DYNAMIC MECHANICAL ANALYSIS OF REXTAC® AMORPHOUS POLYALPHAOLEFINS (APAO) AND BLENDS WITH STYRENE BLOCK COPOLYMERS (SBCs)

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ABSTRACT

Characterization of REXTAC® APAO by dynamic mechanical analysis is reported. The glass transition temperatures, T_gs were dependent on the chemical composition of the copolymers. The elasticity as measured by the storage modulus, G', is a function of the comonomer type and concentration in the copolymer. Blending with Kraton® SBCs yielded immiscible blends, as evidenced by the presence of two distinct T_gs. However, the G' value at 25°C and 1 Hz showed varying levels of compatibility between the SBCs and APAO.

INTRODUCTION

Hot melt adhesives (hot melts) are a fast growing segment of the APAO market. Hot melts are a formulation of a thermoplastic, which is considered the backbone of any hot melt formulation, a tackifier resin, a wax, a thermal stabilizer and sometimes, a modifier. They are used in a diverse array of industries including packaging, book binding, non-wovens, automotive assemblies, etc. Some important polymer parameters that allows for successful use in these type of applications are low viscosity, acceptable cohesive strength, wettability of the substrates and a broad application window.

There are several different types of HMA ranging from the ethylene-vinyl acetate copolymer based HMA, the low molecular weight PE, the elastomer (i.e. styrene block copolymers) and the amorphous poly(alpha)olefin based HMA's to the specialty two component HMA's.

Amorphous polypropylene, APP, which is still used in some HMA formulations is obtained as a by-product of old Ziegler-Natta coordination polymerization technology. However, with the development of new Ziegler-Natta catalyst and process technologies, it has been possible to produce, on-purpose, amorphous polyalphaolefins that have a wide range of closely reproducible properties such as Brookfield melt viscosity, softening point, needle penetration and open times. These properties give only a narrow, partial picture of how a polymer behaves on a macroscopic scale. Other polymer properties, such as tensile strength or rheology, can give a better picture of how a polymer behaves when used as a component in a hot melt adhesive or a sealant formulation. Results on tensile strength testing have been reported elsewhere [1].

Polymeric materials are inherently viscoelastic. Thus, it is important to study both the viscous (loss) and elastic (storage) responses to deformation. These responses can be determined by dynamic mechanical analysis (DMA). DMA is a useful technique to determine how a polymer responds when deformed. It can be used to better understand the role of the polymers in HMA applications. DMA can separate the elastic (storage) modulus G' and the viscous (loss) modulus G''.

Dynamic oscillation over a frequency range can be used to determine the storage modulus G' as the measure of elasticity (or the energy stored by an adhesive). The elasticity of a polymer strongly influences the thickness of the adhesive layer during application [2]. A low elasticity is desirable during application, but a high value is favorable during end-use. This parameter can be easily varied for a given polymer by the temperature of application. In addition, the combination of the storage modulus and the glass transition temperature (the temperature at which the onset of molecular motion starts to take place) show distinct application windows for specific end uses [3]. The glass transition temperature can be easily determined by the peak in tanδ (the ratio between G'' and G') during a temperature sweep at constant frequency.

There a number of papers dealing with the use of styrene based block copolymers in HMA applications [2-8]. The effect of molecular weight distributions on the dynamic mechanical properties of narrow molecular weight amorphous polypropylenes has been previously reported by McLaughlin and Latham [9]. But not much has been reported in the area of amorphous polypropylenes in HMA and dynamic analysis. We have recently set out to determine the rheological properties of REXTAC® amorphous polyalphaolefins and this paper presents some early results of an on-going program set up to study the rheology of RT APAO, both neat and when used as a component in hot melts, sealants, laminations, etc., formulations.

EXPERIMENTAL

There are three distinctive product types of on-purpose APAO produced by our technology:

a.- propylene homopolymers,
b.- copolymers of ethylene and propylene
and
c.- copolymers of butene-1 and propylene.

For hot melts, the homopolymers are designated as the RT 2100 series, the RT 2200, 2300 and 2500 are low, medium and high ethylene copolymers respectively, and the 2700 are butene-1 copolymers. The last two digits indicate the melt viscosity of the polymer in units of *poise*.

