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New Insights into the Elasticity and Multi-level Relaxation of Filler Network with the Studies on the Rheology of Isotactic Polypropylene/Carbon Black Nanocomposite

Luqiong Yang^a, Shilin Huang^{a,c}, Feng Wu^a, Shaodi Zheng^a, Wei Yang^{a,b}, Zhengying Liu^{a,*}, Mingbo Yang^{a,b}

Abstract: The elastic properties and multi-level relaxation behavior of filler network in isotactic polypropylene/carbon black (iPP/CB) nanocomposite were systematically investigated, which was instructive to the development and application of viscoelastic materials. Based on Two-phase model, master curves of the elastic modulus of composites with different CB concentration were built to describe elastic feature of CB networks in composites. From the elasticity of networks it is found that the critical volume of particle for the formation of the elastic network is 2.4vol% and the value of critical exponents is 5.1 ± 0.3 , indicating that the particle-particle interaction in network is strong. Based on Semidilute Fractal theory, the value obtained for the fractal dimension of the filler network was $d_f = 2.0 \pm 0.1$, which was in agreement with reaction limited aggregation mechanism, namely that CB particles must overcome a great barrier to form a cluster. The relaxation behavior of filler network was also studied. For composite with CB content of 2.0vol% (slightly lower than elastic percolation threshold 2.4vol%) relaxation behavior became slower with the extension of the annealing time, CB particles aggregated to form a denser network or backbone and the distribution of relaxation units became narrower, leading to the increase of relaxation modulus. For composite with CB content of 13.6vol%, 0.5h annealing treatment brought a wider distribution of relaxation units, because of the formation of “short chains” of particles, while both relaxation time and relaxation modulus of network increased. Further annealing treatment (>0.5h) made no difference on distribution of relaxation units and relaxation modulus of network, but relaxation time of networks kept increasing. CB concentration dependence of relaxation behavior of network revealed that as CB content increased relaxation modulus of filler network increased monotonously. However, both relaxation time and distribution of relaxation units decreased to a minimum value when CB content increased to 6.4vol%, and then increased with CB content.

Keywords: filler network; elasticity; multi-level relaxation behavior

1. Introduction

Polymer nanocomposites, which combine flexibility and ease of processing of polymers with the excellent functional properties imparted by nanoparticles, have received ongoing interests¹⁻⁵. Filler filled polymer nanocomposites, which can be depicted as a suspension of filler particles and /or agglomerates interspersed within the polymer medium, could significantly change the viscoelasticity of the materials⁶⁻¹¹. In well dispersed nanocomposites with a fine tuning of the microscopic properties, the large interfacial area can be obtained due to the extremely high specific surface area of the nanoparticles, which leads to the strong interaction among the particles or between particle and polymer^{12, 13}. It is generally believed that interfacial interaction between particle and polymer affects the viscoelasticity of the nanocomposites significantly. However, up to now the interaction mechanism study is still in a debate state. Some researchers pointed out that particle-polymer interaction can influence the viscoelastic properties of the system by a

variety of different mechanisms. They further put forward that the effects on the dynamics of polymer segments induced by particles modify the relaxation spectrum of polymers, and particle jamming may lead to slower relaxations¹⁴. While other researchers considered that the segmental relaxation of matrix in composite is not substantially altered by the adsorption of polymer chain onto filler surface¹⁵. Jouault showed that only when the mixed network is formed for a typical rim-to-rim distance equal to twice the gyration radius of the polymer chains, the transmission of stress could be realized in the polymer-particle network, and an additional elastic contribution could appear in modulus⁷. Filler concentration is another important effect for the viscoelasticity of composites. It is described in literature that when filler volume fraction increases to a critical value (rheological percolation threshold), three-dimensional networks of clusters¹⁶, physical jamming^{17, 18}, transient network or entrapped entanglements due to polymer adsorption on the filler surface would be obtained in composites¹⁹, which results in qualitative changes of the relaxation spectra and liquid-solid transition. The second plateau, where the storage modulus (G') of composite becomes almost independent of the frequency as filler loading increases at low frequencies^{6, 9, 20}, is believed to be the result of the formation of particle network. Furthermore, the effects caused by colloidal spherical particles (hydrodynamic effect) make flow field uneven, which would lead to an enhancement of G' for composite melt^{13, 21}. Generally speaking, in order to better understand the influence of nanoparticles on the viscoelasticity of composites, we should take the following factors into account: hydrodynamic effect, polymer-filler interface interaction, filler network. These factors codetermine the viscoelasticity of the composites. However, the respective contribution cannot be determined in details.

