Stress relaxation of ABS polymer melts.
1. Effect of weight fraction of rubber particle

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Abstract

We develop a simple model which can describe and explain abnormal stress relaxation of ABS melt for which stress dose not exponentially decay. The relaxation behavior of ABS melt consists of two distinct relaxation modes. One is the relaxation of the matrix phase similar to the case of homopolymer melt. The other is manifested by the collection of butadiene rubber particles, named as the cluster, where the particles are connected through the interaction between grafted SAN and matrix SAN. The second mode of the relaxation is characterized by the relaxation time, which is a function of the average size and the microscopic state of the cluster. Experimental results reveal that it can be represented as the product of the average size of the clusters by a function of internal variable that represents the fraction of strained SAN chains inside the cluster.

Keywords : ABS, relaxation, percolation

1. Introduction

ABS (acrylonitrile-butadiene-styrene) polymer consists of polybutadiene rubber particles, where grafted SAN polymers (acrylonitrile-styrene copolymers) are chemically attached, and free SAN the constituent of the matrix phase. Hence, the ABS polymer melt may be considered as a particle-filled polymer system whose behavior in stress relaxation is quite different from the behavior of pure components such as SAN or polybutadiene. Although the relaxation modulus of ABS can be described by a conventional linear viscoelastic model as the linear combination of exponential functions in the short time region, it does not decay exponentially in the long time region. The slope in the log-log plot of the relaxation modulus versus time increases with the weight fraction of rubber particles. In the case of extremely high weight fraction, one may consider that there exists non-vanishing fully relaxed modulus.

There are many research results on the rheological behavior of particle-filled polymer-melts and liquids. Aoki and Nakayama (1982) have investigated the effect of rubber particle size on the viscoelastic properties of ABS polymer melts. Aoki (1987) also has examined how the relaxation of ABS varies with the grafting degree of rubber

particles. Bertin *et al.* (1995) studied the abnormal relaxation behavior of ABS melts in long time region. The similar results were reported by Bousmina and Muller (1993) and Memon and Muller (1998) via the research on the influence of concentration and aggregation of dispersed rubber particles on the relaxation behavior of rubber-toughened PMMA. Simhambhatla and Leonov (1995) and Sobhanie *et al.* (1998) proposed the rheological model for particle filled polymers showing frozen memory and the yield. Contrary to the aforementioned researches on particle-filled polymer melts, Rooji *et al.* (1993) and Potanin *et al.* (1995) have investigated the rheological modeling of weakly aggregated dispersions in low-viscosity fluid.

Therefrom, one may conclude that the abnormal relaxation behavior of ABS melts results from certain particle-particle and particle-matrix interactions. In colloidal systems, particle-particle interaction is significant (Rooji *et al.*, 1993; Potanin *et al.*, 1995), since the particles carry some charges which give rise to long-range electrostatic interaction potential. In the case of ABS, both particle-particle and particle-matrix interactions are intricately mixed because the rubber particles are connected with the matrix phase via the grafted SAN polymers (Memon and Muller, 1998; Memon, 1998). In addition, the particles themselves respond to the deformation field. Although the molecular interaction among the monomers in ABS is short-range van der Waals type, the whole effect of the interactions in ABS certainly involves long-range interactions. This is because the inter-

actions mainly originate from the matrix SAN chains trapped by the SAN chains grafted to the rubber particles.

Since it seems very difficult to describe the effect of trapped SAN chains in terms of a molecular model, a phenomenological approach is chosen. Although our approach is similar to that by Simhambhatla and Leonov (1995) in some aspects, the physical meaning of the internal variable defined in the next section is quite different. In this work, we confine our research to stress relaxation phenomena of ABS at small strain instead of developing a complete constitutive equation applicable to general flow fields. We also limit in our study the weight fraction of rubber particles below the percolation threshold since most commercial grade of ABS resin contains the polybutadiene component less than 30 wt.%. However, most theoretical results, for example, results by Simhambhatla and Leonov (1995) and Sobhanie et al. (1997), have been reported for the range above the percolation threshold where the particle-filled polymer shows frozen memory and yield.

