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Rheological Behaviour of Polypropylene/Polyamide-6/TiO₂ Nanocomposites

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ABSTRACT

Polypropylene (PP) and polyamide-6 (PA6) blending has been attempted to achieve improvement in mechanical properties, paintability and barrier properties and adding TiO₂ into polymer matrix might produce nanocomposites with excellent mechanical, high antimicrobial and antioxidation properties. This article investigated the influence of different contents of TiO₂ nanoparticles in the PP/PA6 and PP/PA6/5M (PP-*g*-MAH) on a counter rotating twin-screw extrude, respectively. The results of the PP/PA6/TiO₂ nanometer composites steady-state rheological indication that small amounts of TiO₂ nanoparticles can make PP/PA6 and melt viscosity of PP/PA6 composite decreased and the composites owned favourable rheological properties and improving the shear storage modulus G', loss modulus G'' and complex viscosity η* of composites. It also demonstrated that TiO₂ nanoparticles can give the matrix material with favourable elasticity and viscosity at the same time. On the other hand, when the loading degree of TiO₂ nanoparticles getting higher, parts of TiO₂ nanoparticles react to agglomeration that increase the probability of TiO₂ nanoparticles colliding with each other, which shows the loading degree of TiO₂ nanoparticles have an optimum value and is completely consistent with the result of mechanical properties test of composites.

INTRODUCTION

Polymer rheology [1] is applicable to investigate molecular liquids and mainly refers to nonlinear viscoelastic behaviours of polymer melt [2] and polymer solution [3] in flow state, and the relationships of such behaviour with material structure, other physical and chemical properties [4]. For a long time, the concepts of flow and deformation belong to two areas, the properties of liquid materials are flow and the properties of solid (crystalline) materials are deformation [5-7]. The deformation is non-recoverable and dissipated parts of the energy when liquid flow exhibits viscous behaviour and produces permanent deformation. While solid deformation exhibits elastic behaviour, which generates an elastic deformation at the time of withdrawal of the external force and then recovery and store energy, besides, deformation reduction can recover energy and the material have elastic memory effects. Usually, the liquid flow complies with Newtonian flow

law that suffered material shear stress [8] is proportional to the shear rate [9] ($\sigma = \eta_0\dot{\gamma}$) and current process always is a time course only in a limited period of time to observe the flow of the material. Solid deformation generally complies with the Hooker's law and the responses between stress and strain called transient response [10]. The fluids comply with Newtonian's law as a flower of Newtonian fluid [11-13] and the solids follow with Hooker's law as a flower of Hooke elastomer. Actual materials tend to exhibit far more complex mechanical properties, such as asphalt, clay, rubber, polymer materials and products in particular, they can be flowing and deformed, sticky and elastic and viscous loss. Flow owned an elastic memory effects, binding of sticky and elastic and coexist streaming with denatured. For such types of material, Newtonian flow or just Hooke's law unable to fully describe the law of complex mechanical response [14], so we must develop a new discipline-rheological [15-19] to investigate it. The so-called "rheology'' essence is "solid-liquid two phase'' and deformation under a long time stress to present nonlinear viscoelastic instead a linear viscoelastic under a small deformation [20].

Because of the material to be processed into products is necessary to undergo machining process for the preparation of antibacterial function with a certain high-performance PP/PA6/TiO_2 nanocomposites and due to the isocyanate group (-NCO) at the surface of TiO_2 nanoparticles can react with the amino group (-NH_2) and carboxyl group (-COOH) of polyamide-6, the compatibility between the TiO_2 nanoparticles and PP/PA6 blends has been significantly improved, which results in fine dispersion of nanoparticles [21]. Polypropylene (PP) and polyamide (PA6) blending has been attempted to achieve improvement in mechanical properties, paintability and barrier properties, where polypropylene ensures good processability and insensitivity to moisture, while polyamide-6 contributes mechanical and thermal properties of TiO_2 nanoparticles have strong antibacterial and antioxidation properties [22]. Adding TiO_2 into polymer matrix might produce nanocomposites with excellent mechanical, high antimicrobial and antioxidative properties [23]. Therefore, on the composite's steady-state rheological properties the investigation has been undertaken. Titanium dioxide nanoparticles on the rheological properties of PP/PA6 and the influences of shear rate with temperature to the rheological properties of composite materials also studied. Besides, it's also take effects in the dynamic rheological properties of composite materials tested to study TiO_2 nanoparticles on the composite storage modulus (G') with loss modulus (G'') and complex viscosity.

EXPERIMENTAL

Polypropylene (PP, F401) and polyamide-6 (PA6) were supplied by China Petroleum and Chemical Corporation. Maleated polypropylene (PP-*g*-MAH) with 1 wt % of maleic anhydride (MA) was supplied by Nanjing Deba Chemical Co. Ltd (NDC). Toluene-2,4-diisocyanate (TDI) (Shanghai Chemical Industrial Co., Ltd., China) was used directly without further purification and toluene was distilled under a nitrogen atmosphere from sodium/potassium using benzophenone as an indicator. Titanium dioxide (TiO_2) nanoparticles with an

average diameter of 20 nm were obtained from Zhou Shan Mingri Nanomaterials Co., Ltd., China. They were dried overnight at 110 °C/10^{-2} mbar and functionalized with toluene-2,4-diisocyanate (TDI) according to the method we developed and reported previously [21].

Compounding: Melt compounding of the PP/PA6 blends based nanocomposites was done on a counter rotating twin-screw extruder (Haake Rheodrive 3000, Germany). The extrusion zone temperature ranged from 220 to 245 °C. Prior to extrusion, PP/PA6 blends based pellets were dehumidified by using a vacuum oven at 80 °C for 8 h. The extrudates were pelletized with the Haake pelletizer. The designations and compositions of the materials tested are given in Table-1.

TABLE-1 MELT FLOW INDEX OF PP/PA6 BASED COMPOSITES		
Sample	Parts	MFI (g/10 min)
PP/PA6	70/30	4.60
PP/PA6/5M	70/30/5	2.34
PP/PA6/3T	70/30/3	7.20
PP/PA6/5M/3T	70/30/5/3	2.84
PP/PA6/5M/7T	70/30/5/7	2.56

Determination of melt index: Melt flow rate tester: XRL-400B, manufactured by Jilin University Educational Instrument Factory. According to GB3682-1983, determination of the composite melt flow value of rate (MFR), m = 2.160 kg, T = 230 °C.

Capillary rheometer: Senior double capillary rheometer: Rosand RH7D, product by Melvyn British companies. The length we used during the experiment is 16 mm, to 1 mm diameter capillary die. The temperatures for experiment are 210, 210, 230 and 240 °C.