Most researchers studied the rheology properties especially relaxation behavior of the composite as a whole system. Tian Tang used a micromechanics model to calculate the effective stress relaxation stiffness of linear viscoelastic of the composite²². Hanna J. Maria studied stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites to predict the performance of a material over long periods of time²³. In their study, the research objects are both composites rather than filler networks which mainly determine the function of the materials. In the suspensions with soft particles, as the concentration of colloid particles increases, particles packing together then experience a jamming transition and a colloid network appears. This colloid network could relax in a not very long time range²⁴⁻²⁶. For filled polymer composites, filler networks belong to the scope of colloid as well, so it can be predicted that filler networks in the nanocomposites are not the ideal Hooke solid, they possess the properties of viscoelasticity^{27, 28}. A frequency range of 10^{-2} - 10^2 rad/s has been accepted in the dynamic frequency sweep by extensive researches to investigate the viscoelasticity of nanocomposite melt^{29, 30}. However, in the conventional investigation range (10^{-2} - 10^2 rad/s), the relaxation behavior of the colloid particle network in the polymer matrix can hardly be detected. So the test time is expanded to 10^3 s, guaranteeing most of the relaxation behavior of filler network could be detected (We used cyclic stress relaxation test, and for each sample eight cycles were carried out. Thus, longer test time for each circle may

lead to extremely long test time for a sample, which even causes the degradation of the samples. So we think 10^3 s is the most suitable time scale for our test.). Compared to what have been reported in literatures, we try to describe the elasticity and multi-level relaxation of filler network separately rather than the whole system of nanocomposite. For this purpose, Two-phase model put forward by Filippone³¹⁻³⁴ is proposed to account for the linear dynamic rheology behavior of nanofilled polymer melts and to describe the elastic properties of filler network separated from composite melt. Based on fractal concept raised by Piau³⁵ micro-rheological structure of filler network is disclosed. Furthermore, according to relaxation behavior of the network, we try to analyze the structure evolution of filler or filler network during the whole test domain.

2.1 Materials and processing

A carbon black (VXC 68, Cabot) with a dibutyl phthalate (DBP) volume of 1.23ml/g and a primary particle size of 25 nm was used as received. A commercial isotactic PP (iPP, trade name T30S, melt flow rate is 2.3g/10 min, at 230°C and 2.16 kg load, PD is 3.46, supplied by Lanzhou petroleum Chemical Co, Ltd., China) was used as the matrix. Depending on the volume fraction of carbon black (CB), a series of iPP/CB composites were fabricated by melt processing using a twin-screw extruder with the temperature setting of 185 to 210°C from hopper to die. The test samples were prepared by compression molding at a temperature of 200°C and a pressure of 10MPa for 5min. The diameter of the samples is 25.0mm and the thickness is 1.5mm.

2.2 Characterization

The dynamic rheological measurements were performed on a stress-controlled rheometer (AR 2000, TA Instruments) equipped with parallel-plate geometry (diameter of 25mm). The gap between the two plates was fixed at 1.35 mm to make sure good contact between geometry and test sample. The temperature was 200°C and in order to obtain stable inner structure, a time sweep for 2h was carried out, with the fixed frequency of 0.5rad/s and the strain of 0.1% (It is in the linear viscoelastic region of the composite melts³⁶). Then the frequency sweep was conducted in a frequency (ω) range from 0.05 to 500rad/s with the strain of 0.1% and six data points were collected in every decade (as the time to obtain a data point was $2\pi/\omega$). A stress relaxation analysis was taken out with the initial strain of 0.1%, and in the following 4h, a strain of 0.1% was added every 0.5h. Here it should be pointed out that before adding strain, the former strain in the samples would be removed, so that the accumulation effect of the strain could be avoided.

Strain sweep was carried out at a fixed frequency of 0.5rad/s and the strain from 0.01% to 50% to investigate the nonlinear viscoelastic behavior of the annealed composites. At the same time, Keithley 6517B was used to synchronously monitor the electrical resistivity of the samples with the copper electrodes contacting to the geometry and the voltage of 0.1V. To prevent the thermal degradation of the matrix, all the rheological experiments were conducted in a nitrogen atmosphere.

3. Results and discussion

3.1 Elasticity of the filler network

A model of a solid network interspersed in a background fluid was put forward by Trappe and his coworkers³⁷, where they accounted for the scaling by combining the elasticity of a solid network formed by the particles and the viscosity of the suspending fluid. Later, based on this model Filippone and his coworkers put forward Two-phase model, which made it possible to separate the contributions of each phases in the nanocomposite and proved its application with the hydrodynamic effect of the filler particles being taken into account^{31, 33, 34}. In this model at low frequency the stress response of composites is dominated by the cluster network, which exhibits a ω -independent elastic modulus, while the polymer dynamics prevail at high frequency.

