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# A Study of the Viscoelastic and Rheological Properties of PVC/CPE Blends Modified by Using Polylauryllactam

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Polylauryllactam was used to improve the impact strength of polyvinylchloride (PVC)/chlorinated polyethylene (CPE) blends without sacrificing their tensile properties. The enhancement of the impact strength increased with the increase of the CPE content in the PVC/CPE blends due to the formation of intermolecular hydrogen bonds among PVC, polylauryllactam and CPE macromolecules. A doubled impact strength of the PVC/CPE blend with 20 weight percent of CPE was obtained after the addition of 1.5 phr polylauryllactam. The PVC/CPE blends with polylauryllactam have a better dimensional stability compared with the PVC/CPE blends without the additive, according to their viscoelastic characteristics. Polylauryllactam shortened the processing time to reach a minimum melt viscosity in the processing of the PVC/CPE blends.

**KEY WORDS** Polyvinylchloride, chlorinated polyethylene, blends, polylauryllactam, viscoelasticity.

## INTRODUCTION

Various polymers have been used to improve the impact strength of the brittle and notch sensitive polyvinyl chloride (PVC), such as ABS,<sup>1</sup> EPDM,<sup>2</sup> nitrile rubber,<sup>3</sup> and chlorinated polyethylene (CPE),<sup>4</sup> etc. Polymer blends of PVC with CPE usually have a lower impact strength than that of PVC with other rubbery modifiers, but PVC/CPE blends have excellent chemicals and weathering resistance.<sup>5</sup> Since CPE has some residue polyethylene crystallinity and acts as an elastomer, it only has a partial miscibility with PVC in a PVC/CPE binary blend. It was reported that the impact fracture surface of the blend showed a two phase structure by scanning electron microscope examination.<sup>6</sup>

The further improvement of the impact strength of PVC/CPE blends by using a polyamide with a low melting temperature was explored in this work in order to make a polymer blend with enhanced mechanical properties but still retaining its excellent chemicals and weathering resistance. There was evidence of the formation of intermolecular hydrogen bonds between C—Cl of a PVC molecule and N—H of a polyamide molecule.<sup>7</sup> Therefore, the addition of a polyamide with a lower

melting point than that of the processing temperature to a PVC/CPE blend should decrease the interfacial tension between the CPE phase and the PVC matrix through the hydrogen bonding. The decrease of the interfacial tension should in turn improve the dispersion of the discrete phase and increase the interfacial adhesion. Since polylauryllactam has a melting temperature of 170°C, it was chosen to study its effect on the characteristics of PVC/CPE polymer blends. The modification mechanism, impact strength, stress relaxation, tensile creep behavior and rheological properties were investigated to elucidate the structure-property relationship.

## EXPERIMENTAL

### Sample Preparation

The polyvinyl chloride was produced by suspension polymerization and had a number average molecular weight of 56,000. The chlorinated polyethylene was obtained through a aqueous phase chlorination of polyethylene and had a chlorine content of 36.7 percent by weight.

The polymer powders were first dried at 60°C in vacuo overnight and then mixed with stabilizers (polymer 100 phr, tribasic lead sulfate 5 phr, lead stearate 0.5 phr, barium stearate 1 phr, calcium stearate 0.5 phr, paraffin wax 0.5 phr) and with a predetermined amount of polylauryllactam in a high speed mixer. They were then plasticated in a Banbury mixer at 180°C. The milled sheets were further processed to compression molded sheets for the preparation of test specimens.

### Measurements of Viscoelastic and Rheological Properties

The stress relaxation and tensile creep behavior of the polymer blends were obtained by using a Shimadzu AG-2000A universal tester equipped with a temperature controlled test chamber. The impact strength was measured according to ASTM D256 by a Charpy type impact tester. All the experiments were conducted at 22°C unless otherwise specified.

The rheological parameters and the processability of the polymer melts with or without polylauryllactam were measured by using a Haake Rheocord system equipped with a Rheomix600 standard mixer and sensor. The rotor temperature was 180°C and its speed was 40 rpm.