Rotational rheometer rheological behaviour: Rotational rheometer: AR2000Ex, production from TA company in the United States, Parallel plate model, size is 25 mm, sample in tablet sulfur on hot pressing turn into thick for 1 mm wafer and then cut into wafer, which is 25 mm in diameter. Dynamic measurement of the angular frequency of 0.1-100 rad/s, the sample in a certain temperature under small amplitude dynamic shear, form variables is 1 %, before gathering the formal data advanced line scan should be made to determine whether it was measured in the range of linear sticky bombs. Materials storage modulus (G'), loss modulus (G'') and complex viscosity (η''') viscoelastic parameters along with the change of frequency were recorded.

RESULTS AND DISCUSSION

Melt index of composite materials: Melt index is defined as: under a certain temperature and load, molten state of polymer from the diameter and standard length set by capillary flow of weight (g) in 10 min. The greater the melt index, the better liquidity is.

It is suggested from the definition of melt index that it actually tests the mobility which is given mobility under the shear rate (the viscosity of 1/η). General instrument loads of 2.16 kg, calculated from capillary diameter, shear stress is 200,000 PASCAL and shear rate scope value is about in 10^{-2}-10^{-1} s, so the melt index reflects the low speed of shear zone.

Table-1 listed the different composite material system which at 230 °C and melt index under the condition of loads of 2.16 Kg.

Moreover, that can be seen from the Table-1, although its viscosity increases and the addition of PP-*g*-MAH make blend melt index decreases. When there is little TiO_2 nanoparticles, adding surface-modified TiO_2 nanoparticles will lead to the blends (PP/PA6 or PP/PA6/5M) melt index increases and the viscosity decreases, which improve the fluidity. But when the use of nanoparticles up to 7 copies, the melt index will decrease while the viscosity will increase. To figure out the main reason of changes, we will combine the capillary rheometer for analysis and interpretation.

Working principle of capillary rheometer: Capillary rheometer rheological measurement instrument is currently the most mature, typical and widely used. The main advantages lie in simple operation, accurate measurement and wide measurement range. Material flow in the capillary is similar to the flow of the some material during the processing which has a practical value.

The core of the capillary rheometer is a different aspect ratio capillary and around the barrel, there is a constant temperature heating jacket and in the upper parts of the tank is hydraulically driven plunger. The materials get forced and out from the capillary extrusion after the material is heated into the melt and under high pressure of the plunger, then we can test the viscoplasticity of the materials.

Viscosity of the materials through capillary can be obtained by measuring the pressure gradients to determine shear stress or measuring the volume flows or average flow velocity to calculate shear rate.

For a blood capillary, length is L, radius is R, capillary pressure is P and shear stress on the wall of formula 1 can be expressed:

$$\tau_w = \frac{\Delta PR}{2L} \tag{1}$$

For a Newtonian fluid whose viscosity is η and the volume flow rate is Q, the shear rate at its wall:

$$\hat{\gamma}_w^N = \frac{\Delta PR}{2L\eta} = \frac{4Q}{\pi R^3} \tag{2}$$

For non-Newtonian fluid, the shear rate expressed as:

$$\hat{\gamma}_w = \left(\frac{3n+1}{4n}\right)\hat{\gamma}_w^N \tag{3}$$

where n is non-Newtonian index as defined Rabinovitsch-Mooney equation, n value is:

$$n = \frac{d\ln\tau_w}{d\ln\hat{\gamma}_w^N} \tag{4}$$

Therefore, you can get the corresponding values of n through τ_w and the $\hat{\gamma}_w^N$ double logarithmic differential curve.

Relationships between the shear stress and shear rate: Figs. 1 and 2 are different composite system curves of relationship between shear stress and shear rate. Newtonian fluids flow is not changed with shear rate γ̇ constants viscosity, shear stress σ and shear rate γ̇ of simple linear relations in simple shear flow fields

and the proportion coefficient $\eta = \frac{\sigma}{\dot{\gamma}}$ is called viscosity.

Fig. 1 shows that shear rate increase with shear stress increase, but the shear stress σ and shear rate γ̇ can't maintain a constant linear proportional relationship. Analogy with the

Newtonian fluids, $\eta_a(\dot{\gamma}) = \frac{\sigma(\dot{\gamma})}{\dot{\gamma}}$ can be defined as the apparent

shear viscosity of polymer fluid [24,25].

Apparent viscosity is not a real degree of material measure of irreversible deformation because it always accompany with elastic deformation in the process of flow and elastic recovery in the processing of flow. According to the formula, the actual material is irreversible viscous flow and reversible elastic deformation join together reflects the ratio of shear stress and shear rate and it is smaller than real viscosity values of the material.

We have found that number of the concentrated solution of polymer and polymer melt, the process at the ranges of shear rate (about γ̇ 10^0-10^3 s^{-1}). The shear stress and shear rate satisfies the following empirical formula: σ = K·γ̇^{n} or σ/γ̇ = K·γ̇$^{n-1}$, types of K and n as the material parameters, n is the flow of the materials or non-Newtonian index, it is in lg σ~lgγ̇ log-log curves of the slope. And the parameter of K is related to temperature.

For Newtonian fluids, n = 1, K = η_a and for pseudoplastic fluids [26], n < 1. The greater the value n deviation from 1, the stronger indicating that the material pseudoplastic (non-Newtonian) and the difference between n and 1 reflects the strength of the material nonlinear properties. Usually the significant of the non-Newtonian material and the value of n increase with the shear rate increase. The value of n can be used as a measure of the material' nonlinearity, therefore, all the factors that affect material nonlinear properties have an impact on the value of n.

The shear stress and shear rate of the exponential lg γ̇ is X axis with lg σ to Y axis, drawing in Fig. 2. Fig. 2 gives the relationship of the composites system of lg σ~lgγ̇ log-log curve. From Fig. 2 the incomes curve to linear fitting curve slope is n and lg K is intercept.

From Fig. 2 we can obviously conclude that lg σ and lg γ̇ have a good linear relationship, lg σ linearly follow with lg γ̇ increased and shear rate in the tested range is compliance Ostwald-de Wale powered law equation. It is clear from Fig. 2 a and 2d that TiO_2 nanoparticles make the shear stress decreased in the same shear rate, but the shear stress will be increased when it above a certain level. Addition of macromolecular compatibilizer makes shear stress increase.

From Table-2 it also can be seen that adding 3 parts of TiO_2 nanoparticles in PP/PA6 make the value of n increases. Add a certain amount of the TiO_2 nanoparticles into composite material system of PP/PA6/5M the flow index (non-Newtonian index) n value increases, but flow index n decreased and the pseudoplastic enhanced as the amounts of TiO_2 nanoparticles added exceed a certain amount.