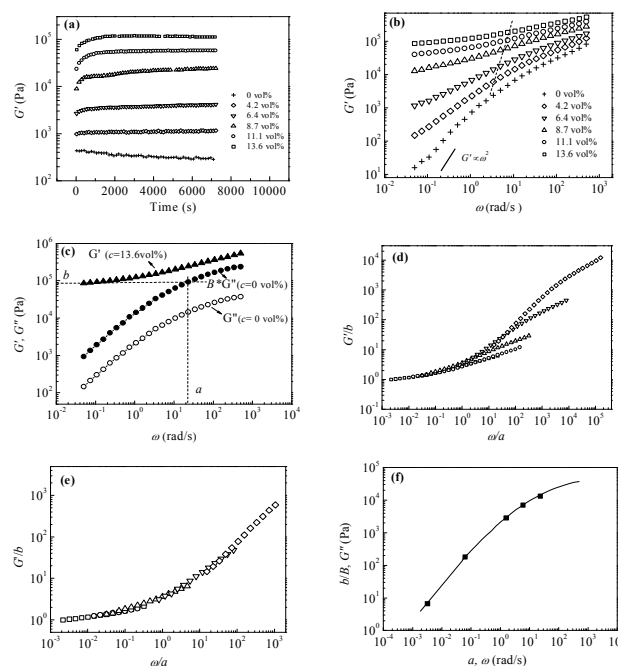


Fig.1. (a) Evolution of storage modulus (G') for the iPP/CB composite melts during melt annealing for 2h. (b) Frequency dependence of G' for the iPP/CB composite melts. (c) Determination of the two shift factors, a and b . (d-e) Fabrication of the master curve of G' for the iPP/CB composite melts with different CB concentration. (f) Comparison between the plots of G'' (iPP) versus ω and $b/B(c)$ versus a .

In iPP/CB composite melt, CB clusters are inclined to reassemble into bigger structures because of inter-particle attraction^{36, 38, 39}. From Fig.1a, the elastic modulus of composite increases during the earlier stage, then it reaches a steady value, meaning that the flocculation of the filler particles leads to enhancement effect on the composite melt. It is assumed that an equilibrium structure of the composite melt can be obtained after 2h melt annealing treatment³⁹. The frequency-dependent storage modulus of iPP/CB composite melt based on the equilibrium state is showed in Fig.1b. It is obvious that CB nanospheres have a dramatic effect on the relaxation behavior of composite. As the particle loading increases, elastic modulus G' increases and linear viscoelastic data indicates a transition to a solid-like response (a second plateau) at low oscillation frequencies for the composite with particle volume fractions of 8.7vol%(Fig.1b). Two-phase model holds the concept that the appearance of the low frequency plateau was contributed to the formation of filler network, and the value of the plateau modulus reflects the strength of filler network elasticity^{31, 33, 34, 37}.

More details are illuminated by the Two-phase model proposed by Filippone^{31, 33, 34}. An empirical amplifying factor $B(c)$ ($B(c)=G^*(c)/G^*(c=0)$, where $G^*(c)$ and $G^*(c=0)$ are complex shear modulus of filled sample and neat matrix in the high-frequency region) is applied to account for the increased gap available to the fluid because of the presence of the particles. Once amplified by $B(c)$, the loss modulus $G''(\omega)$ of the neat polymer crosses the cluster network elasticity, $b(c)=G_n'(c)$, where $G_n'(c)$ is low-frequency plateau of the storage modulus, $b(c)$ and $G_n'(c)$ are both concentration dependent. And a characteristic frequency $a(c)$ is obtained simultaneously which sets the transition from the domain governed by the filler ($\omega < a(c)$) to that dominated by the matrix ($\omega > a(c)$) (Fig. 1c)³². However, for samples without storage plateau scaling the G' curves onto the master curve is not allowed in obedience to the two-phase model which facilitates the identification of the percolation threshold as well. Thus for these samples we assume that the plateau would occur at a lower frequency, and set a series of the $b(c)$ and $a(c)$ with different value, choosing the appropriate value to obtain the master curve. (The correctness of the choosing of $b(c)$ and $a(c)$ is showed in Figure 1f, it is obvious that data b/B vs $a(c)$ is right in the curve of G'' vs ω .) Then a precise track in the plane of $G'(c)/b(c)-\omega/a(c)$ is established³², and it is not difficult to find that excluding the high-frequency domain, the collapse of the G' data sets on the corresponding master curves is perfect for all samples shown in Figure 1d. Filippone pointed that viscosity of composite is dominated by polymer matrix without any contribution from filler particles at high frequency, so that the data of $G'(c)/b(c)$ vs $\omega/a(c)$ in the high frequency domain could be ignored (Fig. 1e).

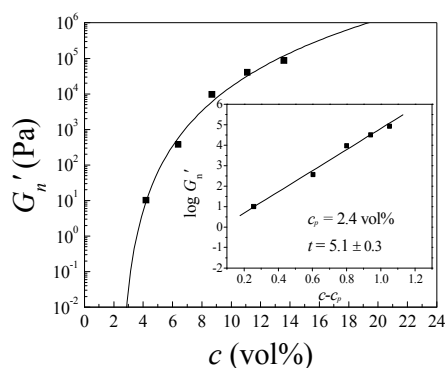


Fig.2. Storage modulus of the CB network as a function of CB concentration. The solid line and the inset represent the result of the fit according to Equation 1.

From the master curve, the elasticity modulus of filler network ($G_n'=b$) in the composite melt can be obtained, shown in Fig. 2d. And the storage modulus of the CB network as a function of CB concentration follows the power law³⁴:

$$G_n' \propto (c - c_p)^t \quad (1)$$

Here, c_p is elastic percolation threshold; c is filler concentration; t is the critical exponent, which relates to the ability of networks to bear stress in microscopic force laws.