## RESULTS AND DISCUSSION

### A. Viscoelastic Behavior of PVC/CPE Blends with Various CPE Contents

Stress relaxation and tensile creep properties of PVC/CPE blends are shown in Figure 1 and Figure 2, respectively. Since CPE is an elastomer at the test condition, its addition to the PVC matrix decreased the stress and increased the elongation in the tensile experiments as expected. The changes in the stress and creep elongation were approximately proportional to the CPE content in the binary blends when the amount of CPE added was from 0 to 20 percent by weight. The rubbery

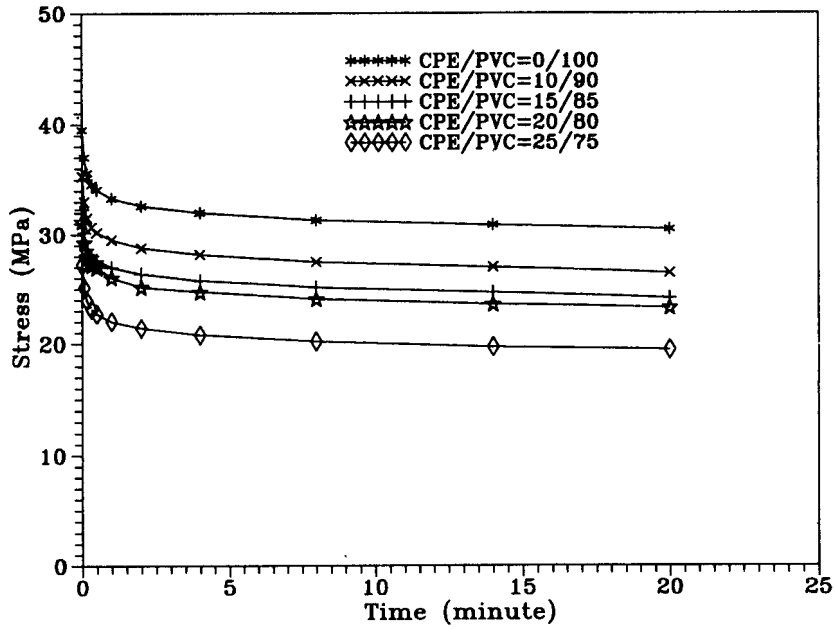


FIGURE 1 Stress relaxation behavior of PVC/CPE blends with various CPE contents (elongation = 10%).

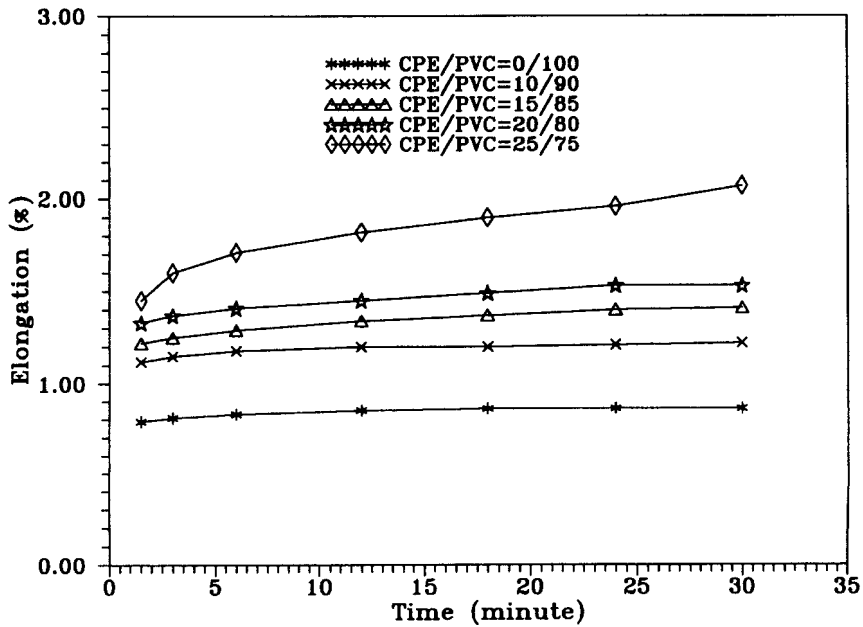


FIGURE 2 Tensile creep behavior of PVC/CPE blends with various CPE contents (stress = 21 MPa).