For this study, three different APAO were chosen: RT 2180, a propylene homopolymer with a melt viscosity of 8000 cps, RT 2585, a high ethylene (ca. 15%) copolymer and RT 2780, a butene-1 copolymer. Each APAO represents a polymer of different chemical composition and were chosen of the highest MW available. The styrene block copolymers (SBCs) chosen were, KRATON® G-1657X, a SEBS SBC and D-1107, a SIS SBC (see Table 5). The blends were prepared by mixing the components in a Sigma-blade Brabender® mixer until the blend "fluxed". Judging by the visual appearance of 50 mil thick compression molded plaques, the blends of RT APAO with the SEBS copolymer appeared as clear whereas the corresponding blends with the SIS copolymer appeared opaque.

The dynamic mechanical analysis of the blends was carried out on Bohlin Reology® AB rheometers. The modulus vs. temperature experiments were carried out using the Variable Oscillation Rheometer in torsion pendulum mode. The samples were prepared as 40 mm long x 3 mm thick x 12 mm wide bars by compression molding ca. 2 g of solid at 260°F. During the runs, the samples were heated at a constant rate of 2°C/min and at a constant frequency of 1 Hz. After the glass transition temperatures, the samples do not recover from the deformation, thus the runs were truncated. The modulus vs. frequency experiments were carried out using the Controlled Stress Rheometer. The samples, disks 25 mm in diameter by 3 mm thick, were prepared in a similar fashion as described above for the VOR experiment. The G' were determined using 25 mm parallel plates and a 3 mm gap. A frequency sweep was conducted and the G' at 1 Hz read from the plot. The data reported for each experiment are the averages of at least two runs.

DISCUSSION

Pressure sensitive adhesives (PSAs) are typically based on SIS copolymers of relatively low styrene content and relatively high molecular weight whereas the majority of the SBCs used in non-PSA HMA applications are SBS or SEBS copolymers. As mentioned in the Introduction, the rheology of styrene block copolymers has been extensively studied and is well understood. As part of our study on the rheological properties of RT APAO, we present herein data obtained for the neat APAO as well as for an intra-APAO blend and blends of APAO with two SBCs.

All adhesives must flow and wet the substrate surface to develop good contact [2]. The strength of the bond between an adhesive and the substrate will depend on surface tension and the adhesives rheology. If the surface tension of the adhesive is higher than the substrate, it will not wet the substrate. Also, its viscosity should be low enough to flow. Blending RT APAO with SBCs, specifically SIS and SEBS, results in blends that have lower melt viscosity than the neat SBCs. The Brookfield MV of the blends, determined at 190°C, are typically ca. 750 K mPa.sec for the 1:3 APAO:SBC blends, ca. 80 K mPa.sec for the 1:1 blends and ca. 20 K mPa.sec for the 3:1 blends.

Figure 1 shows a typical curve obtained in dynamic oscillation at a constant temperature of 25°C. The complex viscosity (η^*) shows a steady decline with frequency, consistent with the narrow molecular weight distribution of RT APAO. The decrease as frequency is increased from 0.01 to 10 Hz is usually 2-3 orders of magnitude. The storage modulus G' shows an increase with frequency. McLaughlin and Latham [9] reported that the G' reaches a plateau at higher frequencies for higher molecular weight APPs. No such behavior is noted here in the materials studied.

Figures 2 and 3 are typical curves obtained in dynamic oscillation at 1 Hz as a function of temperature. For an APAO, for example RT 2215, G' after the glass transition temperature showed a steady decline. In the styrene based block copolymers, after the T_g of the elastomer fraction, G' attains a plateau. As the temperature keeps increasing, the glass transition of the polystyrene phase is reached past which, G' declines further. In SBC's, the styrene phase provides the rigidity below its glass transition. For an APAO/SBC blend, for example RT 2180 and SIS, G' after the glass transition of the SIS reaches a plateau which is delimited by the T_g of the isoprene component of the SIS and the APAO. In this type of blends, it is the APAO which provides rigidity below its glass transition temperature. Past the T_g of the APAO, G' experiences a steady decline. However, due to instrumental limitations, specifically the load cell and the ability of the sample to recover from the torsional deformation after its glass transition, we were not able to determine G', G" and tan δ much above the glass transition temperature of the APAO component.