By plotting G_n' vs CB loading and fitting with the function 1, the critical particle volume for the formation of the elastic network in composite (c_p) is 2.4vol% and the value of critical exponents is 5.1 ± 0.3 (Fig. 2 and the inset in Fig.2). According to percolation power law theory, as long as filler concentration is above critical threshold, particle network could build (In this study, the critical threshold is 2.4vol%, namely that when CB content is above 2.4vol%, a CB network could build). For networks with energetic particle-particle interactions, Arbabi and Sahimi distinguished the systems with central forces dominating when t is about 2.1, in which the particles are free to rotate, and networks with

bond-bending forces dominating when t is about 3.75, in which particles can bear stresses by the unbending of their branches^{32, 40-42}. Surve et al. suggested that for polymer-mediated particle networks a universal trend with $t \approx 1.88$ was obtained⁴³, in contrast to systems with strong particle-particle interactions which exhibited the elasticity exponents as high as $t \approx 5.3$ ³². In our study, the value of critical exponents is 5.1 ± 0.3 , indicating the particle-particle interaction is strong in our system.

3.2 Nonlinear viscoelasticity and Fractal dimension of filler network

Payne effect was first put forward by Payne in 1962 in the study of the dynamic modulus of carbon black-loaded natural rubber vulcanizates^{44, 45}. The effect of amplitude-dependence of the dynamic viscoelastic properties of filled-rubbers, often referred as the Payne effect (non-linear behavior), i.e, the decrease of the modulus with increasing deformation ratio. For pure polymer the non-linear behavior can be imagined to be associated with the mechanism of chain disentanglements. For nano-filled polymer composites the mechanisms of non-linear behavior become more complex. It is generally explained in terms of the breakdown process occurring in the filler network, the disentanglement of polymer chains and the desorption of the polymer chains from the particle surface^{46, 47}.

Fig.3 shows the nonlinear viscoelastic behavior of the composite melts with different CB concentration. For pure iPP matrix, storage modulus almost remains constant during the whole test domain ($\gamma < 50\%$). However, for iPP/CB composite melt, as the strain reaches a critical value (γ_c), the modulus of the composite melt decreases with the increasing of the strain. And the degree of non-linearity increases with filler concentration (As CB concentration increases, the critical strain value reduced from $\sim 2\%$ to $\sim 0.2\%$). There is no doubt that filler network existing in the annealed iPP/CB composites melt play the role of backbones, so at the critical value (γ_c) the decreasing of storage modulus can be contributed to the breakdown of the filler network.

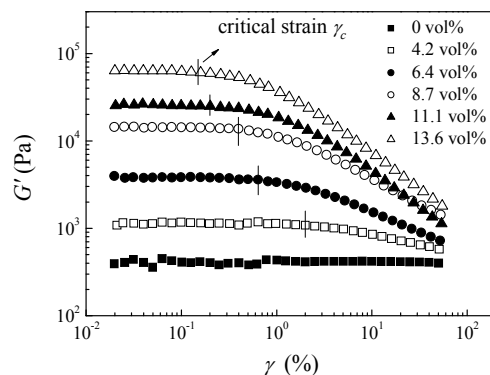


Fig.3. Nonlinear viscoelastic behavior of the composite melts with different CB concentration.

More details about the breakdown of the filler network are obtained by the changing of the resistivity as the function of strain amplitude, as shown in Fig.4. At a fixed frequency, the storage modulus of the iPP/CB (8.7vol%) composite melt decreases dramatically with the deformation increasing to a critical strain ($\sim 0.4\%$), however the resistivity of the sample do not show any synchronous changing, replaced by a lagging increasing of resistivity when the deformation reaches to a higher strain of $\sim 3\%$ which is much larger than that of $\sim 0.4\%$. This indicates that at the beginning of network

deformation, CB particles do not separate immediately with the strain but keep close to each other, which guarantee the existence of the electronic conductive path. Therefore the decrease of storage modulus at the critical strain γ_c only reflects the yield behavior of the filler network under external force effect. However the particle clusters are not separated until a much larger strain (here the strain is $\sim 3\%$) is applied. This deformation may break the touching point of filler network and separate the particle clusters, which leads to the increasing of resistivity. Fig.4b shows the relative resistivity (ρ/ρ_0 , ρ_0 is the resistivity at the lowest strain amplitude) for the composite melts with different CB concentration as a function of strain amplitude. Obviously, the resistivity of samples with higher CB concentration is less sensitive to the deformation, indicating that at higher CB concentration, the separation of network or cluster were more difficult. However, this network is much easier to yield, shown in Fig3. In order to clarify the structural information of filler network in detail, we introduce the concept semidilute fractal theory³⁵.