CPE phase did not contribute to the tensile strength to any significant degree since the PVC phase was still a continuous matrix as reported previously.<sup>6</sup> The further increase in the CPE content might convert the discrete phase to a partially continuous phase as indicated by the viscoelastic behavior of the PVC/CPE blend with 25 weight percent of CPE. Since a part of the stress applied was taken by the rubbery phase, an abrupt change in the stress relaxation and the tensile creep behavior was observed as shown in Figure 1 and Figure 2. The PVC/CPE blend with 25 weight percent CPE even showed viscous flow characteristics under the creep test condition. In order to obtain a polymer blend with an excellent impact strength as well as a dimensional stability, 20 percent by weight of CPE in the PVC/CPE blend was chosen as a maximum CPE content in the modification experiments by using polylauryllactam.

### B. Effect of Polylauryllactam on the Mechanical Properties of PVC/CPE Blends

The impact strength of PVC/CPE blends with or without polylauryllactam is shown in Figure 3. The improvement of the impact strength of binary PVC/CPE blends with the increase of CPE content indicated that the interface between PVC phase and CPE phase had a certain extent of adhesion. Stress whitening phenomenon was also observed in the fracture region of the specimen with a CPE content of 5 weight percent or higher. The impact strength of the specimen with 20 weight percent of CPE was 25.5 kJ/m<sup>2</sup> compared with 6.1 kJ/m<sup>2</sup> of the pure PVC impact strength as shown in Table I.

The addition of a small amount (1.5 phr) of polylauryllactam further enhanced the impact properties of the PVC/CPE blends, especially at high CPE contents as

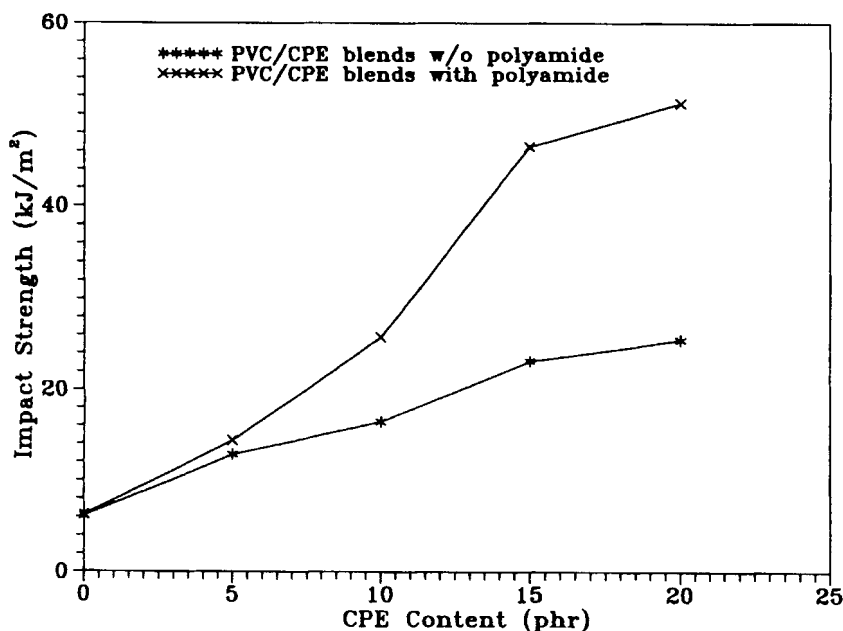


FIGURE 3 Impact strength of PVC/CPE blends with or without polylauryllactam.

TABLE I

The impact properties of PVC/CPE blends with various CPE contents

CPE Content (wt%)	0	5	10	15	20
Impact Strength (kJ/m <sup>2</sup> ) (without polyamide)	6.1	12.8	16.4	23.2	25.5
Impact Strength (kJ/m <sup>2</sup> ) (with polyamide)	6.2	14.3	25.8	46.5	51.2
r value <sup>1</sup>	0	0.03	0.07	0.10	0.14
Efficient Coefficient <sup>2</sup>	1.02	1.12	1.57	2.00	2.01

<sup>1</sup> r value is the ratio of the chlorine content of CPE to the total chlorine content of the PVC/CPE blends.