Relationship of shear viscosity and shear rate: According to the data tested from rheometer to make the changing curve to viscosity and shear rate for the above composite materials system. Fig. 3 provides all composite material's changing curve and shear viscosity followed by shear rate at 230 °C.
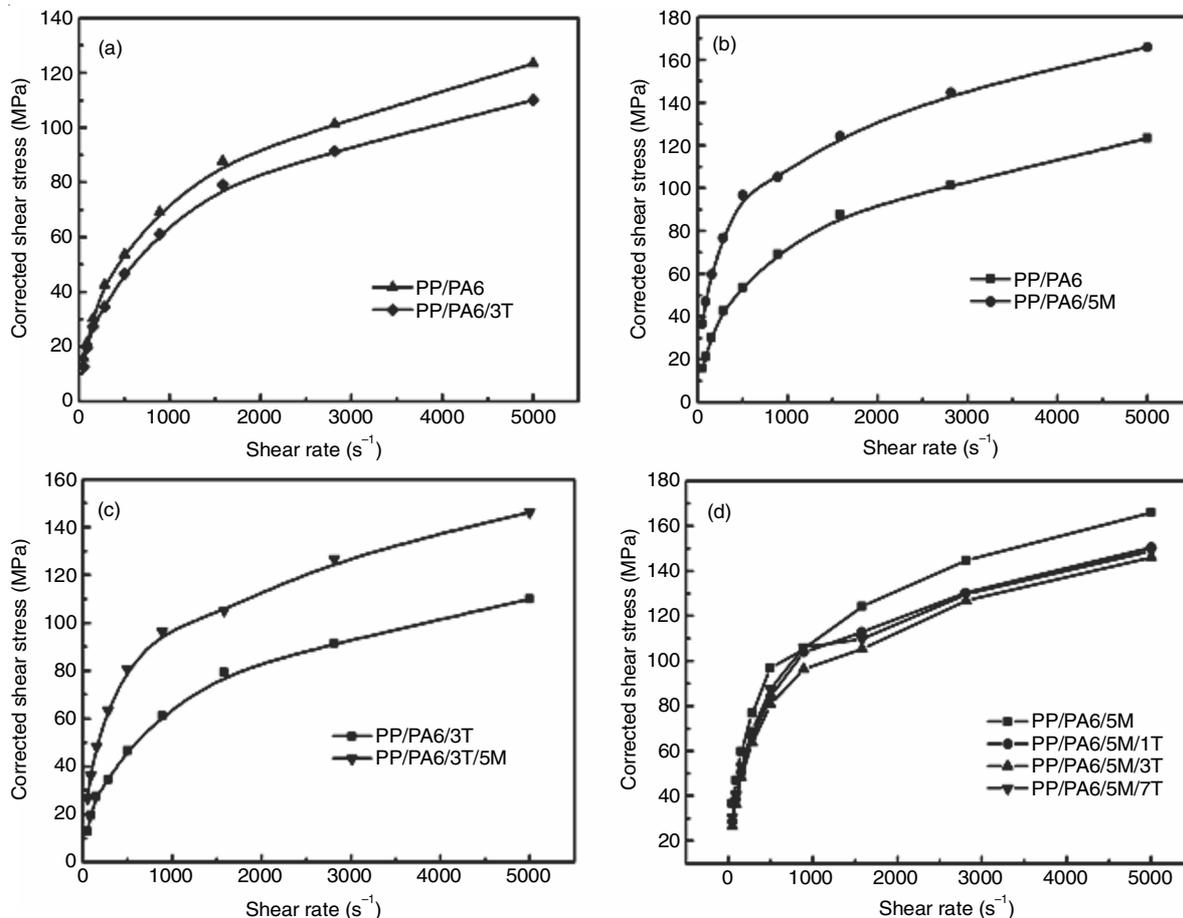
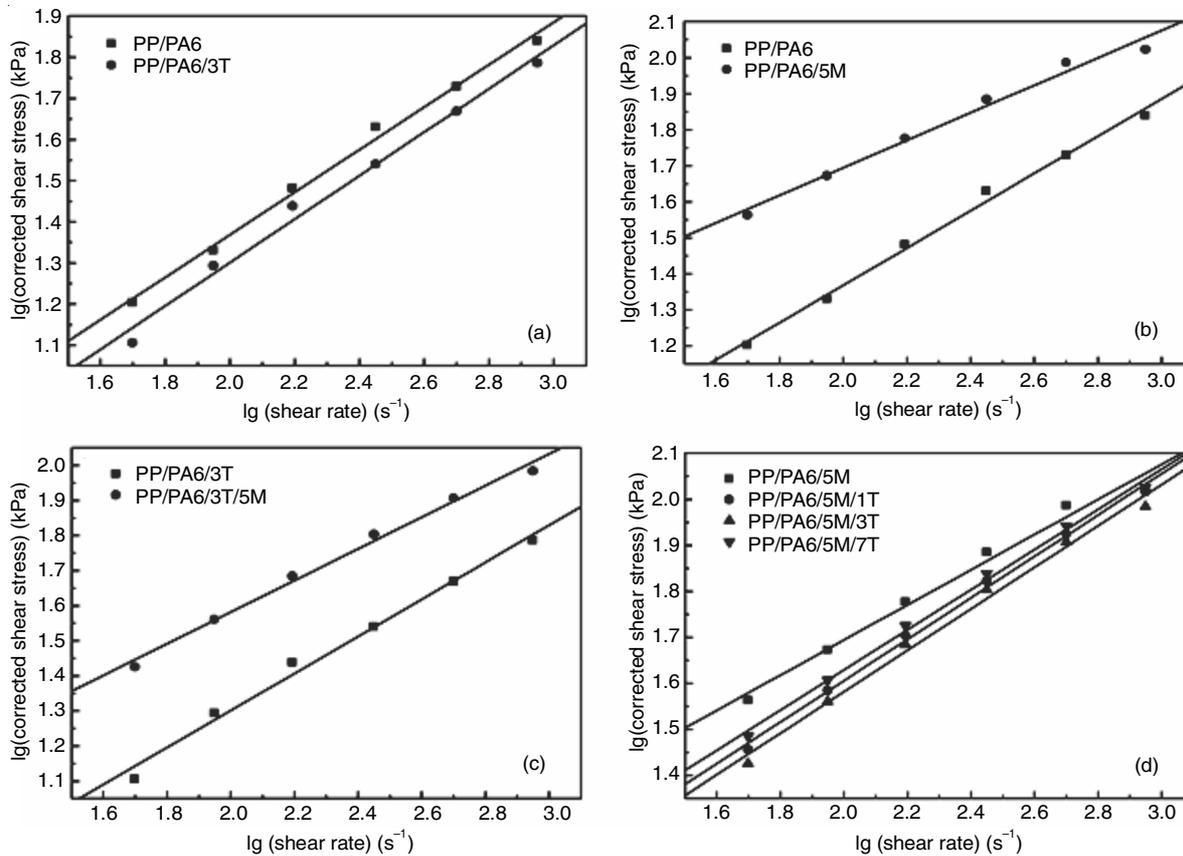Fig. 1. Corrected shear stress *vs.* shear rate