Table I shows G' and the T_g for the RT APAO. The second column shows the polymer type while the third column shows the Brookfield melt viscosities of the polymers used. The fourth column shows the storage moduli for each polymer type and it is evident that G' is strongly dependent on the polymer's structure. The homopolymers show the highest G' values of all APAO. In a prior study, we had determined that the homopolymers also showed the highest tensile strengths [1]. As ethylene is incorporated into the chain backbone, the polymers become less stiff, with the high ethylene copolymers being the softest products, and G' showing a steady decline. This trend can be observed in figure 4. A similar trend was observed for the tensile strength values [1]. The incorporation of 1-butene results in copolymers with G' comparable to the G' of the low ethylene copolymers. We should point out that the G' values found for the APAO are higher than those also found for the SEBS and SIS rubbers used in this study (see Tables 3 and 4). The glass transition temperatures show a compositional and molecular weight dependence. Evidently, by adding a comonomer such as ethylene, the barrier to internal rotation decreases therefore, the T_g of the copolymer decreases.

Table 2, and figure 5, show the data obtained from the determination of G' at constant temperature for different intra-APAO blends. It is evident, within experimental error, the near lineality of the plot of blend composition versus storage modulus. In a previous study [10], we had shown that the glass transition of intra-APAO blends determined by DSC showed single T_g transitions which were composition dependent and indicates their mutual miscibility.

The storage moduli of the different RT APAO/SBC blends is shown in Tables 3 and 4 and in figures 6-11. The G' of the blends is not quite predictable. For example, plots of G' vs. composition for blends of 2180 and 2780 with the SEBS SBC show a nearly linear relationship between G' and blend composition. However, the plots of G' vs composition for their blends with the SIS copolymer depart somewhat from lineality. The largest deviation from lineality is observed for the blends of RT 2585, the high ethylene copolymer and either the SEBS or SIS copolymers.

The most commonly used method for establishing polymer-polymer miscibility is through the determination of the glass transition temperature of the blends. A miscible polymer blend will exhibit a single T_g, somewhere between the T_g's of the components [11]. As shown in Tables 3 and 4, the determination of the T_g of blends of APAO with the SEBS and SIS rubbers indicates that the components are not miscible because the glass transition of the blends, correspond to the glass transition temperatures of the components. Table 3 shows data obtained for blends of APAO with the SEBS rubber and even though the optical appearance of the blends was clear, the presence of the two well defined, unshifted glass transition temperatures of the components indicates that the components of the blends are immiscible. A similar conclusion can be drawn for the blends of APAO with the SIS rubber. A special case is the blend of RT 2780 with SEBS in which the T_g of the SBC experienced a shift towards a lower temperature of ca. -52°C. Although we could think of a few reasons for this phenomenon, at this moment we consider that we do not have sufficient data to sustain any of them.

The nearly linear behavior of G' as a function of composition, figures 6-11, is interpreted to indicate compatibility between the blend components. Thus, RT 2180 and RT 2780 exhibit some compatibility with the SEBS and SIS copolymers whereas RT 2585 shows poor compatibility with the two SBCs. The SEBS blends were clear while the SIS blends were opaque. Usually a clear appearance is an indication of miscibility. However, with the blends showing two distinct T_gs, the observation regarding opacity may be due to the refractive indices of the APAO and SBCs.

CONCLUSIONS

It has been demonstrated that the use of dynamic mechanical analysis is a good tool to determine the rheological properties of APAO. Furthermore, the use of G' as a parameter to study the compatibility of various immiscible blends is simple and effective. APAO do not form miscible blends with SBCs but the compatibility can be affected by the type and concentration of the comonomer in the APAO.

A possible advantage that can result from using RT APAO is that the blend should show an improved heat resistance (SAFT), particularly when using a blend formulated with 2180, as the homopolymer shows a substantially high SAFT of 140°C [1]. Particularly when using RT 2180, the blends will exhibit higher storage modulus. In general, as the blends show the glass transition temperatures of the components, it should be possible to add less tackifier and/or processing oil to lower the MV of the adhesive composition while at the same time exhibiting better low temperature flexibility, as when using RT 2535. As the blends in which RT 2535 is the minor component show a lower modulus, the tack at room temperature should not be affected.