<sup>2</sup> Efficient Coefficient is the ratio of the impact strength of the PVC/CPE blend with polylauryllactam to that without polylauryllactam.

shown in Figure 3 and Table I. The impact strength of PVC with polylauryllactam was almost identical to that of PVC without polylauryllactam. With the increase of *r* value which is proportional to the CPE content in the blends, the effect of polylauryllactam on the impact strength became more and more pronounced. As summarized in Table I, the efficient coefficient which evaluates the improvement of the impact strength increased with the CPE content. At a CPE content of 20 weight percent, the impact strength of the PVC/CPE blend with polylauryllactam was twice as high as that of the PVC/CPE blend without the modification. The improvement of the impact strength in the presence of polylauryllactam can be explained by the interfacial tension changes. K. Yamada and his coworkers<sup>7</sup> reported that there were intermolecular hydrogen bonds between C—Cl of PVC and N—H of poly(*p*-phenylene terephthalamide) determined by using IR spectrophotometer. Since CPE and PVC have a limited compatibility, the hydrogen bonding of the N—H of polylauryllactam with the C—Cl of CPE molecules and with the C—Cl of PVC molecules increased the interfacial adhesion. The hydrogen bonded molecules of PVC-polylauryllactam-CPE acted as a surfactant at the interface to lower the interfacial tension as well as to improve the CPE particle dispersion in the PVC matrix.

The intermolecular hydrogen bonding may form the following structures in the blend, that is, PVC-polylauryllactam-PVC, PVC-polylauryllactam-CPE, CPE-polylauryllactam-CPE, PVC-polylauryllactam, CPE-polylauryllactam. According to the theoretical model<sup>6</sup> by using a probability method, the concentration of PVC-polylauryllactam-CPE hydrogen bonded molecules should increase with the increase of the *r* value until *r* reaches 0.5. Since the PVC-polylauryllactam-CPE molecule

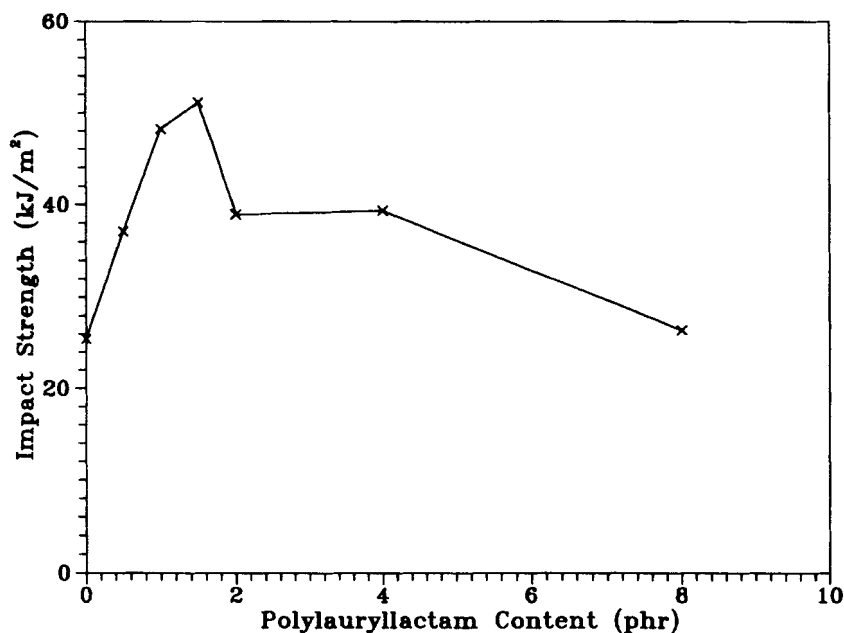


FIGURE 4 Effect of polylauryllactam concentration on the impact strength of modified PVC/CPE (80/20) blends.

was a phase compatibilizer produced in situ, the impact strength of the PVC/CPE blends enhanced after the addition of polylauryllactam, especially at high  $r$  values as shown in Table I.

The effect of polylauryllactam concentration on the impact strength of PVC/CPE blends with 20 wt% CPE is shown in Figure 4. With the addition of polylauryllactam, the impact strength of the blends was enhanced at first and reached a maximum when the concentration of the additive was about 1.5 phr and then decreased afterwards. It can be inferred that the concentration of the PVC-polylauryllactam-CPE hydrogen bonded molecules increases with the increase of polylauryllactam concentration in the range studied. Since these molecules were preferably located at the interface, a saturation concentration similar to the critical micelle concentration (cmc) in the case of emulsion would be reached. The further increase of the PVC-polylauryllactam-CPE concentration would not further decrease the interfacial tension. At the same time the increased concentration of polylauryllactam would also result in the increase of hydrogen bonding in the CPE phase, that is, the increase of the concentration of CPE-polylauryllactam-CPE molecules which cause the decrease of the impact strength. The appearance of impact fracture surface of the specimens showed that the PVC fracture surface did not exhibit stress whitening while the PVC/CPE blends had the stress whitening. The degree of the stress whitening decreased at high polylauryllactam concentration which indicated the decreased elasticity of the CPE phase. This explains the lowering of the impact strength of the blends with the increase of the additive to levels above the optimum amount.