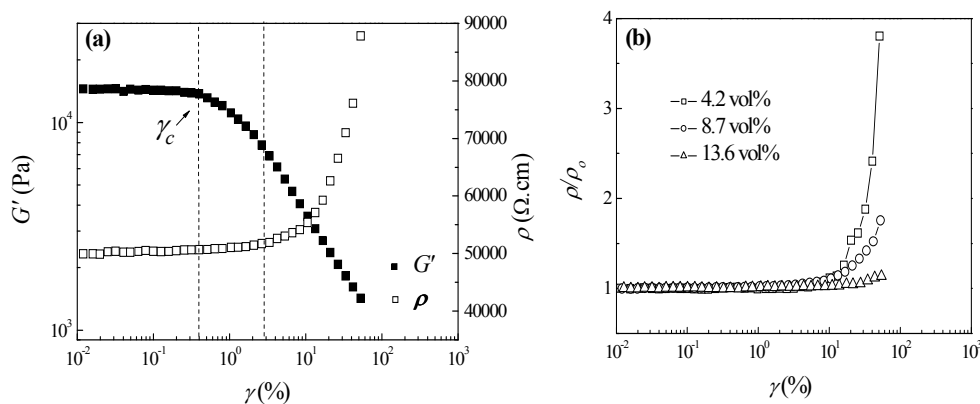


Fig.4.(a) Storage modulus(G')and resistivity (ρ) for the composite melt with 8.7vol% CB as functions of strain amplitude. (b) Relative resistivity (ρ/ρ_0 , ρ_0 represents the resistivity at the lowest strain amplitude) for the composite melts with different CB concentration as a function of strain amplitude (γ).

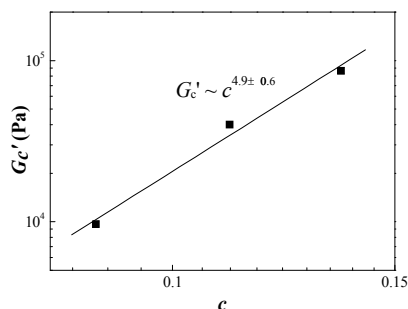


Fig.5. Concentration dependence of the critical storage modulus (G'_c) at the critical strain γ_c , where storage modulus of the composite is about 0.95 times of storage modulus in linear domain. Note that the concentration should be well above the percolation threshold in order to obtain the power-law relationship. Solid lines are the power-law fitting curves for G'_c .

The formulation of the non-fluctuating semidilute fractal concept relates the fractal dimension to the rheological scaling laws³⁵:

$$G'_c \propto c^{5/(3-d_f)} \quad (2)$$

Based on this scaling law, we obtained that the power law of c is 4.9 ± 0.6 and the fractal dimension is 2.0 ± 0.1 for iPP/CB composite with filler network. It is reported that in dilute suspensions, a diffusion limited, cluster-cluster aggregation process yields $d_f \approx 1.75$, while reaction limited aggregation yields $d_f = 2.1 \pm 0.1$, suggesting that suspensions aggregating by these mechanisms should form gels⁴⁸. The exponent reflects the topology of the samples and the motion ability of each part. If the fractal dimension of cluster is relatively large and the cluster is dense, the exponent would be large. Scaling law power values for the elastic modulus found in the literature for similar compounds are⁴⁹: 1) $G_c' \sim c^{3.5 \pm 0.2}$ for the mechanism of diffusion limited cluster-cluster aggregation; 2) $G_c' \sim c^{4.5 \pm 0.5}$ for the mechanism of reaction limited cluster-cluster aggregation. Our result shows that $G_c' \sim c^{4.9 \pm 0.6}$, indicating that when CB particles collide with each other, they cannot aggregate into a cluster directly, only those who overcome the strong barrier could turn into a cluster. Thus in our study, the formation of the CB network meets the reaction limited aggregation mechanism. In order to discuss the kinetics of the aggregation process, the mobility of the polymer matrix was investigated by dynamic rheological measurements. Fig.6 shows the temperature dependence of the gel time for samples with 6.4vol% CB, and the inset shows the Arrhenius plot of the zero shear viscosity of the neat iPP as a function of temperature. It is observed that the activation energy for the formation of gel is larger than that of polymer viscosity ($48.8 \text{ kJ/mol} > 39.7 \text{ kJ/mol}$), indicating that in iPP/CB composite melt the aggregation of CB particles does not comply the mechanism of diffusion limited cluster-cluster aggregation and it has to overcome a great barrier to form a cluster, which meets the mechanism of reaction limited cluster-cluster aggregation (As our previous study shown³⁹). Similar reports has been given by Wu^{50, 51}.

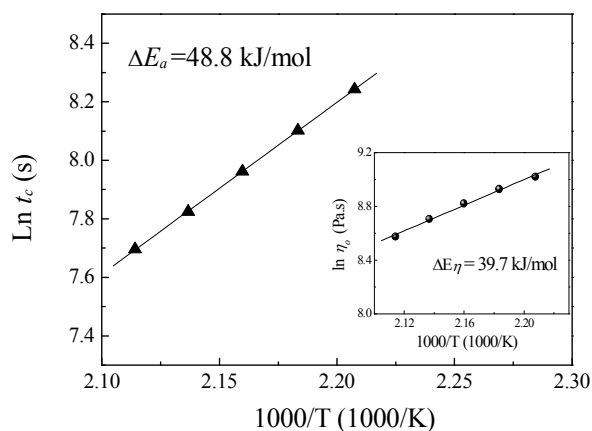


Fig.6. Temperature dependence of the gel time for the sample with the CB concentration of 6.4vol%. The inset shows the Arrhenius plot of the zero shear viscosity of the neat iPP as a function of temperature³⁹.