In this work, we show that the abnormal relaxation behavior of ABS melts is due to the change in the microstructure of the collection of rubber particles. We also develop a simple model and compare its description with experimental data.

2. Theory

It is thought that the abnormal relaxation behavior of ABS melts originates from the following:

(A) The relaxation of the collection of particles, in which the distance between the particles is so small that the interaction between the grafted SAN and the matrix SAN is strong.

(B) The relaxation of deformed rubber particles which contain cross-linked polybutadiene and occlusion SAN.

(C) The hydrodynamic interaction between the rubber particles.

Above the glass transition temperature of SAN, the rigidity of cross-linked polybutadiene is much higher than that of SAN melt. In contrast to colloidal systems, where the matrix phase is usually water, particle-filled polymer system exhibits enormously high viscosity. Hence, we assume that in the case of ABS melt the relaxation mechanism (A) is most dominant and we neglect (B) and (C). To illustrate the relaxation mode (A), we classify the SAN polymer chains and the collection of rubber particles as shown in Fig. 1.

It is certain that the aggregation of rubber particles depends on thermodynamic properties of the interface between rubber particles and matrix phase (Hasegawa et al., 1996). However, the most significant factors are the volume fraction of the rubber particles and the type of percolation process involved in the ABS system, and the

(a)

(b)
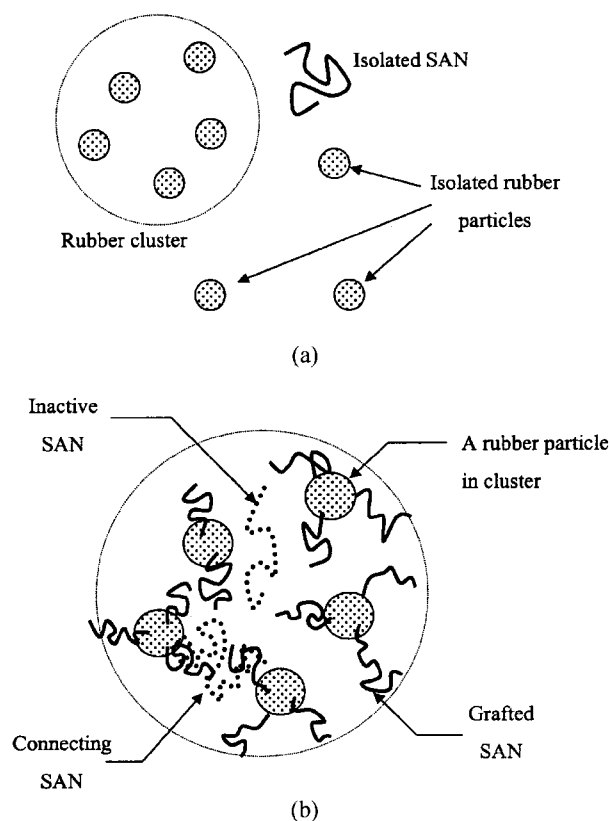
Fig. 1. The schematic representation of the cluster structure and the classification of various SAN chains.

thermodynamic interfacial properties are expected to determine the probability of the percolation process.

We define a cluster as the collection of rubber particles in which the distance between the particles are so small that the interaction between the grafted SAN and the matrix SAN induces an imaginary network structure of the particles. The cluster is schematically shown in Fig. 1(a). An isolated particle is the one that does not belong to any cluster. The matrix SAN is denoted as isolated SAN in Fig. 1(a). To describe the structure of the cluster in detail, the free SAN chains inside the cluster should be classified into two types. We call the free chains in the cluster as the connecting SAN chains if they are associated with the network structure formed by the interaction. These chains play an important role in the relaxation of the clusters while the inactive SAN chains [Fig. 1(b)] are not significant in the relaxation.