**C. Viscoelastic Behavior of PVC/CPE Blends With or Without Polyauryllactam**

Figure 5 shows the effect of polyauryllactam on the tensile stress relaxation behavior of PVC/CPE blends. The addition of 1.5 phr polyauryllactam to the pure PVC changed its stress relaxation behavior significantly. The high retained stress confirmed that the formation of PVC-polyauryllactam-PVC hydrogen bonded molecules would improve the tensile properties although the impact strength of the PVC specimen was not changed as discussed in Section B. The retained stress of the PVC/CPE blend with 20 weight percent of CPE also increased after the addition of polyauryllactam. Since PVC is the continuous phase in the PVC/CPE blend, the tensile behavior of the blend depends mainly on the structure of PVC phase. The similar improvement in the stress relaxation behavior of the pure PVC and the PVC/CPE blend with polyauryllactam indicated that the increased interfacial adhesion in the PVC/CPE blend with polyauryllactam did not contribute to the stress relaxation behavior significantly.

The creep behavior of PVC/CPE blends was also affected by the addition of polyauryllactam. The changes in elongation of PVC/CPE blends with time were measured at a stress of 21.0 MPa as shown in Figure 6. A specimen of the PVC/CPE blend without polyauryllactam showed strong time dependence of its creep behavior at the test conditions. The tensile creep rate decreased with the addition of polyauryllactam. Unlike the impact strength of the PVC/CPE blends, there was no optimum additive level. The higher the polyauryllactam concentration, the lower the tensile creep rate of the PVC/CPE blends. The elongation of the PVC/CPE blend with 8 phr polyauryllactam at 30 minutes was only about 2/3 of that

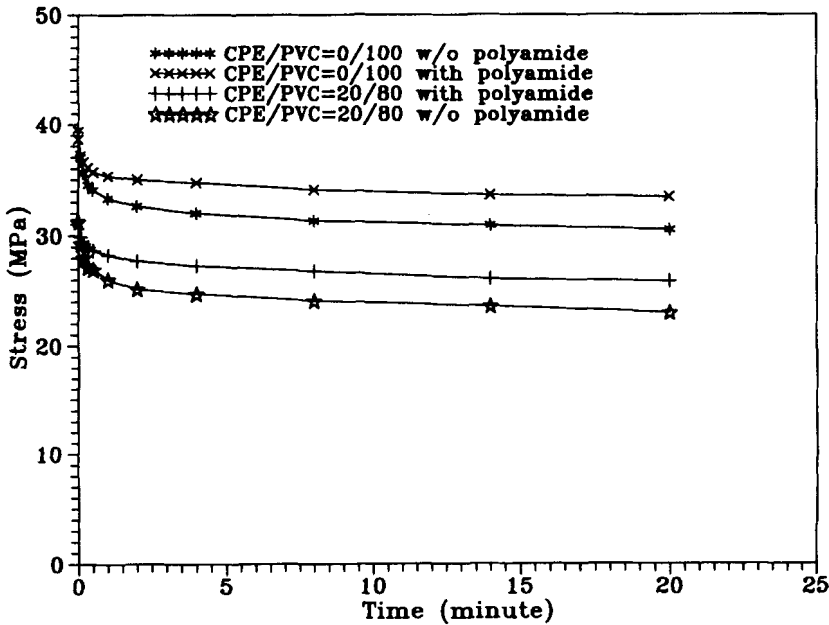


FIGURE 5 Stress relaxation behavior of PVC/CPE blends with or without polyauryllactam (1.5 phr) (elongation = 10%).



