

# Dynamic Properties of an Organic Hybrid of Chlorinated Polyethylene and Hindered Phenol Compound

CHIFEI WU,<sup>1</sup> YOSHIO OTANI,<sup>1</sup> NORIKAZU NAMIKI,<sup>1</sup> HITOSHI EMI,<sup>1</sup> KOH-HEI NITTA,<sup>2</sup> SABURO KUBOTA<sup>3</sup>

<sup>1</sup> Department of Chemistry and Chemical Engineering, Kanazawa University, 2-40-20 Kodatsuno, Kanazawa, Ishikawa 920-8667, Japan

<sup>2</sup> School of Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan

<sup>3</sup> Toyama Industrial Technology Center, 150 Futagami, Takaoka, Toyama 939-0981, Japan

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**ABSTRACT:** The dynamic mechanical properties of hybrids of chlorinated polyethylene (CPE) and 3,9-bis[1,1-dimethyl-2( $\beta$ -(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl]-2,4,8,10-tetraoxaspiro[5,5]-undecane (AO-80) were investigated. The CPE/AO-80 hybrids showed a novel relaxation in addition to the glass transition of CPE. The novel relaxation is attributed to the dissociation of intermolecular hydrogen bonds within the AO-80-rich domain. The Payne effect, that is, the decrease of the storage modulus  $E'$  with increasing strain amplitude and the appearance of a loss modulus  $E''$  maximum at a strain of 0.6%, was observed for the CPE/AO-80 hybrids. This result demonstrates that the AO-80-rich domains within matrix polymer CPE form a network. The Payne effect is considered to be attributed to the mechanical disruption of segment-segment contacts at a sufficiently great strain. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1788–1793, 2001

**Key words:** chlorinated polyethylene; hindered phenol; dynamic mechanical property; Payne effect; filler networking

## INTRODUCTION

Elastomers are used in a wide range of applications, particularly in the automotive industry, under several conditions of temperature, frequency, and deformation. However, elastomers are seldom used commercially in a pure state. Different types of inorganic fillers such as carbon black and silica are added to adjust the performance of elastomers.<sup>1</sup> Most recently, the additive effects of the polymeric microparticulates as an organic filler on mechanical properties of base polymer, were also reported.<sup>2,3</sup> However, much less attention

has been devoted to the examination of the effects of the low molecular weight additives on elastomer performance.

In general, low molecular weight additives such as stabilizers and vulcanizing agents have been investigated extensively in a very low concentration range in which the polymer is the major component. Very few fundamental studies have been reported on the moderate concentration range in which the content of the additives is comparable to the content of the matrix polymer. So far, it has been recognized that a plasticizer usually leads to a decrease of the glass-transition temperature and to an increase of molecular mobility.<sup>4</sup> This phenomenon is related to the processing method of the polymer. On the other hand, in our recent studies<sup>5–10</sup> attention has been focused

Correspondence to: C. Wu (wucf@cc.tuat.ac.jp).

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on the discovery of some unknown function of a polymer resulting from the addition of low molecular weight additives. It was found that adding 3,9-bis[1,1-dimethyl-2{ $\beta$ -(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]-2,4,8,10-tetraoxaspiro[5,5]-undecane (AO-80) into chlorinated polyethylene (CPE) caused a novel relaxation above the glass-transition temperature of CPE.<sup>5</sup> Consequently, some additional properties such as broad damping and shape-memory effects were accompanied by this novel relaxation. This novel relaxation is attributed to the intermolecular interaction between the AO-80 molecules and the CPE chains. It is suggested that AO-80 molecules aggregate to form an AO-80-rich domain, which forms a network structure with the CPE matrix.

