Dynamic and Modulated Thermomechanical Behaviour of Toughened Polypropylene Composites

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Polypropylene (PP) composites have been prepared with mineral filler particles encapsulated in polar elastomers to increase toughness as well as tensile modulus and strength. Composites were prepared in a single screw extruder with special Gateway screw for enhanced dispersion. Mechanical testing demonstrated enhanced properties using both stress–strain and modulated frequency viscoelastic analysis. The viscoelastic analysis determined mechanical properties as a function of frequency and temperature, with emphasis on the glass transition phenomenon.

1. Introduction

Polypropylene (PP) has been known as a widely used polymer. Nevertheless, its glass transition temperature (T_g) in ambient temperature has limited its utility. Many investigations had shown that blending PP with elastomers (polymers with instantaneous reversible deformation response) or a dispersed phase mineral (filler) should enhance physical and mechanical performance [1, 2].

In this study, PP was blended with three elastomers for surface modification between the PP matrix and filler respectively. There will be three possible discrete morphologies existing in the composites: separate mineral particles in PP, separate elastomer particles in PP, elastomer encapsulated mineral particles in PP [3, 4]. The latter are surface energetically preferred due to the polar sites on elastomer chain segments that aid in binding well with fillers. The mechanical properties of the composites would be characterised using dynamic force (stress–strain) analysis and modulated force thermomechanometry.

2. Experimental

2.1 Materials

Table 1 shows the composition of each blend system in this research, respectively. Polypropylene (KM6100) was supplied by Bastell with MFI: 3.5 dg·min⁻¹, density: 0.905 g·cm⁻³, and softening temperature: 152 °C. Ultra-high molar mass polysiloxane masterbatch (MB50-001) was supplied by Dow Corning with siloxane content: 50 % and density: 0.95 g·cm⁻³. Propylene-maleic anhydride graft copolymer (A-C 597A) was supplied by Honeywell with density: 0.94 g·cm⁻³, free maleic anhydride content <0.9 %, and drop point: 143 °C. Poly(ethylene-co-vinyl acetate) (FL00212) was supplied by Exxon Mobil with density: 0.933 g·cm⁻³ and VA content: 12 %. Talc (T20A) was supplied by Unimin with density~2.7 g·cm⁻³. Kaolin (Polyester 200R) was supplied by IMERYS Minerals with density: 2.6 g·cm⁻³.

2.2 Composite preparation

Blend tapes were prepared by melt-blending in a single screw extruder, with Gateway screw of 12 mm diameter with a length:diameter ratio of 1:26 (Axon B12). The temperature settings of each zone were: 165 °C for the feeding zone, 180 °C for the melting zone, 180 °C for the metering zone, and 165 °C for die zone and the rotator speed was set at 90 rpm. After cooling the tape, a thermal treatment at 140 °C for 2 h was conducted.

2.3   Dynamic force stress–strain test

A dynamic (changing with time) force tensile test was conducted to explore the hardness, toughness and strength change after adding fillers and elastomers. Tensile mode was chosen as the geometry of test-scan. Rectangular samples of 10 mm x 25 mm were cut from the thermal treated tape then put into the clamp of an Instron Universal Test Instrument, the crosshead speed was set at 2 mm·min⁻¹, and the scan was carried out at 25 °C.

2.4   Modulated force thermomechanometry

Modulated-force (sinusoidal oscillation with time) thermomechanometry (mf-TM) (Perkin-Elmer Diamond DMA) was used to characterize the viscoelastic properties. Rectangular specimens of 8 mm x 25 mm were cut from the blend tapes, and a complex frequency or synthetic multi-frequency of 0.5, 1, 2, 5, 10 Hz was selected. Scanning was carried out from -40 °C to 140 °C at 2 °C·min⁻¹. A constant deformation of 20 μm was used for control of the variable modulated force. Nitrogen purge gas was used at a flow rate of 25 mL·min⁻¹ and 100 mN of initial static force was used.

3.   Results and Discussion

3.1   Dynamic force tensile analysis

Table 1 lists the results of dynamic force modulus, yield stress and peak strain, which shows that addition of PMAC and EVA in the PP-filler composites increased the Young's modulus. Addition of PSil did not significantly alter the Young's modulus, referring to the elastomer encapsulated mineral particles dispersed into the PP morphology that contributed to increasing the strength of composites. Though PSil contributed the least in strength among all three elastomers, the toughness of PP-PSil-filler increased most while other composites decreased the toughness. Silicone elastomer has a lower modulus than PMAC or EVA and the silicone was more able to absorb stress thereby increasing toughness.

Table 1 Mechanical properties of composites, tan(δ) peak, E_{act} for composite glass transitions.

PP composite	Ratio (%)	Modulus (MPa)	Stress (MPa)	Peak Strain (%)	Tan(δ) peak at 1 Hz (°C)	E_{act} of T_g (kJ·mol⁻¹)
PP	100	636	34.0	22.8	0.26	84.8
PP-PSil-talc	90-5-5	628	21.5	25.1	2.47	165.3
PP-PSil-talc	85-10-5	602	21.2	9.3	2.49	108.8
PP-PSil-kaolin	90-5-5	685	24.6	41.0	3.79	82.9
PP-PMAC	95-5	575	28.1	15.3	1.68	78.9
PP-PMAC	90-10	488	21.9	16.0	3.30	123.8
PP-PMAC-talc	90-5-5	766	26.7	11.4	1.11	71.6
PP-PMAC-talc	85-10-5	805	28.4	12.6	0.29	63.8
PP-PMAC-kaolin	90-5-5	755	31.6	15.7	0.32	83.1
PP-EVA	90-10	495	24.3	13.7	0.32	64.9
PP-EVA-talc	90-5-5	770	31.6	18.0	1.73	111.9
PP-EVA-talc	85-10-5	641	27.0	19.8	5.06	73.1
PP-talc	95-5	684	28.9	14.5	-0.355	87.1
PP-kaolin	95-5	665	28.8	14.5	3.64	99.5