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TABLE 1. REXTAC® AMORPHOUS POLYALPHAOLEFIN

PRODUCT PROPERTIES

Product Type	Polymer Type	Brookfield Visc. (mPa.s)	G', Storage Modulus x 10^6 (Pa)	T_g (°C)
2115	Propylene homopolymer	1500	6.5	-10
2180		8000	8.2	-7
2215	Low ethylene copolymer	1500	2.3	-16
2280		8000	3.0	-13
2304	Medium ethylene copolymer	400	2.8	-17
2315		1500	2.9	-17
2330		3000	2.2	-17
2385		8500	1.8	-17
2535	High ethyl. copolymer	3500	0.8	-25
2585		8500	1.8	-25
2715	1-Butene copolymer	1500	3.4	-15
2730		3000	3.2	-14
2780		8000	2.1	-12

TABLE 2. STORAGE MODULUS, G', AT 25°C AND 1 Hz FOR AN RT 2535/RT 2180 intra-APAO BLEND

BLEND	G' (10^6 Pa)
RT 2535	0.84
RT 2535:RT 2180 = 3:1	1.2
RT 2535:RT 2180 = 1:1	3.5
RT 2535:RT 2180 = 1:3	6.1
RT 2180	8.2

TABLE 3. STORAGE MODULUS, G', AT 25°C AND 1 Hz FOR RT APAO/KRATON G-1657X RUBBER BLENDS

Sample	G' (10^6 Pa)	T_g (°C)
G-1657X	0.98	-44
RT 2180	8.2	-7
2180/G-1657X = 1:3	1.4	N.D.
2180/G-1657X = 1:1	2.6	-40/-8
2180/G-1657X = 3:1	3.9	-44/-9
RT 2585	1.8	-25
2585/G-1657X = 1:3	0.74	N.D.
2585/G-1657X = 1:1	0.67	N.D.
2585/G-1657X = 3:1	0.73	-45/-24
RT 2780	2.1	-12
2780/G-1657X = 1:3	1.1	N.D.
2780/G-1657X = 1:1	1.43	N.D.
2780/G-1657X = 3:1	1.7	-52/-10

N.D. = Not Determined

TABLE 4. STORAGE MODULUS, G', AT 25°C AND 1 Hz FOR RT APAO/KRATON D-1107 RUBBER BLENDS

Sample	G' (10^6 Pa)	T_g (°C)
D-1107	0.44	-52
RT 2180	7.7	-7
2180/D-1107 = 1:3	0.65	N.D.
2180/D-1107 = 1:1	1.65	N.D.
2180/D-1107 = 3:1	5.23	-55/-6
RT 2585	1.8	-25
2585/D-1107 = 1:3	0.35	N.D.
2585/D-1107 = 1:1	0.41	-53/-23
2585/D-1107 = 3:1	0.50	-56/-24
RT 2780	2.2	-12
2780/D-1107 = 1:3	0.49	N.D.
2780/D-1107 = 1:1	0.75	-54/-12
2780/D-1107 = 3:1	1.50	-56/-10

N.D. = Not Determined

TABLE 5
LIST OF SUPPLIERS

TRADEMARK	SUPPLIER	DESCRIPTION
KRATON® D-1107	SHELL CHEMICAL Co.	Styrene-Isoprene-Styrene Block Copolymer
KRATON® G-1657X	SHELL CHEMICAL Co.	Styrene-(Ethylene-Butylene)-Styrene Block Copolymer

Fig. 1. Storage Modulus ,G', and Complex Viscosity, η^*, vs. Frequency @ 25°C for RT 2304.