Fig. 2. lg (corrected shear stress) *vs.* lg (shear rate)

TABLE-2 VALUES OF n AND K FOR PP/PA6 BASED COMPOSITES			
Sample	lg K	n	K
PP/PA6	0.34	0.52	2.16
PP/PA6/3T	0.25	0.53	1.76
PP/PA6/5M	0.93	0.38	8.53
PP/PA6/5M/1T	0.71	0.45	5.09
PP/PA6/5M/3T	0.68	0.45	4.80
PP/PA6/5M/7T	0.76	0.44	5.72

At a certain temperature, η_a mainly is a function of shear rate if shear stress has no time-dependent. As can be seen from Fig. 3, composites melt shear viscosity gradually decreases with increases shear rate, the variations in line of shear rate on shear viscosity of the liquids polymer of the general rule, *i.e.*, the effect of ''shear thinning''. Polymer flow is not coincidence the Newtonian equations of fluid, while lower-molecular liquid flow, the flow rate increased to increase resistance, shear stress

σ is direct proportion with shear rate $\dfrac{d\gamma}{dt} = \dot{\gamma}$.

$$\sigma = \eta\frac{d\gamma}{dt} = \eta\dot{\gamma} \qquad (5)$$

Eqn. 5 is the Newtonian fluid' formula, proportional constant η is viscosity, it is resistance (shear stress) in unit area when the rate gradient of liquid flow (shear rate) is 1 s^{-1}. The liquids of viscosity would not change follow by the size of shear stress and shear rate and keep constants all the time.

Those who do not conform the fluid Newton's fluid formula, collectively referred as non-Newton fluid rheological behaviour, which has nothing to do with time are pseudoplastic fluid, dilatant fluid [27] and Bingham fluid (Bingham) [28].

The viscosity of the polymer melts and conc. colutions of pseudoplastic fluid decreases with increase of shear rate. This is because the polymers in the flow of the liquid layers between the total liquid layers exist certain velocity gradients, if the macromolecules with thin and long at the same time through several different flow liquid layered, each part of the same molecule make progress to different speed and this situation is clearly not lasting. Therefore, the long chain molecules are always tries to make all parts of them into the same velocity flow layers in the flow. Parallel distribution of different flow velocities of molten layer leads to the orientation of molecules in the direction of flow. This kind of phenomena are always naturally along the flow direction of longitudinal arrangement, increases of polymer in the flow process with shear rate or shear stress and the orientation of macromolecule makes melt viscosity reduction.

Relationship between shear viscosity and shear rate

Influence of TiO₂ nanoparticles for shear viscosity: Fig. 4(a) and 4(b) are surface modified TiO₂ nanoparticles on
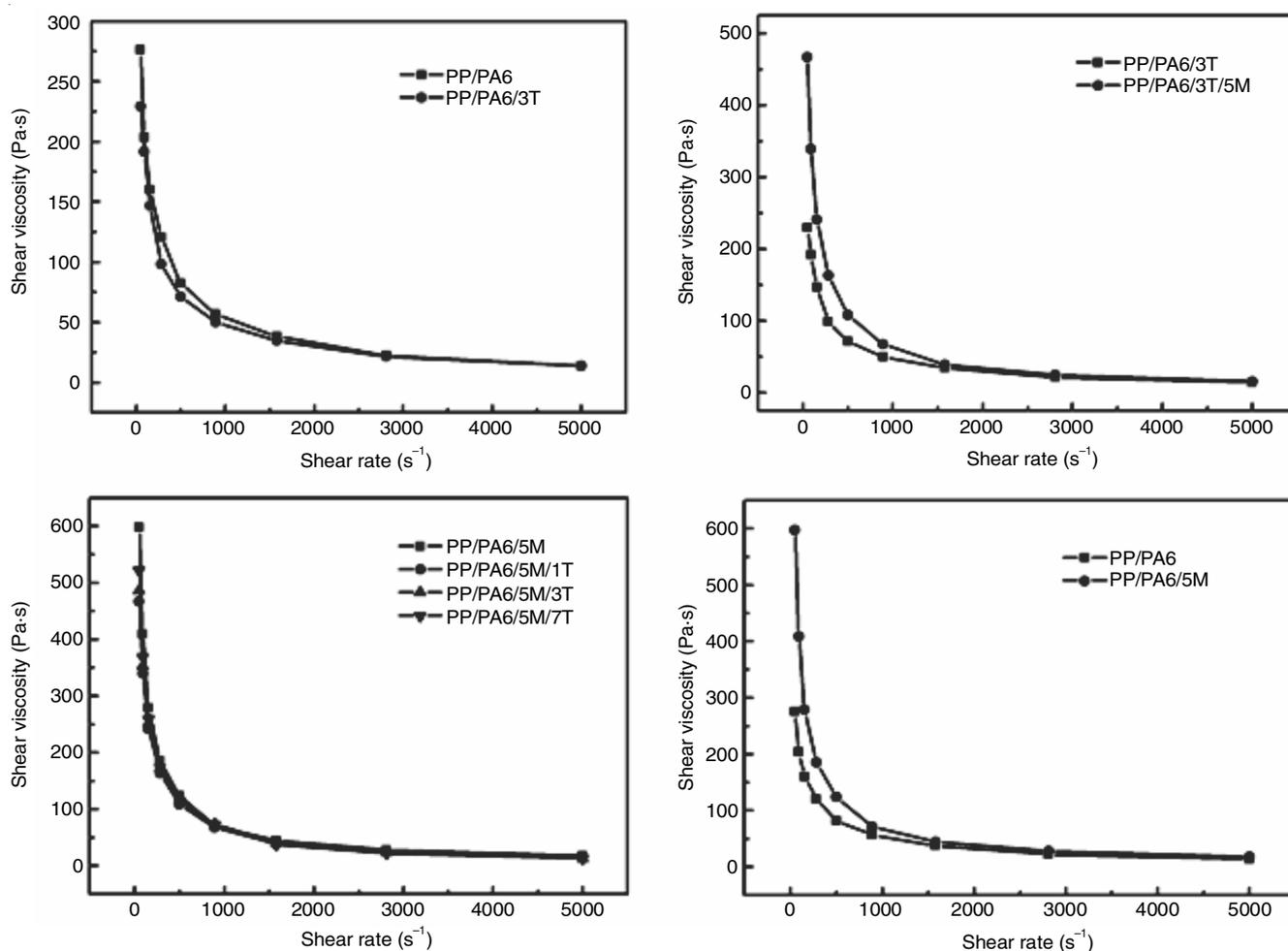