3.2   Modulated force thermomechanometry

The mf-TM was conducted with a synthetic frequency scan in tensile deformation mode. The maximum of each tan(δ) peak was determined as T_g. The synthetic frequency

mode imparts a composite modulated force that is the sum of each of the five frequencies shown. Fourier analysis is used to deconvolute the response into the component frequencies, whereby the modulus is resolved into in-phase (storage) and out-of-phase (loss) components. They provide both frequency and temperature response of the storage modulus (E') and loss modulus (E") and their ratio is the damping factor, $\tan(\delta)=E''/E'$. The storage modulus is the instantaneous reversible (elastic) response and the loss modulus is the time dependent reversible (viscoelastic) response.
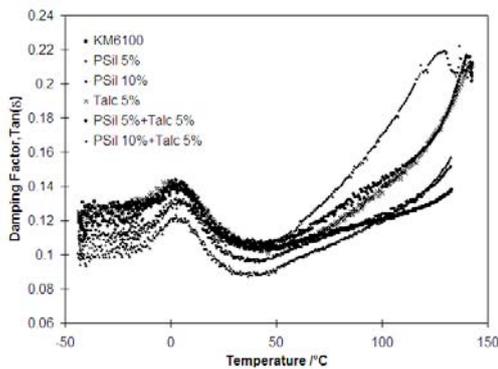
Fig. 1. Tan(δ) curves of PP-PSil-talc
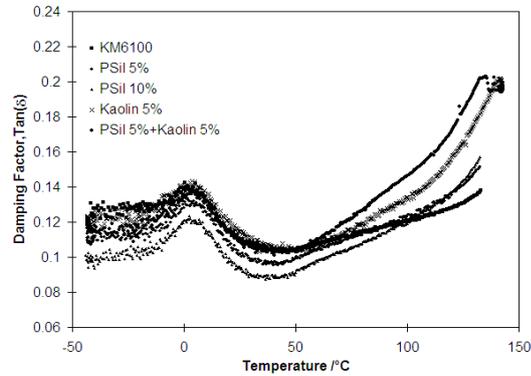
Fig. 2. Tan(δ) curves for PP-PSil-kaolin.
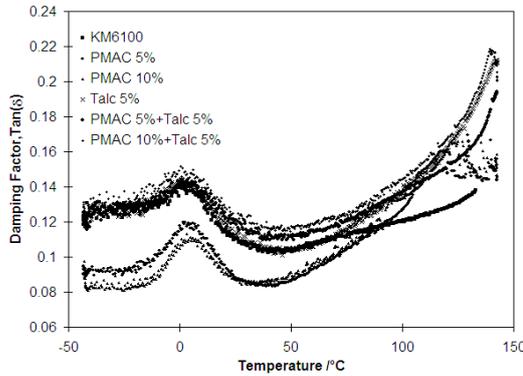
Fig. 3. Tan(δ) curves for PP-PMAC-talc
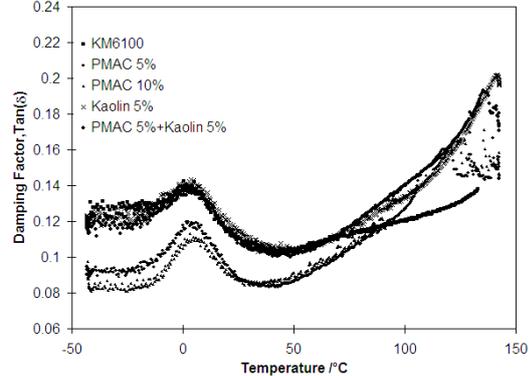
Fig. 4. Tan(δ) curves for PP-PMAC-kaolin.
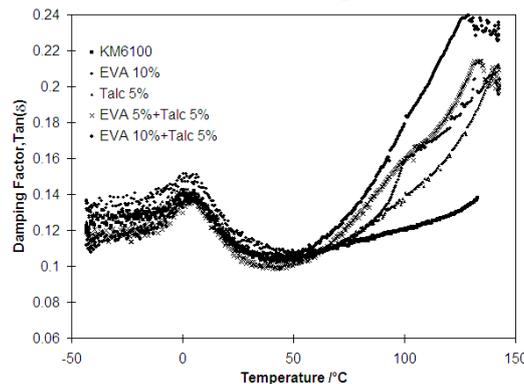
Fig. 5. Tan(δ) curves for PP-EVA-talc.

Table 1 and Figures 1 to 5 show that blending any of the elastomers or kaolin with PP slightly increased the T_g of the composites while blending talc with PP decreased the T_g. PP-elastomer-talc and PP-elastomer-kaolin blends exhibit a slightly higher T_g than pure PP. 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 = $-E_{act}/R$, where R is the gas constant. Table 1 shows the E_{act} value of PP and each blend.

4. Conclusions

Blending with mineral fillers increased the strength of the composites, while blending with elastomers contributed in increased toughness. The compatibilising elastomers aid in the binding between matrix and fillers and enhance the strength of the composites significantly with slight decrease or even increase in toughness, and the filler particles are enveloped by elastomer. The T_g was shifted to higher temperature with addition of each elastomer and kaolin and conversely shifted to lower temperature with addition of talc. Furthermore, the T_g of each PP–elastomer–filler composite was higher than that of pure polypropylene. The temperature dependence of PP molecular mobility, the activation energy, was greater in PP–PSil–filler blends and lower in PP–PMAC–filler and PP–EVA–filler composites.

References
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