3.3 Long time relaxation behavior of filler network

3.3.1 Relaxation phenomenon of filler network

Two-phase model proposed by Filippone holds the view that the elasticity of the network can maintain a constant at the low frequency domain because the filler networks do not relax with the relaxation of the polymer matrix. In reality, filler networks in the iPP/CB composite are not ideal Hooke solid, when the time scale is long enough, the relaxation behavior would occur. We compare the relaxation behavior of neat iPP with that of the iPP/CB composite (CB content is

2.0vol%, which is slightly lower than elastic percolation threshold 2.4vol%.) after melt annealing at 200°C for 2h, as shown in Fig.7a. It is obvious that stress can relax quickly in the pure iPP matrix. We find that relaxation modulus (G_t) of pure iPP is about 3×10^4 Pa when the time is as short as 0.01s, and it decreases to 0.8Pa when time reaches to 50s. The reason for this phenomenon is that at 200°C iPP molecular chains can disentangle from each other and can relax fully. However, the stress relaxation behavior of iPP/CB composite becomes more complex. Within the time of 1s the stress relaxation behavior of iPP/CB composite is similar to that of pure iPP. Beyond 1s a slow relaxation behavior appears, which gradually evolves in the process of the annealing, as shown in Fig.7b. As for the composite sample (2.0vol%) without annealing treatment, only short time relaxation behavior can be observed. However, after melt annealing for 0.5h, a transition of relaxation modulus (G_t) of the composite arises, namely that a slow relaxation behavior emerges. As annealing time increases, relaxation behavior becomes slower and slower, which indicating that the appearance of slow relaxation behavior is caused by constantly changing of the internal structure during annealing treatment. Exactly, the aggregation of the CB particles in melt annealing process may significantly affect the viscoelasticity of composite, leading to appearance of the slow relaxation behavior. At the same time, it should be pointed out that beyond the time scale of 100s relaxation modulus decreases as the extension of time, indicating that CB network still can relax, although it is very slow. Therefore, the filler networks should not be regarded as the ideal Hook solid, and they should belong to viscoelastic solid. Furthermore, we find that annealing time only affects the long time relaxation behavior and makes no difference to the short time relaxation behavior (within 1s), as shown in Fig.7b. This can be explained that the short time relaxation behavior is dominated by the relaxation of the polymer matrix and it is independent of the annealing treatment.

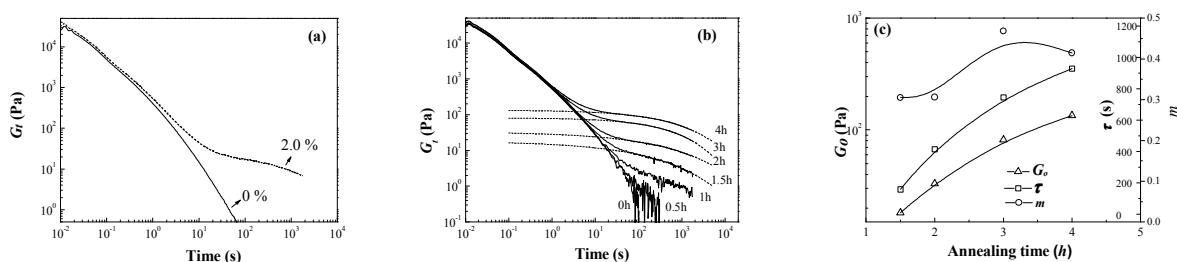


Fig.7.(a) Relaxation behavior of neat iPP and the iPP/CB composite (2.0vol% CB) after melt annealing at 200°C for 2h. (b) Influence of the melt annealing time on the slow relaxation process of the iPP/CB composite (2.0vol% CB). (c) The fitting parameters of the KWW function (Equation 3) as functions of annealing time.

The relaxation process of filler network can be described by Kohlrausch-Williams-Watts (KWW) relaxation function^{52, 53}:

$$G_n(t) = G_0 \times e^{-(t/\tau)^m} \quad (3)$$

Here, $G_n(t)$ is relaxation modulus of filler network at the time of t ; G_0 is relaxation modulus of filler network at the time of 0 (initial modulus) (As shown in Fig7b, G_0 is the intersection point of extension of dash line and vertical coordinate); τ is characteristic relaxation time of the network, reflecting an “average” relaxation time; m ($0 < m \leq 1$) is stretched exponential constant, which is a measure of the distribution of relaxation times ($m \rightarrow 1$ represent a narrow distribution of the relaxation time).