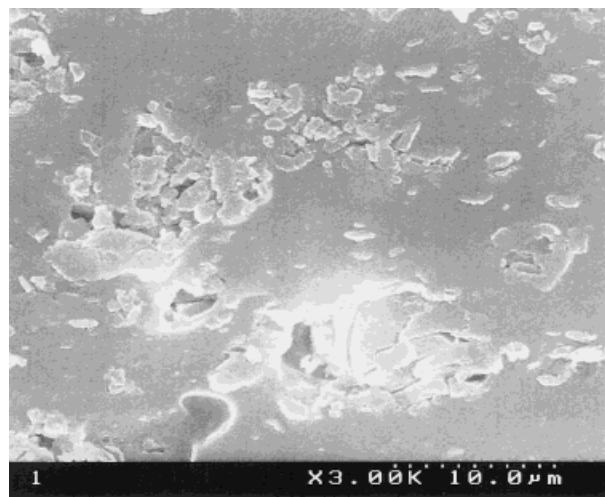
It is well known that rubbers filled by either inorganic or organic fillers show a typical nonlinear viscoelastic behavior: dynamic moduli depend on the strain amplitude and a significant decrease of storage modulus occurs at strains of about 1%. This effect, generally termed the "Payne effect,"<sup>11,12</sup> is exponentially increased by increasing filler loading<sup>13,14</sup> and was found to be dependent on structure and surface behavior,<sup>14–16</sup> surface chemical modification,<sup>17</sup> and physical modification,<sup>18</sup> as well as the mixing time<sup>19</sup> and mixing method.<sup>14</sup> It has been widely accepted that the Payne effect is related to the filler network formed in the polymer matrix and was considered to serve as a measure of filler network.<sup>1</sup> Similarly, the Payne effect is considered to be of use to confirm the existence of a network of the AO-80-rich domains in the CPE matrix.

This study deals with how the dynamic properties of CPE over a wide range of strain amplitudes are affected by the dispersion state of the AO-80 additives. Furthermore, we propose a dispersion model of the AO-80-rich domain in matrix polymer CPE. This new approach successfully accounts for the Payne effect observed in the dynamic properties.

## EXPERIMENTAL

### Materials

The CPE used as a matrix in this study, with a chlorination degree of 40 wt %, was a rubbery grade (Elaslene 401A; Showa Denko Co., Japan). The low molecular weight compound used as a dispersing material was commercial antioxidant



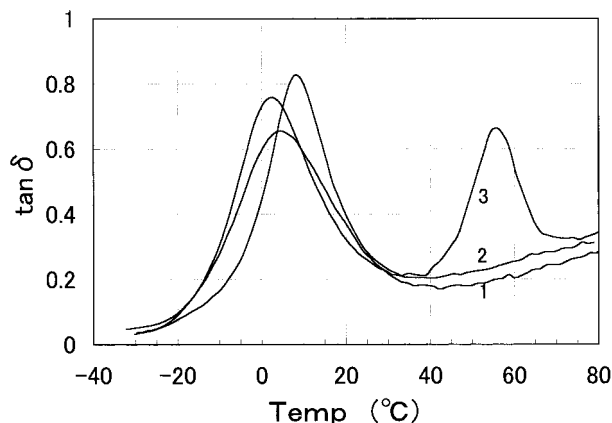
**Figure 1** SEM photomicrograph of unpressed CPE/AO-80 (25%).

(ADK STAB AO-80, whose chemical structure is shown in Fig. 1 of Wu et al.<sup>5</sup>; Asahi Denka Industries Co., Japan).

The CPE powders were first kneaded with a mixing roller for 5 min. AO-80 powder (as shown in Fig. 2 of Wu et al.<sup>5</sup>) was then added to the kneaded CPE. The mixture was kneaded again for 10 min at room temperature into sheets that were directly cut into rectangular pieces for the measurements. Thus the obtained sample, in which the AO-80 compound was dispersed into the CPE matrix in the form of the crystalline particles, as shown in Figure 1, is called as unpressed sample. Then this sample was made molten for 3 min and was then pressed in a laboratory hot press at 160°C, which is above the melting point of AO-80, for 7 min under a pressure of 180 kg/cm<sup>2</sup>. Finally, the sample was quenched in an ice-water bath (pressed sample).

### Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties measurements were carried out using a dynamic mechanical analyzer (DVE-V4; Rheology Co.) on sample specimens 20 mm in length, 5 mm in width, and about 1 mm in thickness. The temperature dependence of the dynamic tensile modulus was measured at a constant frequency of 1.1 Hz and at a heating rate of 3°C/min. In addition, the strain dependence of the dynamic tensile modulus was determined by increasing the strain amplitude from 0.05 to 5% at a constant temperature of 23°C and frequency of 1.1 as well as 11 Hz.