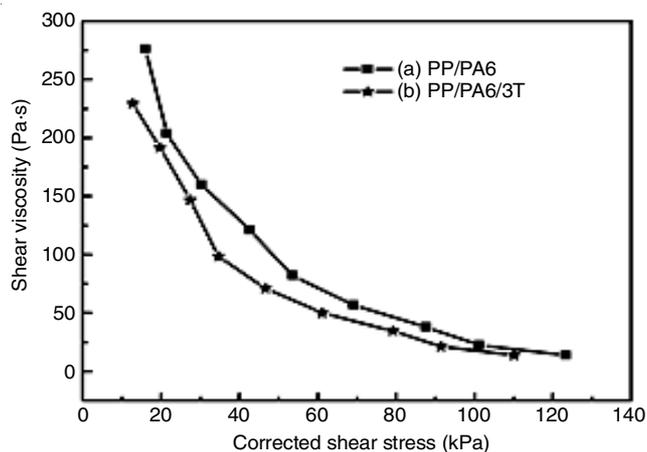Fig. 3. Shear viscosity *vs*. shear rate (230 °C)

Fig. 4(a). Relationships of shear viscosity and shear stress at 230 °C, (a) PP/PA6, (b) PP/PA6/3T
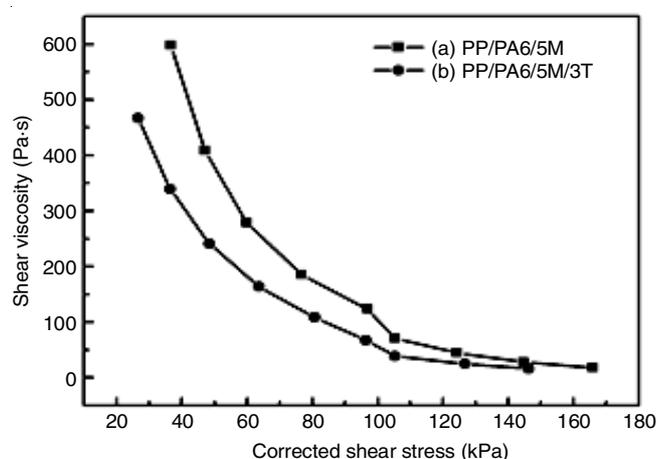

Fig. 4(b). Relationships of shear viscosity and shear stress at 230 °C, (a) PP/PA6/5M, (b) PP/PA6/5M/3T

PP/PA6 and PP-*g*-MAH capacity PP/PA6 complex system of shear viscosity and shear stress impact curves.

From Fig. 4(a) and 4(b), it can be seen that for all of the composite materials system, shear viscosity changes with shear stress trend is consistent and the melt viscosity decreased with the increases of shear stress. "Shear thinned" can be thought of the mechanism of materials within the original macromolecular chains bound nodes is opened or decreased concentration around nodes under the actions of external force. The action of external force can also be understood that the original chains orientation along the flow directions make the materials viscosity decreased as original macromolecular chains conformation changes. The change rules coincidence with the influence of shear stress general rules for the polymer fluid shear viscosity general laws.

From Fig. 4(a) and 4(b), it's not difficult to see in the PP-*g*-MAH (eqn. 5) expansion or capacity of PP/PA6 system after adding 3 times of the surface modification of TiO₂ nanoparticles, shear stress PP/PA6 and PP/PA6/5M shear viscosity decreased in a wide range. The PP/PA6/3T and PP/PA6/5M/3T composites system of shear viscosity were lower than PP/PA6 and PP/PA6/5M blends of shear viscosity. It is generally believed that nanoparticles added into the polymer systems will have two kinds of effects, one is the friction results the higher shear

viscosity polymer melts between nanoparticles, the other is lubrication added to the polymer matrix make polymer melts shear viscosity deceased. The two functions which as the dominant mainly depend upon the state of nanoparticles dispersion in polymer matrix and the compatibility of nanoparticles with polymer matrix. If nanoparticles dispersed evenly and have good compatibility with polymer, the probability of the nanoparticles collide with each other friction is small and could come into the polymer chains which have good lubrication effects and make the matrix polymer materials have good process rheological properties. In PP/PA6/3T and PP/PA6/5M/3T material systems, due to the nanoparticles after dealing with the TDI effectively improve the interfacial interaction between the polymer TiO₂ nanoparticles and polymer can make the TiO₂ nanoparticles dispersed evenly in polymer matrix, reduce the friction collision between the nanoparticles. The TiO₂ nanoparticles can make lubrication effects between the large molecules polymer chain segments and reduce the interaction between the chain segments. The lubrication is greater than the friction effects and make the melt shear viscosity getting smaller. It is suggested that the addition of surface modification of TiO₂ nanoparticles can effectively improve the rheological properties of PP/PA6 matrix composites. As shown in Fig. 4(b), while the melt shear viscosity of PP/PA6/5M complex system is 40 s⁻¹, PP/PA6/5M/3T melt shear viscosity of the composite system is 243 s⁻¹, which is the addition of 3 times TiO₂ nanoparticles to make materials of PP/PA6/5M melts shear viscosity decreased to 39 %.