Parameter τ and m are estimated by curve fitting according to the KWW equation, and the fitting results are shown in Fig.7 c. It is obvious that with the increasing of annealing time, both initial modulus G_0 and characteristic relaxation time τ increase, which indicate that more CB particles take part in the formation of the filler network with time increasing, leading to a denser network structure. Thus the motion of the CB “chains” would be restricted by the surrounding particles. Similar researches on the relaxation behavior have been widely reported^{24, 26}. After 4h annealing treatment G_0 and τ keep increasing, indicating that inner structure of network do not reach the equilibrium state yet. At the same time, the value of stretched exponential constant m is within the range of 0.3-0.4. During the annealing treatment, stretched exponential constant m increases with time, from which we can speculate that the distribution of relaxation unit becomes narrower after the annealing treatment. Moreover, in addition to the network backbone, there are also many branched structures of CB “chains” in CB network, whose motion ability is better than that of the backbone. As the annealing performed, surrounding CB particles may take part in the growth of the “chains”, thus these “chains” would become longer and denser, and eventually connected to a new backbone, as shown in Fig.8a. In this way, the motion of the whole CB network would be restricted, leading to a narrower distribution of the relaxation units.

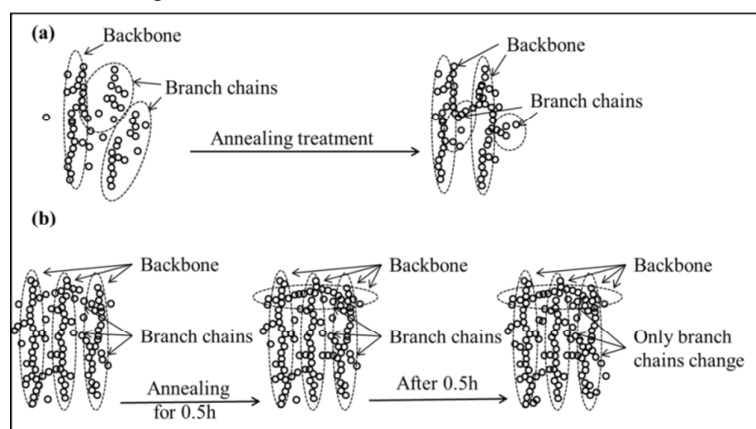


Fig.8. Evolution of network structure:(a)in composites with low CB concentration(2.0vol%), annealing treatment may give rise to the grows of CB branch chains and finally turn into backbones;(b)in composites with high CB concentration(13.6vol%), filler networks can be very dense, in early annealing treatment (0.5h) may lead to the touching of longer CB chains, further touching between short CB chains can be very hard in long time annealing, however these chains can restrict the motion of backbones, making the relaxation behavior of backbone or network more difficult.

As for the composite with higher CB concentration (13.6vol%) the development of the relaxation process during melt annealing is shown in Fig. 9. Slow relaxation behavior of samples without melt annealing is observed, indicating that filler network formed before annealing treatment. And with increasing of annealing time, significant change in slow relaxation of filler network takes place. KWW function is used to fit the slow relaxation behavior, shown in Fig.9a (dashed line), and the fitting results are shown in Fig.9b. The G_0 increases with annealing time in first 0.5h, however, shows no increase in further annealing treatment (>0.5h), which indicates that network in composites with high filler concentration would be much easier to reach the state of equilibrium. During the whole annealing treatment relaxation time of networks keeps increasing and finally reaches to a state of stability after 3 hour's annealing treatment. This kind of phenomenon suggests that some changes emerging within the network structure makes the network difficult to relax. Before annealing, $m \approx 0.41$, after 0.5h annealing treatment m decreases to 0.33 and further annealing only makes slight decrease on the stretched exponential constant m . It is believed that in high concentration filler filled composite filler network would be very dense and later joined CB particles only formed short CB “chains”, leading a wide distribution of relaxation unit, so that the value of m decreases. After annealing for 0.5h short CB “chains” is hard to contact with each

other, thus these short “chains” could not make significant contribution to the modulus of filler network. However, the existence of short CB “chains” would restrict the motion of backbone, resulting in a longer relaxation time of filler network, details shown in Fig8b.

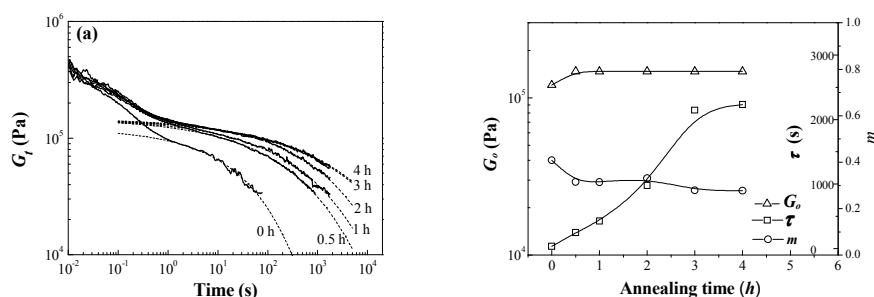


Fig.9. (a) Development of the slow relaxation process in the composite melt with 13.6vol% CB during melt annealing. (b) The fitting parameters of the KWW function (Equation3) as functions of annealing time.