**Figure 2** Temperature dependence of storage modulus  $E''$  at 1.1 Hz for (1) CPE, (2) unpressed CPE/AO-80, and (3) pressed CPE/AO-80 (25%).

### Scanning Electron Microscopy (SEM)

A section of the sample was coated with gold, after which the photomicrographs were taken with a Hitachi S-4500 field emission gun scanning electron microscope (Hitachi, Japan) under an applied voltage of 25 kV.

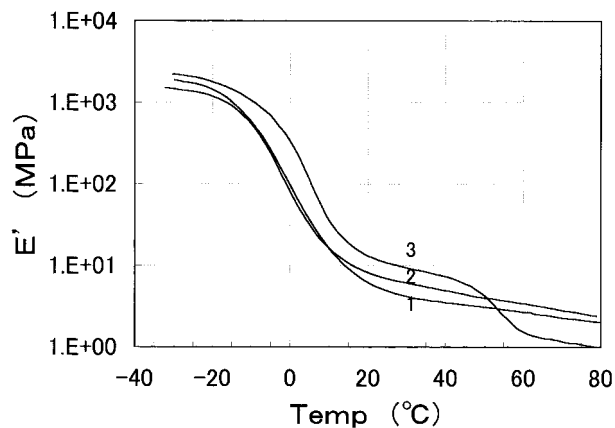
## RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the loss tangent ( $\tan \delta$ ) for CPE and both unpressed and pressed CPE/AO-80 (25%), respectively. Whereas the pure CPE exhibited only one peak, the CPE/AO-80 sample clearly exhibited two peaks. According to our previous studies,<sup>5–10</sup> we found the CPE-rich continuous phase and the AO-80-rich domains where the CPE chains are incorporated for CPE/AO-80 blends; these two relaxations are attributed to the onset of micro-Brownian motion of the CPE chains within the CPE-rich phase and to dissociation of the intermolecular hydrogen bonds between CPE and AO-80 within AO-80-rich domains, respectively.

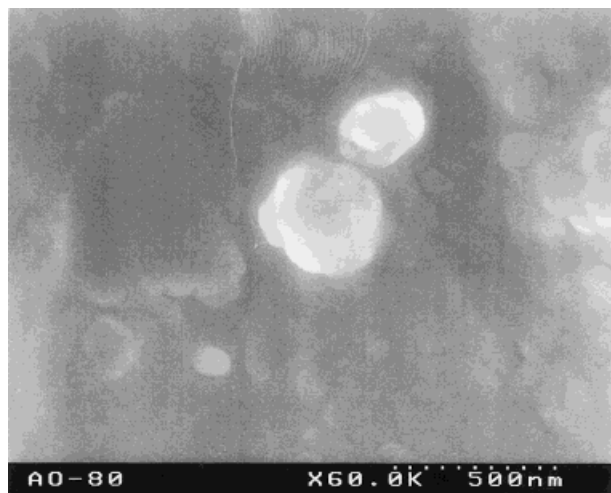
Figure 3 shows the temperature dependence of the storage modulus  $E'$  for CPE and both unpressed and pressed CPE/AO-80 (25%), respectively. The unpressed CPE/AO-80 (25%) exhibited a relatively high value of the plateau modulus  $E'$  after glass transition of CPE. As shown in previous studies,<sup>20,21</sup> the increase of the  $E'$  in the rubbery region can be interpreted as the addition effects of AO-80 crystals, as seen in Figure 1, which act as reinforcing fillers.

In contrast, for the pressed CPE/AO-80 (25%) the  $E'$ -temperature curve clearly shows two dispersions in which the  $E'$  drops stepwise with temperature, as well as three plateau regions. The value of  $E'$  at the first plateau, which corresponds to the glassy modulus, is higher than that of the unpressed CPE/AO-80 (25%) and pure CPE. Studies of plasticizer have been active on poly(vinyl chloride), and the modulus was increased by blending some low molecular weight compounds.<sup>22,23</sup> About this phenomenon, Caldwell carried out a systematic work and named these organic compounds that increased the modulus by blending "antiplasticizers."<sup>24–26</sup> Therefore, AO-80 can be regarded as an antiplasticizer.