As rubber particles are added to pure SAN melt, the state of stress of the mixture becomes different from that of pure SAN. When we denote the contribution of the clusters to the total stress σ as σ_c, the total stress of the ABS melt may be expressed as

$$\sigma = (1 - \phi)\sigma_m + \phi\sigma_c, \tag{1}$$

Where ϕ is the weight fraction of polybutadiene in the

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ABS and the matrix stress σ_m is the stress for the pure SAN. In Eq. (1), it is assumed that stress of ABS melt results from two contributions. One is the matrix stress σ_m which represents the stress acting on the isolated chains, and the cluster stress σ_c stands for the contribution of the cluster of the rubber particles connected by the grafted and the connecting SAN chains. The simple mixture rule involved in Eq. (1) will be valid if the initial stress of ABS is linearly proportional to the weight fraction of the rubber particles. We assume that the viscoelastic property of the matrix can be described by the multi-mode Maxwell model.

To describe the cluster stress, the relaxation process of the cluster should be understood. It is assumed that the relaxation of the cluster is governed by that of the connecting SAN. Upon a sudden deformation, elastic energy is stored both in the connecting chains and in the other chains. If the release of elastic energy by dissipation can be interpreted as stress relaxation, then the relaxation of the cluster stress should be pertinent to the total effect of the release of the elastic energy stored in the connecting SAN chains. After the relaxation is completed, it is assumed that the connecting SAN chains are not effective in the formation of the rubber-particle network containing elastic energy just as the inactive SAN chains.

It is also assumed that the relaxation time for the cluster stress is dependent upon the connectivity of the rubber particles and the mean size of the clusters in the beginning of the relaxation. In other words, the relaxation time depends on structural changes in the cluster. To describe this in a quantitative manner, we introduce an internal variable q defined as the fraction of the connecting SAN chains:

$$q = \frac{N(t)}{N_o}, \quad 0 \leq q \leq 1, \tag{2}$$

where N_o is the total number of connecting chains just after the sudden deformation and $N(t)$ is the number of the connecting SAN chains at time t. Another variable to be introduced is the initial mean size of the cluster. For its quantitative description, the theory of percolation (Sahimi, 1994; Gould and Tobochnik, 1988) is adopted. The percolation theory states that the mean size of finite clusters below the percolation threshold, is

$$S(p) \propto (p_c - p)^{-v}, \text{ for } p < p_c, \tag{3}$$

where S is the mean size of the finite clusters, p is the percolation probability, p_c is the probability at the percolation threshold and v is the critical exponent for the mean size of the finite cluster. As shown in the percolation theory, the value of v is about 1.8 for 3-D case (Sahimi, 1994).

Evolution equation of q in a general flow field has to be formulated in order to complete a constitutive relation of ABS melt. However, since the scope of this study is confined to the stress relaxation phenomena at small strains,

only the followings are suggested.

(i) The relaxation time of the cluster stress is assumed to depend on the initial mean size of the finite clusters and the fraction q at time t.

(ii) The time dependence of q is simplified as

$$\frac{dq}{dt} = f(q, |\dot{\gamma}|), \tag{4}$$

where $f(q, |\dot{\gamma}|)$ is positive until a given deformation is dominant over relaxation and becomes negative afterwards. In Eq. (4) $\dot{\gamma}$ is shear rate. For stress relaxation, $f(q, |\dot{\gamma}| = 0)$ has to guarantee that $q(t)$ is a monotonically decreasing function of time, since $\dot{\gamma} = 0$.

(iii) As a first order approximation, we presume that the relaxation time of the cluster stress $\tau_c(q, S)$ is linearly proportional to S:

$$\tau_c(q, S) = \frac{S}{\lambda(q)}, \tag{5}$$

where $\lambda(q)$ is a positive function of q.