Influence of PP-*g*-MAH on shear viscosity: Fig. 4(c) and 4(d) is PP-*g*-MAH on PP/PA6 and PP/PA6/3T complex systems and the effects of shear viscosity and shear stress change curves respectively. From Fig. 4(c) and 4(d), it can be seen that adding 5 copies in the PP/PA6 or PP/PA6/3T composite materials system PP-*g*-MAH can make the composites melt shear viscosity increases, which mainly has the following several reasons: (1) Due to MAH and polyamide-6 amino makes chemical reaction in the process of melting, *in situ* generated the PP-*g*-PA6 graft copolymers, possibly chemical reaction as shown in Fig. 4(a)-4(c), *In situ* generation of PP-*g*-PA6 graft copolymer exists in two phase interface to reinforce two phase interactions. Interface will be cut off in the process of flow deformation of dispersed phase particles, so as to make the system improves the overall pressure drop and expression as viscosity increased. (2) The interfacial tensions reduce after add PP-*g*-MAH system, droplet deformation and fracture are more likely to happen and when the droplets burst will absorb energy due to the increase of surface energy, the viscosity will increase as the overall pressure drop increases if the droplet occurred in the process of flow is broken. (3) graft copolymer dispersed in polypropylene and polyamide-6 two-phase interface makes the composite internal macromolecular chain bound nodes concentration increased, (4) the high viscosity of PP-*g*-MAH may also be one of the reasons that causing PP-*g*-MAH compatibilizing system has the high melts viscosity. Because of the above several aspects, the shear stress makes PP-*g*-MAH capacity of PP/PA6 and PP/PA6/3T composites system shear viscosity were higher than composite system in a very wide range. As shown in Fig. 4(d), for PP/PA6/3T
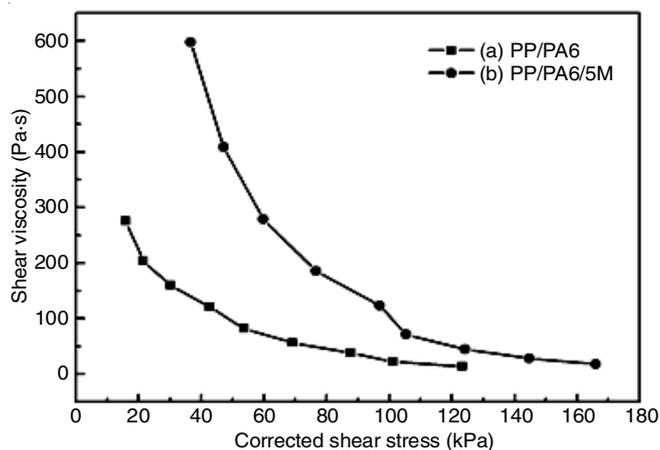
Fig. 4(c). Relationships of shear viscosity and shear stress at 230 °C, (a) PP/PA6, (b) PP/PA6/5M
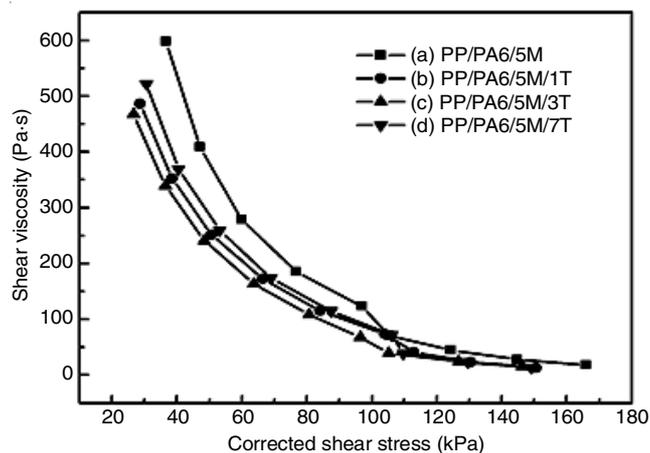

Fig. 4(e). Relationships of shear viscosity and shear stress at 230 °C, (a) PP/PA6/5M, (b) PP/PA6/5M/1T, (c) PP/PA6/5M/3T, (d) PP/PA6/5M/7T
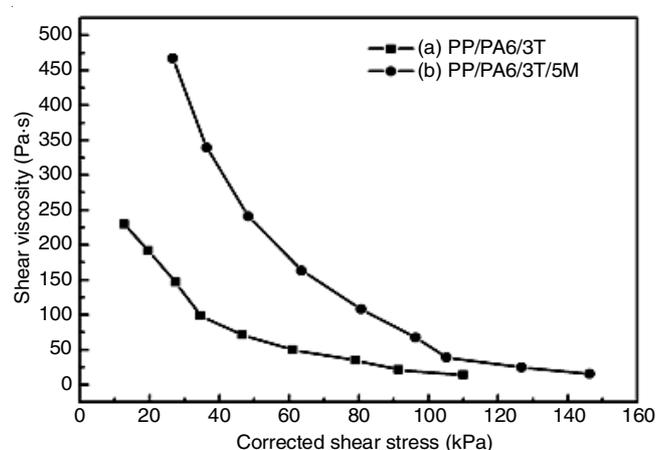

Fig. 4(d). Relationships of shear viscosity and shear stress at 230 °C, (a) PP/PA6/3T, (b) PP/PA6/3T/5M

composites material system, when the shear stress is 47 KPa, PP/PA6/3T composite materials system of the melt shear viscosity of 71 Pa·s and PP/PA6/3T/5M composite materials system is 243 Pa·s, *i.e.*, the melts shear viscosity increased more than four times (417 %) after adding 5 times PP-*g*-MAH.

Influence of dosage of TiO₂ nanoparticles on shear viscosity: Fig. 4(e) is a different amount of TiO$_2$ nanoparticles, PP/PA6 compatibilized composites of shear viscosity and shear stress change curves. As observed from Fig. 4(e), PP/PA6/5M composites system with TiO$_2$ nanoparticles additions increase and the melt shear viscosity gradually decreased in a wide range of shear stress while the surface modification of TiO$_2$ nanoparticles amounts does not exceed 3 times. When the TiO$_2$ nanoparticles filling amount reaches 7 times, the proceeds of the composites melt shear viscosity increased instead. The change rules causes the shear viscosity change with the dosage of TiO$_2$ nanoparticles composite materials system change can still be analysis from TiO$_2$ nanoparticles in the matrix polymer of two kinds of role. One reason is that TiO$_2$ nanoparticles filled into the polymer matrix friction may collide with each other and results in higher viscosity, another part is the lubrication for polymer matrix and led the melt viscosity decrease. Which of the two function roles how dominant mainly depends on the interaction between nanoparticles with matrix polymer and

the disperse of nanometer particles in polymer matrix situation. If the nanoparticles can be evenly dispersed in polymer matrix and has good interface bonds, the polymer nanoparticles can enter into the inter-macromolecular chains and less the chance of nanoparticles collide with each other, lubrication excel cause a decline in the melt shear viscosity at this moment. At low dosage of TiO$_2$ nanoparticles, the TiO$_2$ nanoparticles can be evenly dispersed in PP/PA6 matrix, the lubrication is greater than the friction effects with the dosage of TiO$_2$ nanoparticles increase and the composites system of the melt shear viscosity decrease. When TiO$_2$ nanoparticles filling quantity reach 7 times, parts of the TiO$_2$ nanoparticles arise reunion because of the high amounts of TiO$_2$ nanoparticles filling, the probability of collision increases between TiO$_2$ nanoparticles and its aggregate and the collision with lubrication of nanoparticles to polymer matrix friction role offsets each other, so the melts viscosity of PP/PA6/5M/7T larger than the melts viscosity of PP/PA6/5M/3T and demonstrates the loading level of nanoparticles have an optimum value. But the nanocomposites melt viscosity of PP/PA6/5M/7T is still less than the melt viscosity of composite materials of PP/PA6/5M, shows that the TiO$_2$ nanoparticles are still for composite materials of PP/PA6/5M has the lubrication.