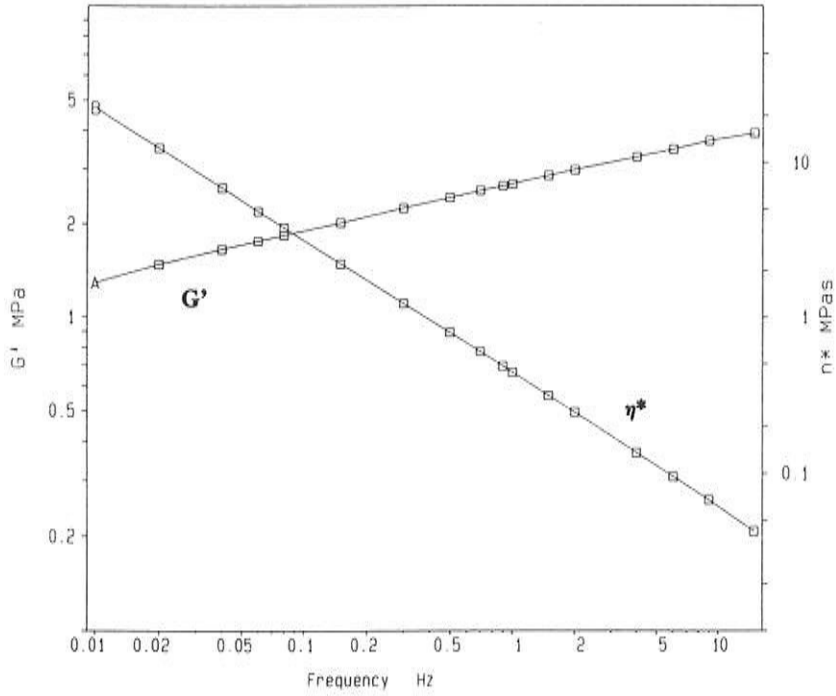

Fig. 2. Dinamic Oscillation @ 1Hz as a Function of Temperature for RT 2115.

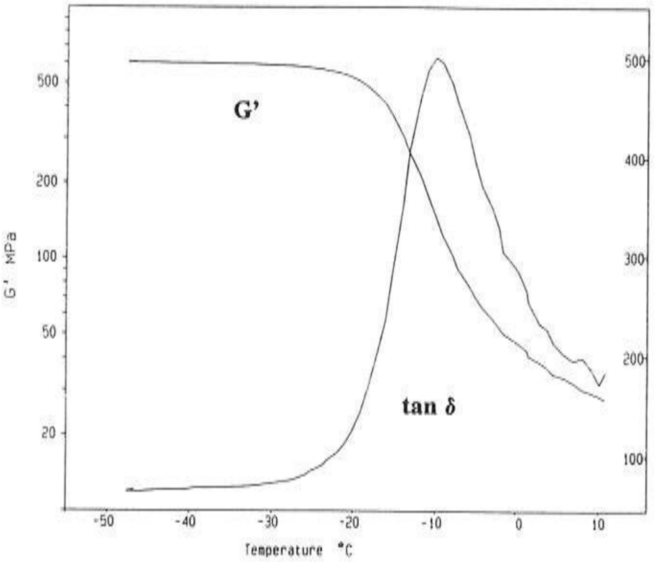

Fig. 3. Dinamic Oscillation @ 1Hz as a Function of Temperature for RT 2180:D-1107 = 3:1 Blend.