3.3.2 The Influence of Filler Concentration on Relaxation Behavior of Network

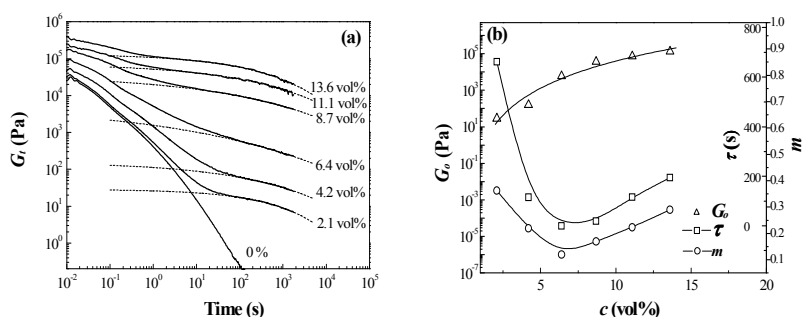


Fig.10. (a) Relaxation behaviors of the iPP/CB composites melt (after annealing at 200°C for 2h) with different CB concentration. (b) The fitting parameters of the KWW function (Equation3) for the slow relaxation process in the composite melts.

In this part, the effect of filler concentration on relaxation behavior of filler network is studied. Fig.10 (a) shows relaxation behavior of iPP/CB composite with different CB concentration after annealing at 200°C for 2h. It is obvious that as CB concentration increases, the relaxation modulus of iPP/CB composite melt increases and within the entire test the amount of relaxation modulus reduction decreases. Fitting for the slow relaxation process by KWW equation the value of G_0 , τ and m are obtained, shown in Fig.10 b. For all samples G_0 monotonically increases with increasing of CB concentration. However, it is unexpectedly to find that when the concentration of CB increases from 2.1 vol% to 6.4 vol%, the relaxation time of samples decreases from 662s to 0.08s and at the same time m decreases, which indicates that the dispersion units of networks become wider. It is not common to find that relaxation time decreases with increasing of colloidal particles. It is generally believed that in nanocomposite with the increasing of particles, mutual restraint between particles would become stronger, resulting in a longer relaxation time of filler network, which is in contrast with our results. It is speculated that when CB concentration is low (2.1 vol%), CB particle aggregates to form a network

throughout the sample and this network can be very loose. The movement of network is the overall movement of CB particles. Thus relaxation time of CB network would be relatively longer and the distribution of relaxation units would be narrower. As CB concentration increases the branches of network increase too. In this case not only network backbone (long time relaxation) but also branches of network (short time relaxation) exists inner filler network, so the distribution of relaxation units become wider, thus the value of m decreases and the average relaxation time of overall network decreases. However, with further increasing of CB particles (6.4vol%) both relaxation time and stretched exponential constant m increase (relaxation units become narrower). Since higher filler concentration would help to form a denser network and to make the branches contact with each other which finally forms the backbone of network. In this case the length of relaxation units would become homogeneity, leading to the increase of stretched exponential constant m . On the other hand, restriction effect among each relaxation units (especially branches) would lead to a longer relaxation time, showing the increasing of τ .

4. Conclusion

In summary, the elastic properties and multi-level relaxation behavior of filler network in iPP/CB composite were systematically studied. Firstly, a master curve of G' of composite with different CB concentration was built based on Two-phase model proposed by Filippone. The rheological threshold, 2.4vol%, was determined on the basis of a power law relation, and the critical exponent was in the vicinity of 5.1 suggesting strong interaction among CB particles. In non-linear viscoelasticity study, the degree of non-linearity of composite increased with filler concentration. A formulation of the nonfluctuating semidilute fractal concept proposed by Piau allowed us to relate the fractal dimension to the rheological scaling laws ($G_c' \propto c_f^{5/(3-d_f)}$), and the fractal dimension $d_f \approx 2.0$ was obtained, which was good agreement with reaction limited cluster-cluster aggregation. The decreasing of storage modulus at the critical strain γ_c reflected the yield behavior of the filler network.

KWW equation was used to systematically study the relaxation behavior of filler network. The results showed that in iPP melt CB network was not the ideal Hooke solid and in long time scale it could relax as well. This relaxation behavior of filler network was closely related to annealing time and filler concentration. For composite with low CB concentration, relaxation behavior became slower during annealing treatment, CB particles or networks became denser and the distribution of relaxation units became narrower, leading to the increasing of relaxation modulus. For composite with high CB concentration, short time annealing treatment brought a wider distribution of relaxation units, as the formation short chains, while both relaxation time and relaxation modulus of network increased, however, in further annealing treatment the relaxation time of network keep increasing, but the distribution of relaxation units and relaxation modulus of filler network did not show any difference. CB concentration dependence of relaxation behavior revealed that as CB content increased relaxation modulus of filler network increased monotonously. However, both relaxation time and distribution of relaxation units decreased to a minimum value when CB content increased to 6.4vol%, and then increased with CB content.

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Notes and references

^aCollege of Polymer Science and Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China

^bState Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China

^cMax Planck Institute for Polymer Research, 55128 Mainz, Germany

*To whom correspondence should be addressed. Tel: +86-28-8540-5324

Email: (Zhengying Liu) liuzhying@scu.edu.cn

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