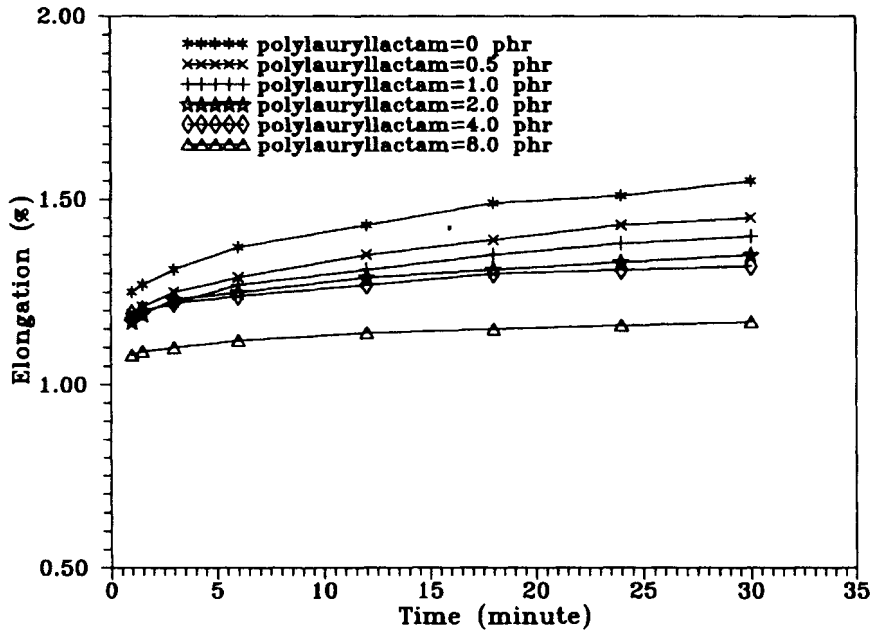


FIGURE 6 Tensile creep behavior of PVC/CPE (80/20) blends with various concentrations of poly-lauryllactam (stress = 21 MPa).

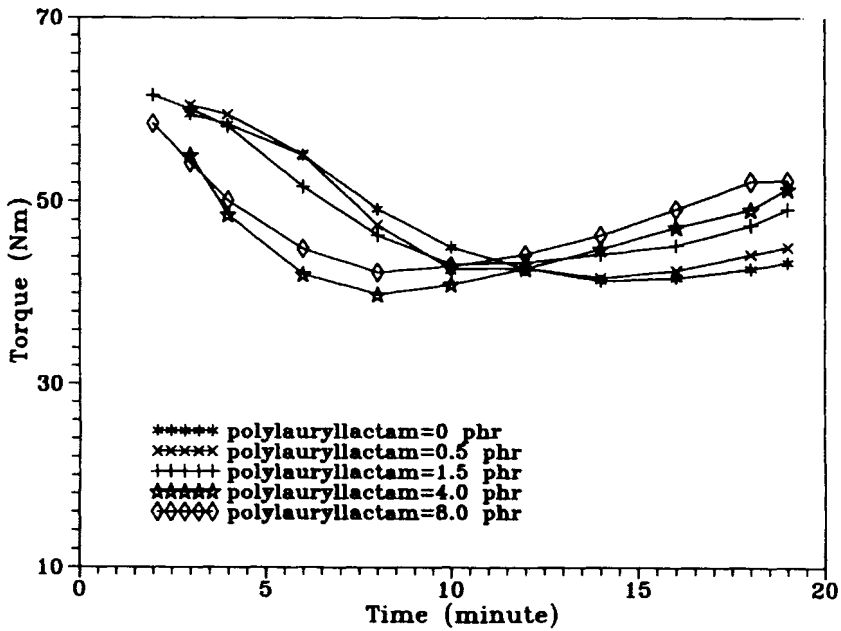


FIGURE 7 Effect of poly-lauryllactam concentration on the torque of PVC/CPE melts during processing.