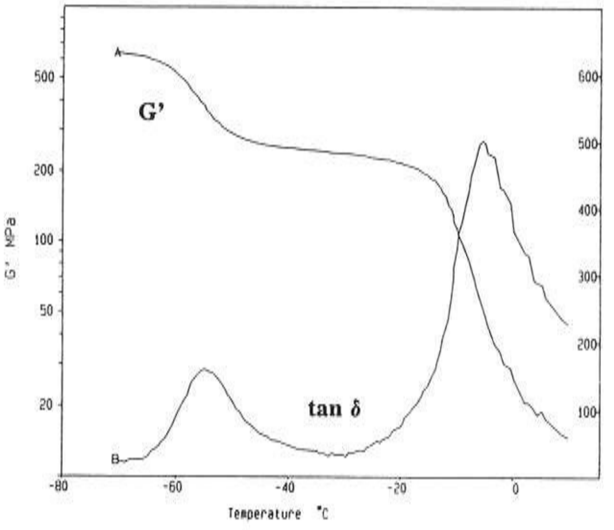

Fig. 5. Storage Modulus @ 1 Hz and 25°C for RT 2535:RT 2180 Intra-APAO Blends

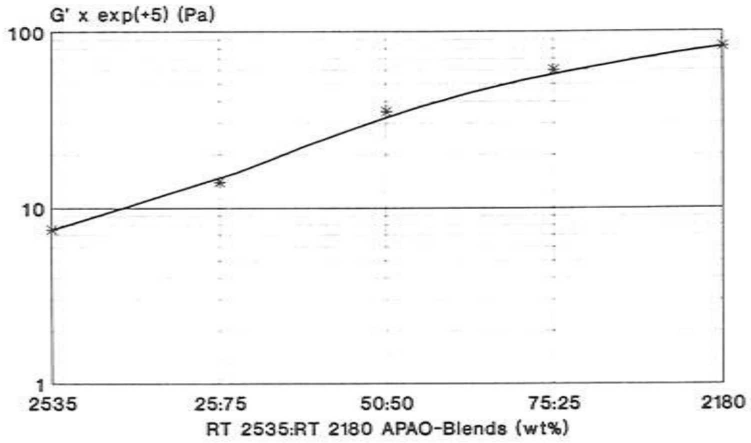

Fig. 4. Storage Modulus, G', of RT APAO Homopolymer, Ethylene and Butene-1 copolymers