(iv) We employ the modified Maxwell model for the cluster stress:

$$\frac{d\sigma_c}{dt} + \frac{1}{\tau_c(q, S)}\sigma_c = G_c\dot{\gamma}, \tag{6}$$

where G_c is a modulus.

Since there is no clear reason why the connecting chains in the clusters of different sizes relax differently, we assume that the function $f(q, |\dot{\gamma}|)$ in Eq. (4) is independent of the weight fraction of the rubber particles. As a first approximation, we suggest that the relaxation time τ_c is linearly proportional to the mean size of the cluster, since the bigger the size, the longer it takes to relax. In addition, it is also a reasonable assumption that the percolation probability p is proportional to the volume fraction of the rubber particles and the proportionality depends on the thermodynamic properties of the interface between the rubber particles and the matrix. Thus, we can rewrite Eq. (3) and (5) as follows:

$$S(p) = S(\phi) = S_o(\phi_c - \phi)^{-v} \tag{7}$$

$$\tau_c(q, S) = \tau_c(q, \phi) = \frac{S_o(\phi_c - \phi)^{-v}}{\lambda(q)}. \tag{8}$$

Here S_o is the proportionality constant dependent upon the interfacial properties that may change due to the difference of AN (acrylonitrile) contents between the grafted and the free SAN, the molecular weight of the grafted SAN, the density of the grafted SAN on the surface of the rubber particles and so on. Even though it is ignored in this study, there exists a possibility that the function $\lambda(q)$ also depends on the AN contents of the grafted and the matrix SAN and other thermodynamic properties. However, Eqs. (4), (7) and (8) suggest a possibly crude but simple way to deter-

mine the relaxation stress in terms of measurable quantities such as weight fraction of the rubber particles and observation time.

Integration of Eq. (4) should yield a monotonically decreasing function of time, $q(t)$. For simplicity, we presume that $q(t) \approx \exp(-t/\theta)$ where θ is a positive constant. Since the shear rate is zero in the stress relaxation test, with the help of Eqs. (6) and (8), we obtain

$$\sigma_c(t) = \sigma_c(0) \exp\left[-S^{-1}(\phi)\int_0^t \frac{ds}{\lambda[q(s)]}\right]. \tag{9}$$

Regarding σ_m, we employ the conventional multi-mode Maxwell model:

$$\sigma_m(t) = \sum_i \sigma_{m,i} \exp\left(-\frac{t}{\tau_i}\right), \quad \sigma_m(0) = \sum_i \sigma_{m,i}. \tag{10}$$

As we have already postulated, $\sigma_m(t)$ can be determined by the relaxation test of the pure SAN ($\phi = 0$). Rearrangement of Eq.(1) gives

$$\sigma_c(t) = \frac{1}{\phi}[\sigma(t)-(1-\phi)\sigma_m(t)]. \tag{11}$$

On the basis of Eq. (11), the stress deviation $\sigma_c(t)$ is completely measurable since all terms in the right-hand side can be determined from the experiment. By taking the logarithm on both sides of Eq. (9) and differentiation, the relaxation time $\tau_c(q,\theta)$ may be expressed as

$$\frac{1}{\tau_c(q,\phi)} = -\frac{d \ln \sigma_c}{dt} = -\frac{d}{dt} \ln \frac{\sigma-(1-\phi)\sigma_m}{\phi}. \tag{12}$$

Plotting the derivative of experimentally obtained $\ln \sigma_c$ versus time verifies the approximate mathematical form of $\lambda[q(t)]$.

3. Experimental

3.1. Materials

We produced the mixture of SAN and grafted ABS provided by Cheil Ind. Inc. of Korea by extrusion with a co-rotating twin screw extruder at 210°C. The weight average molecular weight of matrix SAN is about 120 kg/mole and its AN (acrylonitrile) content about 28.5 wt.%. The mean diameter of rubber particles in the grafted ABS is about 3,000 Å. The grafted ABS contains AN and polybutadiene of about 25.0 wt.% and 45 wt.%, respectively. The weight fractions of the polybutadiene used in this study are 0, 13.5, 15.8, 18.0, 20.3, 22.5, 24.8 and 27.0 wt.%.