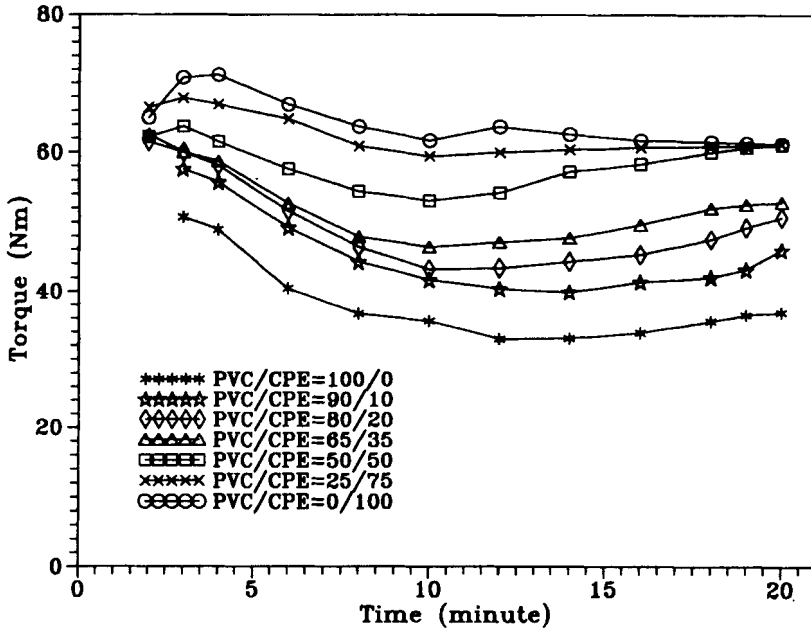


FIGURE 8 Effect of CPE contents on the torque of PVC/CPE melts with 1.5 phr polylauryllactam during processing.

of the blend without the additive. The improvement of the creep behavior after the addition of polylauryllactam can also be attributed to the increase of the hydrogen bonding in the blend. Since there was an optimum concentration of polylauryllactam in the PVC/CPE blend for the impact strength enhancement, the amount of the additive should be determined for specific applications in order to satisfy both the impact strength and the tensile property requirements.

**D. Rheological Behavior of PVC/CPE Blends With or Without Polylauryllactam During Processing**

The polymer processing characteristics were measured at 180°C in terms of the total torque applied versus the processing time. Figure 7 presents the effect of polylauryllactam concentration on the torque of PVC/CPE blends with a CPE content of 20 weight percent. Since the melt viscosity of the polymer blends is proportional to the torque applied to the mixing chamber, the torque change during the processing reflects the viscosity change at various conditions. All samples showed a minimum torque during processing. The mixing torque was high at the beginning and then decreased with the increase of the processing time. After the minimum torque was reached, the total torque increased with processing time. The initial drop in the measured torque resulted from the melting process and the elongation of polymer chains in the direction of shear. For the PVC/CPE blend without polylauryllactam, it took longer time to reach the minimum torque compared with the blends with polylauryllactam. This might indicate that polylauryllactam acted as a lubricant at the beginning of the melt mixing process. The hydrogen bonding

between the polylauryllactam, PVC and CPE molecules caused the melt viscosity increase after the minimum viscosity was reached. A certain degree of thermal degradation or crosslinking usually associated with PVC processing was also observed because the PVC/CPE melt without polylauryllactam showed a slight increase in its viscosity after passing the minimum point.

The CPE content in the PVC/CPE blends with 1.5 phr polylauryllactam had a significant influence on the processing characteristics as shown in Figure 8. The melt of PVC with polylauryllactam had the lowest viscosity throughout the whole time window studied. The melt viscosity increased with the increase of CPE content in the PVC/CPE polymer blends. The total torque applied to the CPE melt with polylauryllactam was about double of that to the PVC melt with the same amount of polylauryllactam. This is of course attributed to the characteristics of the CPE elastomer under the processing conditions.

## SUMMARY AND CONCLUSIONS

The changes of the stress relaxation and the tensile creep behavior of PVC/CPE blends were approximately proportional to the CPE content in the range of 0 to 20 weight percent. A significant change in the viscoelastic characteristics of the blend with 25 weight percent CPE indicated the formation of a partially continuous CPE phase.

The addition of polylauryllactam to the PVC/CPE blends improved the impact strength of the blends, especially at high CPE concentrations. The impact strength of the PVC/CPE blend with 20 weight percent of CPE was doubled after the addition of a small amount of polylauryllactam (1.5 phr).

The optimum concentration of polylauryllactam in the PVC/CPE blend with 20 weight percent of CPE was about 1.5 phr in order to obtain the maximum impact strength enhancement.

A slower stress relaxation rate and a higher retained stress were observed for the PVC/CPE blends with polylauryllactam compared to those of the blends without the additive. The tensile elongation of PVC/CPE blends at a constant stress decreased with the increase of polylauryllactam concentration.

The addition of polylauryllactam shortened the processing time required to reach the minimum melt viscosity of the PVC/CPE blends. The melt viscosity increased with the increase of CPE content in the PVC/CPE blends with 1.5 phr polylauryllactam.

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