increased crystallinity in blends and shear banding of PP in the interphase region near the elastomer dispersed particles. The T_g of composites increased with increasing of polysiloxane content. The activation energy, or temperature dependence of PP molecular segmental mobility, was greater in the blends than for pure polypropylene.

References
[1]   Renger C J, Burrows S J, and Shanks R A 2001 *J. Appl. Polym.* Sci. **82** 3091.
[2]   Chipara M, Lozano K, Hernandez A and Chipara M 2008 *Polym. Degrad. Stab.* **93** 871.
[3]   Munoz P M P, Werlang M M, Nachtigall S M B, Cardozo N S M and Mauler R S, 2007 *J. Appl. Polym. Sci.* **104** 226.
[4]   Mohanty S. and Nayak S K, 2007 *J. Appl. Polym. Sci.* **104** 3137.