3.2. Rheological measurements

We performed static stress relaxation experiment with ARES (Advanced Rheometric Expansion System) of Rheometric Scientific Inc., with a parallel plate geometry.
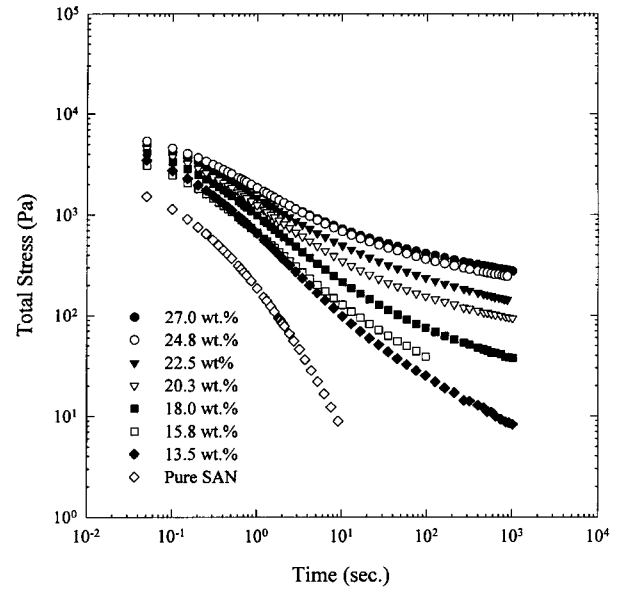

Fig. 2. Stress relaxation of ABS melt with various weight fraction of rubber particles.

The sample discs were 25 mm in diameter and 2 mm in thickness. We increased the magnitude of shear strain up to 0.06 for 0.08 sec. and fixed the strain. The measurement was carried out at 190°C.

4. Results and discussion

Fig. 2 is the log-log plot of stress with respect to time passed just after reaching 6% of strain. Although the stress decrease for ABS melt in the short time region is similar to that of the pure SAN, it shows some functional behavior proportional to t^{-m} (m>0) in the long time region. This peculiar relaxation behavior of ABS melt may be characterized in terms of the exponent m that decreases as the fraction of the rubber particles increases. However, the curves in Fig. 2 cannot be satisfactorily fitted with the linear combination of the Porony series and the power series of time. However well the combination may describe experimental data, the possible awkward procedure of fitting is not meaningful enough to give physical insight for the relaxation behavior.

In order to check the validity of the linear dependence of σ upon the fraction of rubber particles, we plot the initial stress against the weight fraction ϕ. If we consider errors possibly present in the assumption of step strain and uniform distribution of rubber particles as well as crudeness in our modeling, the linearity claimed in Fig. 3 is reasonable in our opinion. Thus, the assumption used in Eq. (1) seems valid. In other words, we may decompose the total stress into the two parts shown in the right-hand side of Eq. (1).