The  $E'$  in the last plateau, which is denoted as the rubbery modulus, is lower than that of pure CPE. Therefore, the AO-80 molecules above the second relaxation temperature are considered to act as a plasticizer of CPE. The  $E'$  in the intermediate plateau is higher than those of pure CPE and the unpressed CPE/AO-80 (25%). For the pressed CPE/AO-80 sample, because AO-80 dispersed into CPE in this temperature range is in a rubbery state after the glass transition, its modulus should be lower than that of the crystal. However, the modulus observed for the pressed sample was greater than that of the unpressed sample. This result suggests that the phase-separated AO-80 domains, the size of which is in the submicron order (as seen in Fig. 4), act as junction crosslink points in addition to their additive effect as filler. Consequently, the  $E'$  in the intermediate plateau can be considered to be composed of the following two parts. One is independent of strain,



**Figure 3** Temperature dependence of loss tangent  $\tan \delta$  at 1.1 Hz for (1) CPE, (2) unpressed CPE/AO-80, and (3) pressed CPE/AO-80 (25%).



**Figure 4** SEM photomicrograph of pressed CPE/AO-80 (25%).

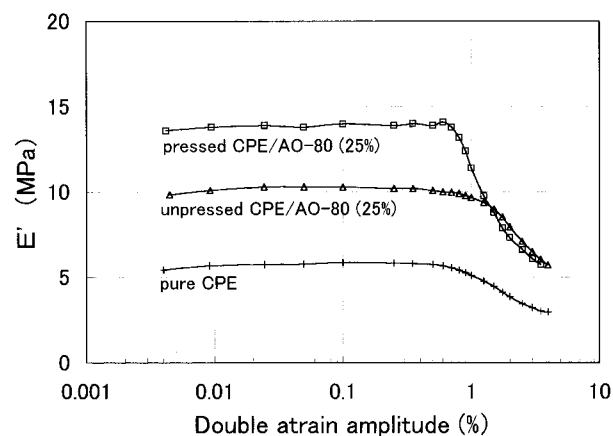
including the pure CPE network, the hydrodynamic effect of the AO-80-rich domain, specific interactions between AO-80-rich domains, and the CPE matrix. Another is a strain-dependent part caused by the AO-80-rich domain network expected. If the latter were the case, the Payne effect as a measure of filler network would be observed. In this study, we limit the focus to the strain dependence of  $E'$  in the intermediate plateau.

Figure 5 shows the strain dependencies of  $E'$  at 23°C and 1.1 Hz for CPE and both unpressed and pressed CPE/AO-80 (25%), respectively. It was found that the  $E'$  of pure CPE slightly changes upon increasing strain amplitude over the range tested. In general, pure elastomer does not essentially show the Payne effect.<sup>11,12</sup> Minor changes in the  $E'$  observed here might be the result of networking by the CPE macrocrystals. A comparison of pure CPE with unpressed CPE/AO-80 (25%) shows that the AO-80 crystalline particles do not affect the strain dependence of  $E'$ . In the case of the polymeric fillers, it has been found that the filler-networking is strongly dependent on the filler particle size,<sup>2,13</sup> that is, there is no Payne effect when added filler is relatively large, whereas a significant Payne effect is observed in the case of smaller particles. As seen in Figure 1, the AO-80 crystals within the unpressed CPE/AO-80 sample are relatively large ( $\sim 2 \mu\text{m}$ ). Those results are in full agreement with a finding by Vieweg et al.,<sup>3</sup> that is, there is no Payne effect when added filler is relatively large.

Moreover, whereas the  $E'$  for the pure CPE and unpressed CPE/AO-80 (25%) is relatively insensi-