In addition, as can be seen from the Fig. 3, horizontal ordinate as the shear rate, y-ordinate as the shear viscosity, the different shear viscosity of blend components almost identical clearly and difficult to discern the difference. However, from Fig. 4(a)-4(e), it is observed that the use of the shear stress instead of the shear rate can obviously make out the difference between different composites shear viscosity. But for two-phase incompatible polymer blends of viscoelastic melt, characterized with the shear rate is not very accurate, because deformation degree of dispersion of the dispersed phase droplets is different when the two-phase of melt viscoelasticity of polymer blending system flows through the capillary. At the interface the shear rate varies with the different shape of the dispersed phase to different, where the variation of the shear rate different from the continuous phase. However, as long as the two-phase interface does not slip, the changes of the shear stress at the interphase is continuous, it has nothing to do with the shape of the dispersed phase.
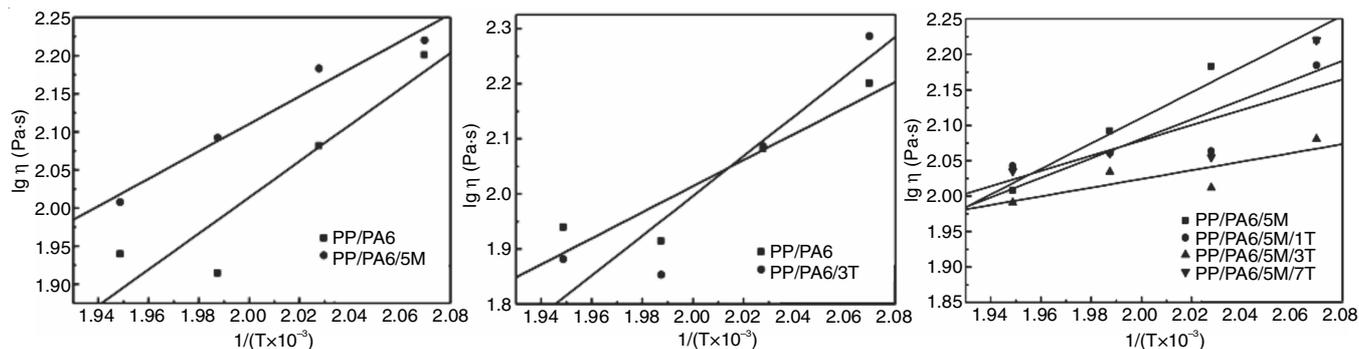
Fig. 5. Relationship of shear viscosity and temperature of PP/PA6 based composites

Influences of temperature on the melt viscosity: Fig. 5 shows the relationship curves between the melt viscosity and the temperature of the PP/PA6 based composites at a shear rate of 501 s⁻¹.

As we can see from the Fig. 5, the composites melt viscosity reduces with the rise of the temperature. The influences of temperature on the composites melt viscosity can be represented by viscosity flow activation energy (ΔE), the smaller the ΔE value is, indicating the sensitivity is smaller which the composites melt viscosity to temperature. According to lg η_a = A + ΔE$_\eta$/RT, the composite materials viscosity flow activation is calculated from the scope of the curve listed in Table-3.

As can be seen from Table-3, the addition of PP-*g*-MAH into PP/PA6 blends make the melt flow activation energy decreased, while the addition of 3 parts TiO$_2$ nanoparticles enable make the melt flow activation energy increased. Adding a small amount of TiO$_2$ nanoparticles in PP/PA6/5M composite materials system can make the melt flow activation energy decreased, but when you add 7 parts TiO$_2$ nanoparticles the melts flow activation energy will increase, which indicate the presence of a small amount of TiO$_2$ nanoparticles make temperature sensitivity decrease of the melt viscosity. This is because in capacity PP/PA6 composites system, TiO$_2$ nanoparticles take lubrication on PP/PA6 blends matrix polymer and make viscosity flow activation energy decreases, but too much TiO$_2$ nanoparticles may lead to particle aggregates and weakened lubrication.

Dynamic rheological behaviour: From many steady flow properties, we can see different material system express different rheological characteristics duo to its different viscoelastic properties. Since at high shear rate, the inter-phase structures and molecule structures within the system are likely to change a lot, it is difficult to obtain accurate information about internal structure of materials. In the dynamic rheological, deformation is small since the measure frequency is low, thus the material structures of the system obtained, provides a good condition for the study of internal structures of composite material system properties, especially in the study of interaction between the two phases. The main purpose of the test about material's

dynamic rheological properties is through dynamic testing methods to study influence of TiO$_2$ nanoparticles on composite material dynamic rheological properties.

The linear viscoelastic polymer materials behaviour can be used as a means to characterize the internal structures of the material. Linear viscoelastic behaviour is linear elastic [29] (elastic behaviour Hooke constant) and linear viscous [30] (stress proportional strain rate) simple additivity and only met a small deformation conditions generally. Viscoelasticity theory suggests that elastic is the solids behaviour of the system and the viscosity is the liquids behaviour of the system. They can respectively use the energy storage modulus (G') and energy consumption modulus (G'') to show the values of the system of elasticity and the strength of the adhesive. While η'' is a measure of the materials on the dynamic shear impedance. It is made of energy storage viscosity (elastic component) and dynamic viscosity (viscosity component).

Fig. 6(a)-6(c) are the dynamic frequency scanning of composite materials respectively. The shear energy storage modulus G', the loss modulus G'' and the plural viscosity η' changed with the change of frequency.

Fig. 6(a)-6(c) showed that (1) Energy storage modulus increase after adding 3 parts TiO$_2$ nanoparticles in PP-*g*-MAH capacity of PP/PA6/5M. Adding 7 parts TiO$_2$ nanocomposites can make energy storage modulus maximum in the low frequency ranges. Adding 3 parts TiO$_2$ nanocomposites can make energy storage modulus maximum in high frequency areas. In terms of energy consumption modulus and complex viscosity, the maximum shows up when adding in three biggest TiO$_2$ nanoparticles. It suggests that an excess of TiO$_2$ nanoparticles affects composite energy storage modulus. And energy consumption modulus increase shows that the filling amount of TiO$_2$ nanoparticles have an optimum value. (2) It's not difficult to find that when compared energy storage modulus curve with energy consumption modulus curve, the modulus of energy consumption is greater than the energy storage modulus of the composite materials in the range of test frequency. It suggests that the composites show. (3) Adding 3 parts the surface modification of TiO$_2$ nanoparticles, PP/PA6/5M