To obtain σ_c from the experiment, we performed the regression analysis on the data of $\sigma_m(t)$. With this analysis and the application of Eq.(11), we then obtain the data set
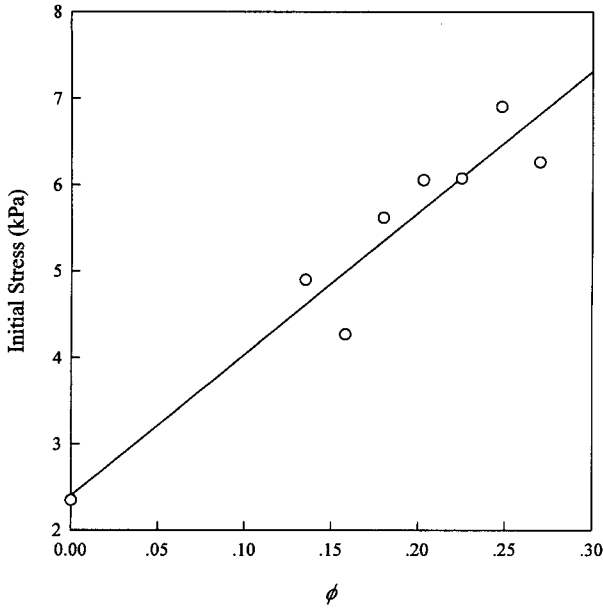
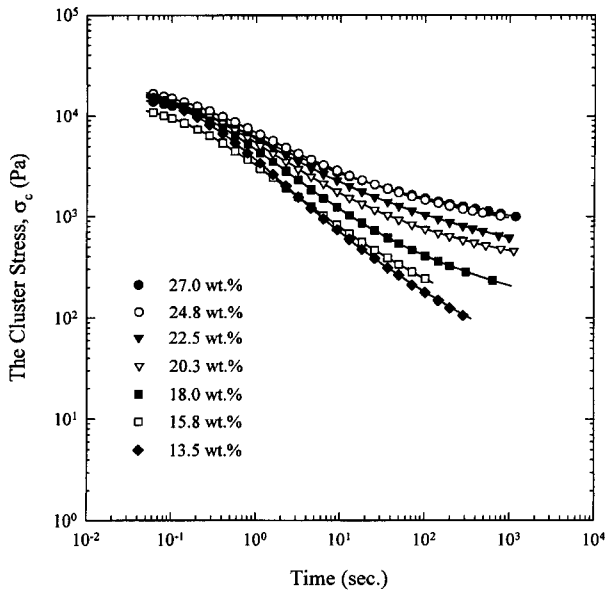Fig. 3. The the initial stress of ABS melt as a function of the weight fraction of rubber particles.

Fig. 4. Pade approximation of the cluster stresses for various weight fractions of rubber particles.

for σ_c. For the sake of reliable numerical differentiation, we applied Pade approximation for σ_c:

$$\ln \sigma_c = \frac{a_o + a_1 \ln t + a_2(\ln t)^2 + a_3(\ln t)^3 + a_4(\ln t)^4 + a_5(\ln t)^5}{b_o + b_1 \ln t + b_2(\ln t)^2 + b_3(\ln t)^3 + b_4(\ln t)^4}$$

(13)

Eq. (13) gives very good fit for the curves of $\ln \sigma_c$ with the determination coefficient $r^2 \geq 0.999$ irrespective of the spec-
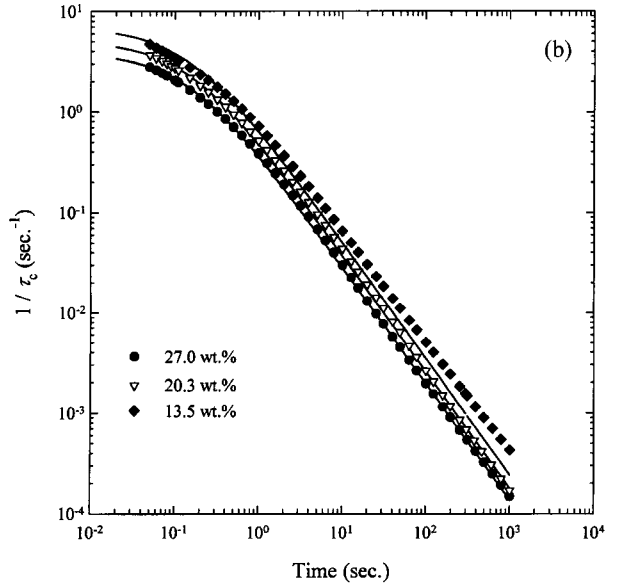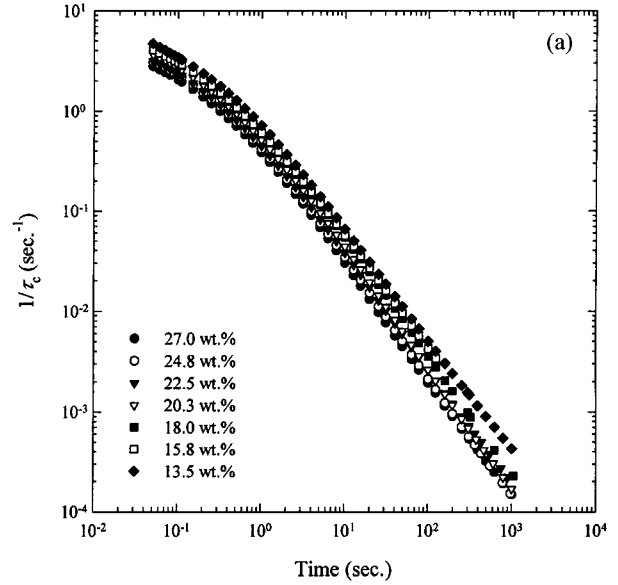