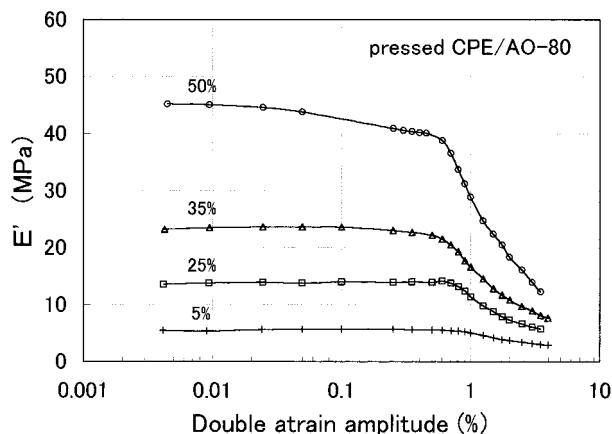
tive to strain amplitude, for the pressed CPE/AO-80 (25%) the effect of strain amplitude on the  $E'$  is very pronounced. Thus, a temporary secondary networking by the AO-80-rich domains within the pressed CPE/AO-80 (25%) was illustrated by the observed Payne effect.

Briefly, the preceding discussion suggests that there is a networking by the AO-80-rich domain for a given CPE/AO-80 system. Now the questions arise as to why and how this network can be formed in the CPE/AO-80 system. The answer is probably related to a particular morphology for pressed CPE/AO-80 (25%). This can be explained in terms of the phase diagram. In the case of pressed CPE/AO-80, according to preliminary studies,<sup>5,7,8</sup> those blends are compatible when the AO-80 content is less than 15%, whereas blends become partly compatible when AO-80 content exceeds 15%. This partly compatible state can be attributed to a result memorizing the phase separation according to the spinodal decomposition by the formation of intermolecular hydrogen bonds between CPE and AO-80. As a result, some segment of the CPE chain is incorporated into the phase-separated AO-80 domain. For an organic hybrid consisting of CPE and another hindered phenol, tetrakis[methylene-3-(3-5-di-*tert*-butyl-4-hydroxy phenyl)propionyloxy]methane (AO-60), the dynamic mechanical properties of which are nearly identical to those of the CPE/AO-80 hybrid, the chlorine within the AO-60 domain was confirmed by elemental analysis.<sup>6</sup> Therefore, it is assumed that the microstructure of the AO-80 domain is basically similar to that of the AO-60 domain.



**Figure 5** Strain dependence of storage modulus  $E'$  at 23°C and 1.1 Hz for CPE and both unpressed and pressed CPE/AO-80 (25%).



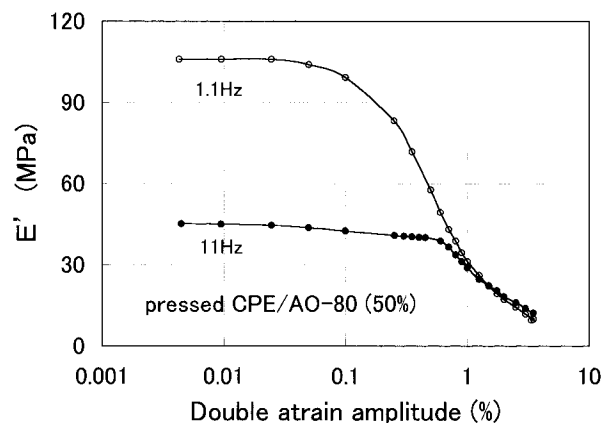


**Figure 6** Strain dependence of storage modulus  $E'$  at 23°C and 1.1 Hz for pressed CPE/AO-80.

These results demonstrated that two components, CPE and AO-80, are hybridized during the quenching process. We consider pressed CPE/AO-80 as a hybrid. Thus, the interactions between segments of a CPE chain and of another CPE chain, which are projecting out from the AO-80-rich domains, produce a three-dimensional mobile physical network. This intersegment interaction is probably attributable to van der Waals force, which can be broken when the strain (or stress) is large enough. A decrease in  $E'$  at a high strain amplitude (seen in Fig. 5) is considered to be the result of the mechanical disruption of segment-segment contacts. It should be noted here that the Payne effect also does not originate in either the CPE component or the AO-80 component, but rather arises from their hybridization.

The strain dependencies of  $E'$  for CPE/AO-80 hybrids with different loadings of AO-80 at 23°C and 1.1 Hz are presented in Figure 6. The  $E'$  values of all hybrids at high strain amplitude are close; an exponential augmentation of  $E'$  at low strain amplitude with increasing AO-80 content was observed. The decrease in the  $E'$ , that is, the Payne effect is exponentially increased by increasing the AO-80 content. On the other hand, whereas  $E'$  greatly decreases for highly filled hybrids, that of CPE with AO-80 of 5% (similar to pure CPE) does not change significantly. Therefore, the Payne effect in CPE/AO-80 blends can be considered as a measure of an AO-80-rich domain networking that originates from intersegment interaction.