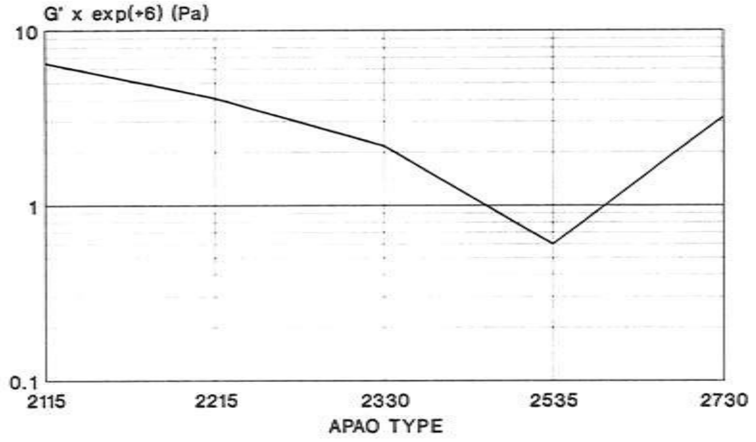

Fig. 7. Storage Modulus @ 1 Hz and 25°C for RT 2180:Kraton D-1107 Rubber Blends

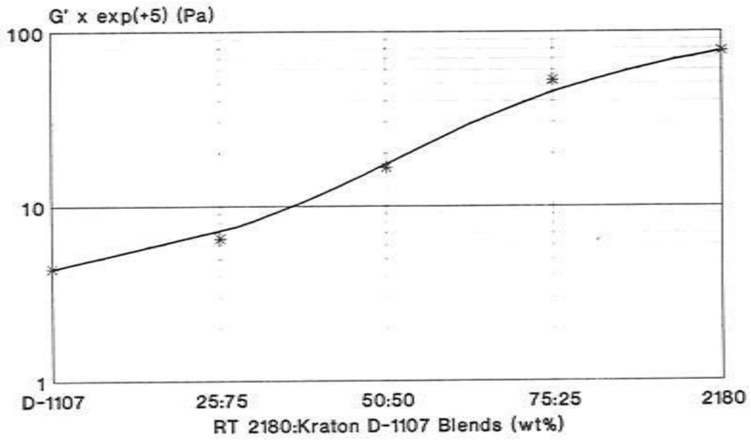

Fig. 6. Storage Modulus @ 1 Hz and 25°C for RT 2180:Kraton G-1657X Rubber Blends

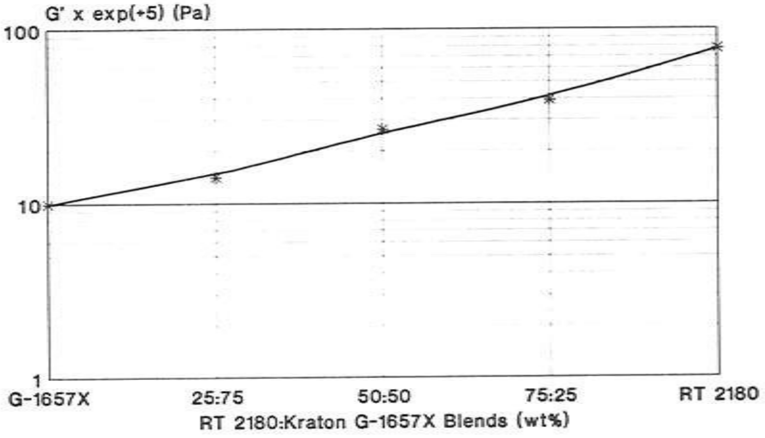

Fig. 9. Storage Modulus @ 1 Hz and 25°C for RT 2585:Kraton D-1107 Rubber Blends

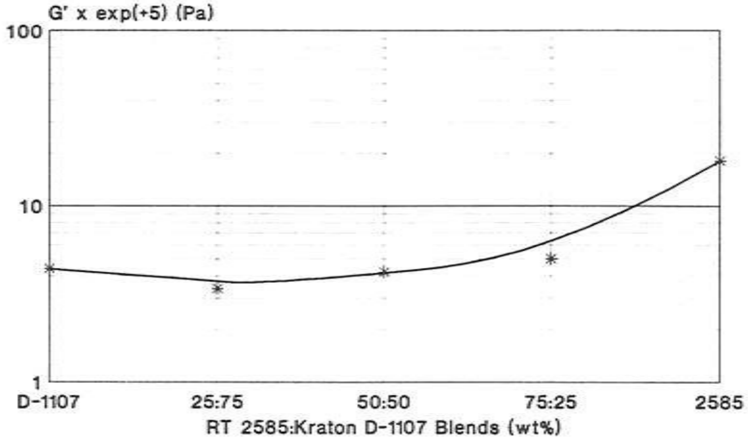

Fig. 8. Storage Modulus @ 1 Hz and 25°C for RT 2585:Kraton G-1657X Rubber Blends

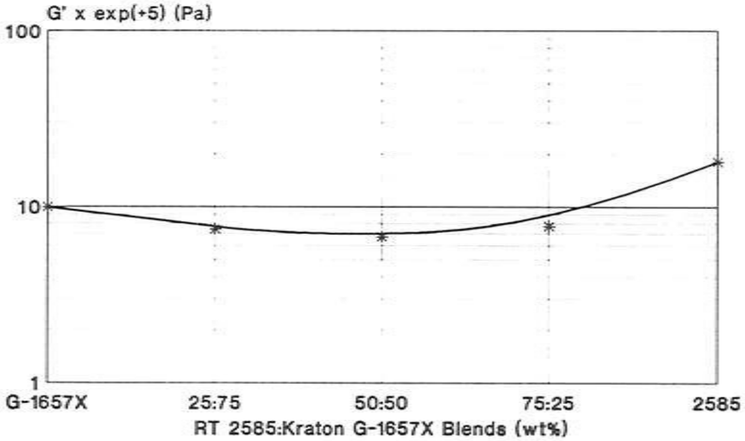

Fig. 11. Storage Modulus @ 1 Hz and 25°C for RT 2780:Kraton D-1107 Rubber Blends

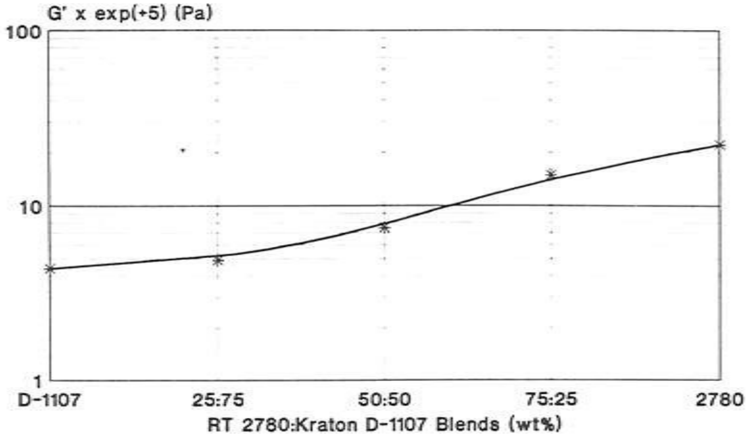

Fig. 10. Storage Modulus @ 1 Hz and 25°C for RT 2780:Kraton G-1657X Rubber Blends