Fig. 5. The reciprocal relaxation time of the cluster stresses for various weight fractions of rubber particles. (a): experimental data; (b): regression results.

imens with various ϕ. Fig. 4 shows the results of the regression. The symbols and the lines in the figure indicate the experimental results obtained from Eq.(11) and the regression results from Eq. (13), respectively.

Then with the following equation,

$$\frac{1}{t} \frac{d \ln \sigma_c}{d \ln t} = \frac{d \ln \sigma_c}{dt} = -\frac{1}{\tau[q(t), \phi]},$$

(14)

we can obtain Fig. 5 whose curves resemble those of steady shear viscosity versus shear rate. All the curves in Fig. 5(a) are nearly parallel and have similar shape. It seems that there is a vertical shift factor that is a function of ϕ. Eq.(8) suggested in this study explains this obser-

vation. It states that the curves of the reciprocal relaxation time $\tau_c(q,\phi)$ for various ϕ can be superposed if we normalize them in terms of the mean size of the cluster, that is, if we employ $\tau_c[q(t),\phi]/S(\phi)$. Only to demonstrate this, we presume a mathematical form of $\tau_c[q(t),\phi]$, the modification of the empirical equation for shear viscosity:

$$\frac{1}{\tau_c(q,\phi)} = \frac{S^{-1}(\phi)}{1+[-\beta \ln q(t)]^n} = \frac{S^{-1}(\phi)}{1+(\beta t/\theta)^n}, \qquad (15)$$