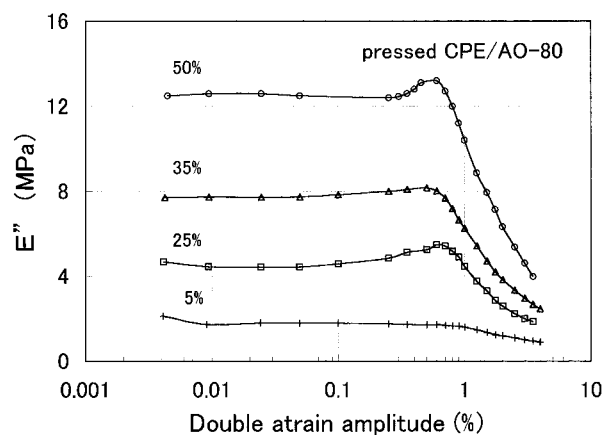
In general, in the case of filler-filled rubbers, it is known that those dynamic properties depend



**Figure 7** Strain dependence of storage modulus  $E'$  at 23°C and 1.1 Hz as well as 11 Hz for pressed CPE/AO-80 (50%).

not only on the strain amplitude but also on the frequency. Figure 7 shows the strain dependence of the  $E'$  under different frequency conditions. The same tendency is evident, although the difference in the  $E'$  between low strain and high strain is much greater because of the frequency dependence of intersegment interaction.

Whereas  $E'$  is mainly related to the AO-80-rich domain network that is reduced during dynamic strain,  $E''$  is related to the breakdown and reformation of those structures. Figure 8 shows the strain dependence of the  $E''$  for various samples at 23°C and 1.1 Hz. Apparently, the addition of AO-80 in CPE will substantially increase  $E''$  of the material regardless of the strain amplitude. It is also evident that, in contrast to  $E'$ , which decreases monotonously with increasing strain,  $E''$  shows a maximum value at a moderate strain



**Figure 8** Strain dependence of loss modulus  $E''$  at 23°C and 1.1 Hz for pressed CPE/AO-80.

amplitude (about 0.6%). After passing through a maximum, the  $E''$  decreases rapidly with further increases in strain amplitude. In the case of filler-filled rubber, it is well known that the  $E''$  is dependent on the rates of network breakdown and reformation, which are related to the strain amplitudes. If the strain amplitude is small enough so that the network is unable to be broken, the  $E''$  value seems to be determined mainly by the hydrodynamic effect of the AO-80 domain so that the strain dependence was eliminated. To the contrary, the strain is high enough that the network is destroyed to such an extent that it cannot be reconstructed in the time scale of dynamic frequency, and thus the effect of the network on the  $E''$  will disappear. However, at a moderate strain, the network can be broken and then be reconstructed rapidly, so that it causes an additional energy loss.  $E''$  is made up of the sum of the hydrodynamic effect and the lost energy effect, so that it shows a maximum at a critical strain. On the other hand, for pure CPE or the low content samples, such a maximum was not observed.

## CONCLUSIONS

The dynamic mechanical properties of a hybrid of CPE and AO-80 were investigated. The CPE/AO-80 hybrids show another novel relaxation in addition to the glass transition of CPE. This novel relaxation on the higher-temperature side in the mechanical spectrum is attributed to the dissociation of intermolecular hydrogen bonds within the AO-80-rich domain. For CPE/AO-80 hybrids the storage modulus  $E'$  curve clearly shows three plateau regions. The strain dependence of  $E'$  in the intermediate plateau was measured. Consequently, the Payne effect, that is, the decrease of the storage modulus  $E'$  with increasing strain amplitude and the appearance of a loss modulus  $E''$  maximum at a strain of 0.6%, was observed. This result demonstrated the existence of a three-dimensional mobile physical network including an AO-80-rich domain for the CPE/AO-80 hybrid. The Payne effect is considered to be attributed to the mechanical disruption of segment-segment contacts at a sufficiently great strain.

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