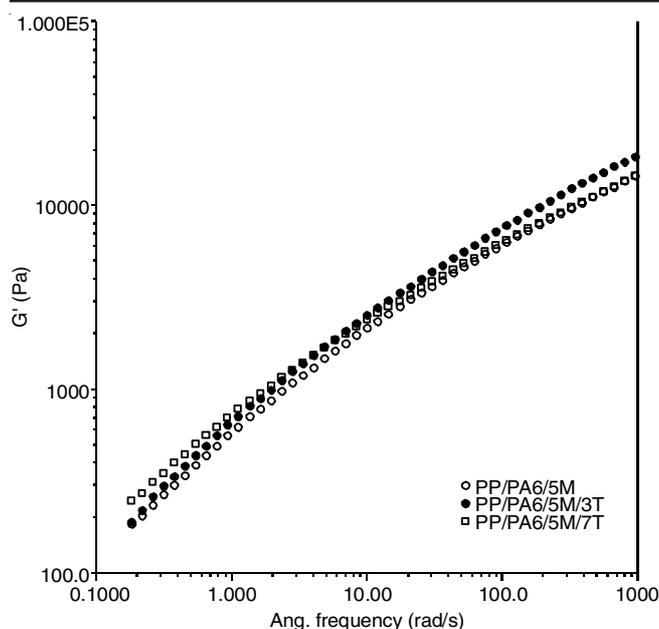| TABLE-3					
DATA OF FLOW ACTIVATION ENERGY FOR PP/PA6 BASED COMPOSITES					
Sample	PP/PA6	PP/PA6/5M	PP/PA6/3T	PP/PA6/5M/1T	PP/PA6/5M/3T	PP/PA6/5M/7T
ΔE$_\eta$/RT	2.37	1.80	3.61	1.08	0.61	1.37
ΔE$_\eta$	19.68	14.96	30.02	8.94	5.09	11.42

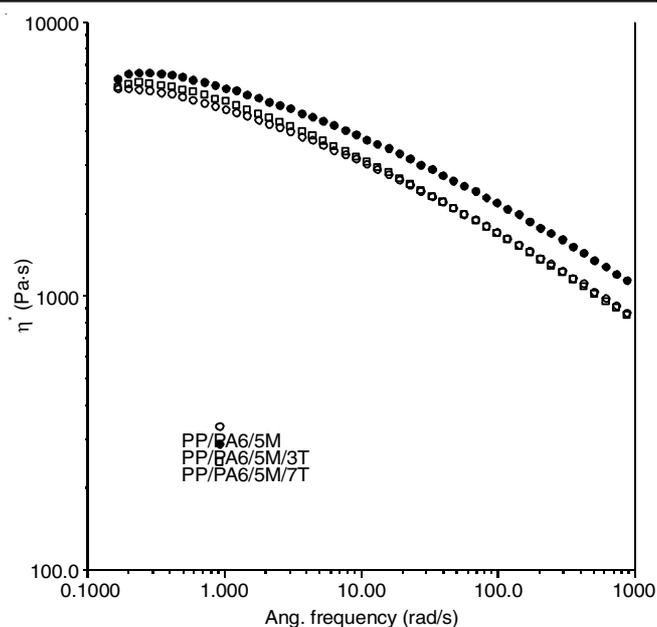Fig. 6(a).   Storage modulus (G2) *vs.* frequency plots for PP/PA6 based composites at 220 °C

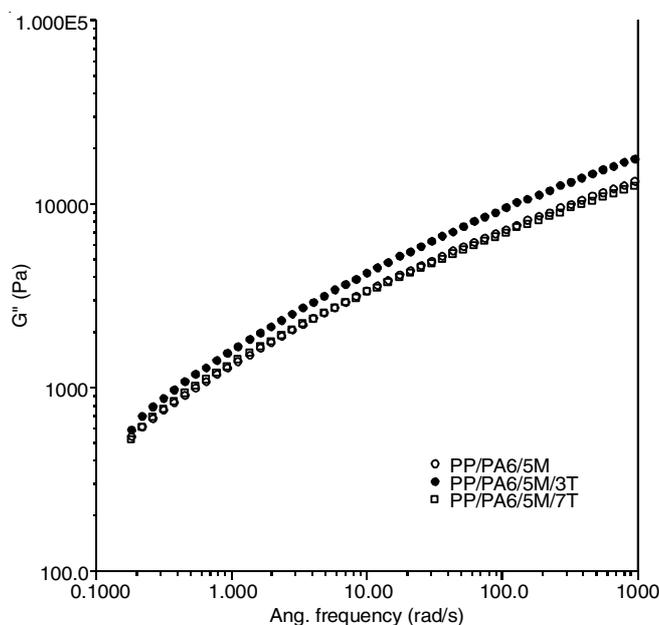Fig. 6(c).   Complex viscosity (η^*) *vs.* frequency plots for PP/PA6 based composites at 220 °C

Conclusions

• Based on PP/PA6/TiO_2 nanometer composites steady-state rheological test, it studied the relationships of shear viscosity, shear stress and shear temperature. The result shows that a small amount of TiO_2 nanoparticles can make the PP/PA6 and capacity of PP/PA6 composites melt viscosity reduce and make the composite material have a good process deformation property. In the capacity of PP/PA6 composites system, adding a certain amount of TiO_2 nanoparticles can make the flow index (non-newton index) n increase. But as the amount of TiO_2 added more than a certain amount, the flow index n reduce instead and make the pseudoplastic of composite increased.

• A small amount of TiO_2 nanoparticles can make the viscous flow activation energy of PP/PA6 compatibilized composites decrease, the sensitivity of melt viscosity on the temperature drop, which is due to the TiO_2 nanoparticles uniformly dispersed in the matrix polymer and TiO_2 nanoparticles have a good lubrication for the matrix polymer.

• It was reported that the rheological properties of composite materials that a small amount of TiO_2 nanoparticles can make the shear storage modulus of the composites G2, loss modulus G'' and complex viscosity η^* are improved, this shows that TiO_2 nanoparticles can also give the matrix material with good elasticity and viscosity.

Fig. 6(b).   Loss modulus (G3) *vs.* frequency plots for PP/PA6 based composites at 220 °C

and complex viscosity η'' of the blend melt was obviously higher than that of pure PP/PA6/5M blend system. Because it is in the melting process, surface modification of TiO_2 nanoparticles surface-NCO and PP-*g*-MAH will react with amino polyamide-6 molecules. Surface modification of TiO_2 nanoparticles surface-NCO and PP-*g*-MAH anhydride group chemically bonded with polyamide-6 end amino. The dispersed phase deformation under the action of a shear stress is much harder, at the same time, matrix molecules do not bound because of the braking action of dispersed phase. They lead to the melt viscosity increase, in addition, with the increase of ω, the composites complex viscosity η'' is on the decline. Through the above analysis, a small amount of TiO_2 nanoparticles can make composite materials have a good elasticity and viscosity at the same time.

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