where β and n are positive constants. The nonlinear regression analysis of the data for $\phi = 0.27$ yields the values of parameters $S^{-1}(\phi) = 3.909$, $\beta/\theta = 6.857$ and $n = 1.161$. With the assumption that β, θ and are independent of the weight fraction of the rubber particles, we simply apply these values of β/θ and n for the analysis of the other specimens. The lines in Fig. 5(b) are drawn based on the regression analysis of Eq. (15). Fig. 5(b) illustrates that Eq. (15) gives reasonable fit for various weight fraction of the rubber particles. Again the regression analysis for the other specimens with β/θ and n fixed, yields data of $S^{-1}(\phi)$. Fig. 6 shows that the values of $S^{-1}(\phi)$ obtained for various ϕ agree well with Eq. (7). In Fig. 6, we used $v = 1.8$ derived theoretically for the 3-D percolation. Here, we have determined the values of the parameters for Eq. (7); $S_o^{-1} = 23.61$ and $\phi_c = 0.6314$. The existence of $\phi_c = 0.6314$ implies that above this weight fraction the complete relaxation of the cluster stress is never possible. Then, non-vanishing fully relaxed stress appears. Using these values of S_o^{-1}, ϕ_c and v, we can obtain the superposition of the curves in Fig. 5(a). Fig. 7 demonstrates that our factorability assumption on the
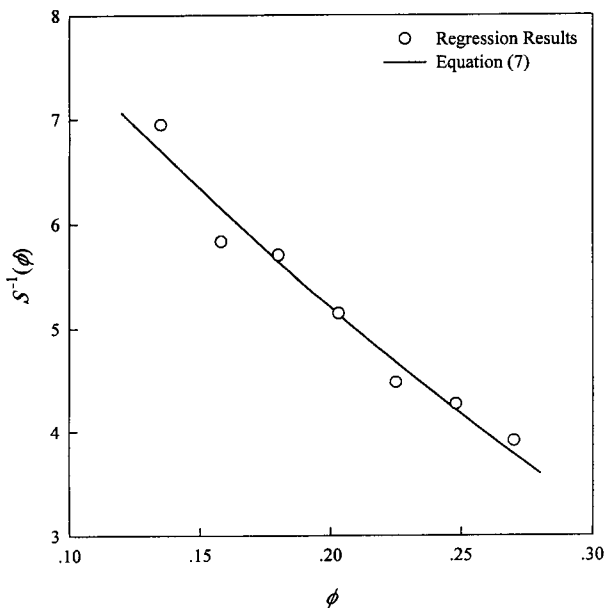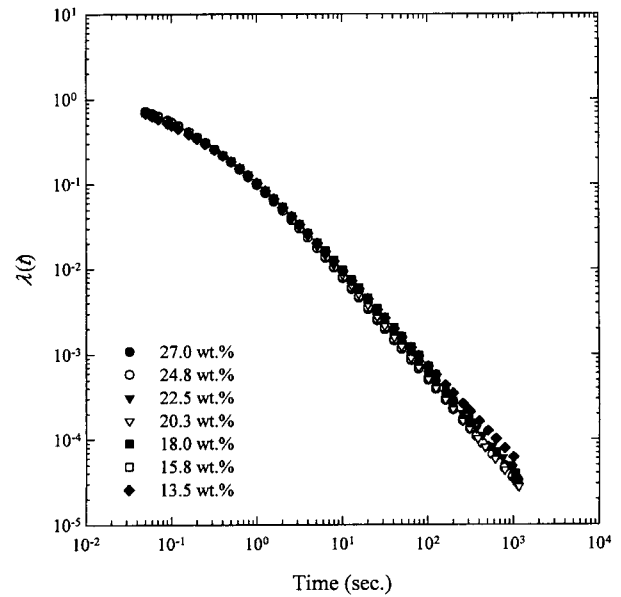

Fig. 7. The superposition of the reciprocal relaxation time for the cluster stresses.

relaxation time $\tau_c(q,\phi) = S(\phi)/\lambda(q)$ is acceptable.

5. Conclusions

In stress relaxation, abnormal behavior of ABS melt is observed in the long time region. We thought that this behavior is related to the network structure present in rubber particles (or the cluster) formed by the connecting SAN chains. In our model, the total stress of the ABS melt is separated into the contributions of the pure matrix and the network. To describe the stress of the cluster, we used the modified Maxwell model, of which the relaxation time is assumed to be a function of the mean size of the clusters and the internal variable q.

The model developed in this work describes the abnormal relaxation of ABS melts satisfactorily. Comparing the description of our model with the relaxation data of ABS melts, we confirm that the relaxation time of the cluster stress is proportional to the mean size of the clusters of the rubber particles. We determined the critical weight fraction of polybutadiene which corresponds to the percolation threshold. In addition, the model for the mean size of the clusters in the percolation theory agrees well with the shift factor of the relaxation time of the cluster stress over the weight fraction of polybutadiene ϕ.

Acknowledgements

Fig. 6. $S^{-1}(\phi)$ obtained experimentally and calculated from the percolation model.

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