

Short communication

# Experimental investigations on PVC–LiAsF<sub>6</sub>–DBP polymer electrolyte systems

S. Rajendran \*, T. Uma

*Department of Physics, Alagappa University, Karaikudi, 630 003, India*

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## Abstract

Poly(vinyl chloride) (PVC)-LiAsF<sub>6</sub> polymer electrolytes plasticized with dibutyl phthalate in different mole ratios have been studied by means of X-ray diffraction (XRD), infrared spectroscopy (IR) and a.c. impedance spectroscopy. The complexation has been confirmed from XRD and IR studies. A maximum room temperature conductivity ( $3.938 \times 10^{-5} \text{ S cm}^{-1}$ ) has been observed for PVC: LiAsF<sub>6</sub>: DBP (10:5:85 mol%) complex. The  $\log \sigma$  vs.  $1/T$  plots ( $\sigma$  = electrical conductivity;  $T$  = temperature) show Arrhenius behaviour. The activation energy is estimated and the results are discussed. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Polymer electrolyte; Poly(vinyl chloride); XRD, IR and conductivity studies

## 1. Introduction

There is currently wide interest in the area of polymer electrolytes because of their potential use in electrochemical applications such as lithium batteries with high energy density [1,2]. Among the polymer systems reported, poly(ethylene oxide) (PEO) is the most widely studied in terms of its complexation behaviour with several metal salts [3–6]. PEO/metal–salt complexes exhibit high ionic conductivities at (or) near ambient temperature and thus are attractive candidates for electrochemical applications. The poor mechanical strength of PEO electrolytes in the high conduction region is, however, a severe drawback.

Poly(vinyl chloride) (PVC) is a commercially available, inexpensive polymer and is compatible with many plasticizers such as dibutyl phthalate (DBP) and dioctyl adipate (DOA). The resulting plasticized PVC has good mechanical strength and is widely used in the form of films, sheets, and moldings for plastic leather and curtains, lead-wire coating, flooring, wallboard, etc. A reduction in the resistivity of plasticized PVC is sometimes required to obtain anti-electrostatic properties. Elasticized PVC has been widely used as membranes in ion-selective electrodes [7–9].

Further, a PVC-based polymer electrolyte system plasticized by ethylene carbonate and propylene carbonate has been reported [10] as being applicable to lithium and lithium-ion secondary batteries. In this context, it is important to optimize the conductivity and electrochemical properties of plasticized PVC systems.

In the present paper, we report a new polymer electrolyte PVC–LiAsF<sub>6</sub> system with DBP in various mole ratios for Li<sup>+</sup> conduction. Investigations with X-ray diffraction (XRD), infrared spectroscopy (IR), and a.c. impedance spectroscopy are undertaken and measurements of electrical conductivity are reported.

## 2. Experimental

PVC (molecular weight:  $1.5 \times 10^5$ ) and LiAsF<sub>6</sub> were mixed with DBP in various mole ratios. Solution-cast films with thicknesses of about 80 to 160  $\mu\text{m}$  were obtained by pouring the solutions of PVC and LiAsF<sub>6</sub> in distilled tetrahydrofuran (THF) on to Teflon bushes and then drying at room temperature (304 K). The films formed were again dried in a vacuum oven at 323 K at a pressure of  $10^{-3}$  Torr for 24 h. The polymer films thus obtained were stored in a desiccator.

XRD studies of pure PVC and polymer complex films were performed using a JEOL, JDX 8030 X-ray diffrac-

\* Corresponding author. Tel.: +91-4565-35205-200; fax: +91-4565-35202; e-mail: alagappa@md3.vsnl.in

tometer. The IR studies were carried out using a Perkin-Elmer model 577 IR spectrophotometer. The bulk electrical conductivities of polymer complexes were evaluated from the complex impedance plots at different temperatures (304–373 K) using a Keithley 3330 LCZ meter. The plots were recorded in the frequency range 40 Hz to 100 KHz with a signal amplitude of 10 mV. For conductivity studies, the polymer films were sandwiched between stainless-steel electrodes. The electrode area was 3.14 cm<sup>2</sup>. The sample holder was kept inside a sealed glass tube with a dynamic vacuum to prevent uptake of moisture by the

polymer–salt electrolyte films and the experiments were performed in the temperature range 304 to 373 K.

### 3. Results and discussion

#### 3.1. Evidence of complex formation

The XRD patterns of pure PVC, LiAsF<sub>6</sub> and complexed PVC are presented in Fig. 1a,b and c–f, respectively. The

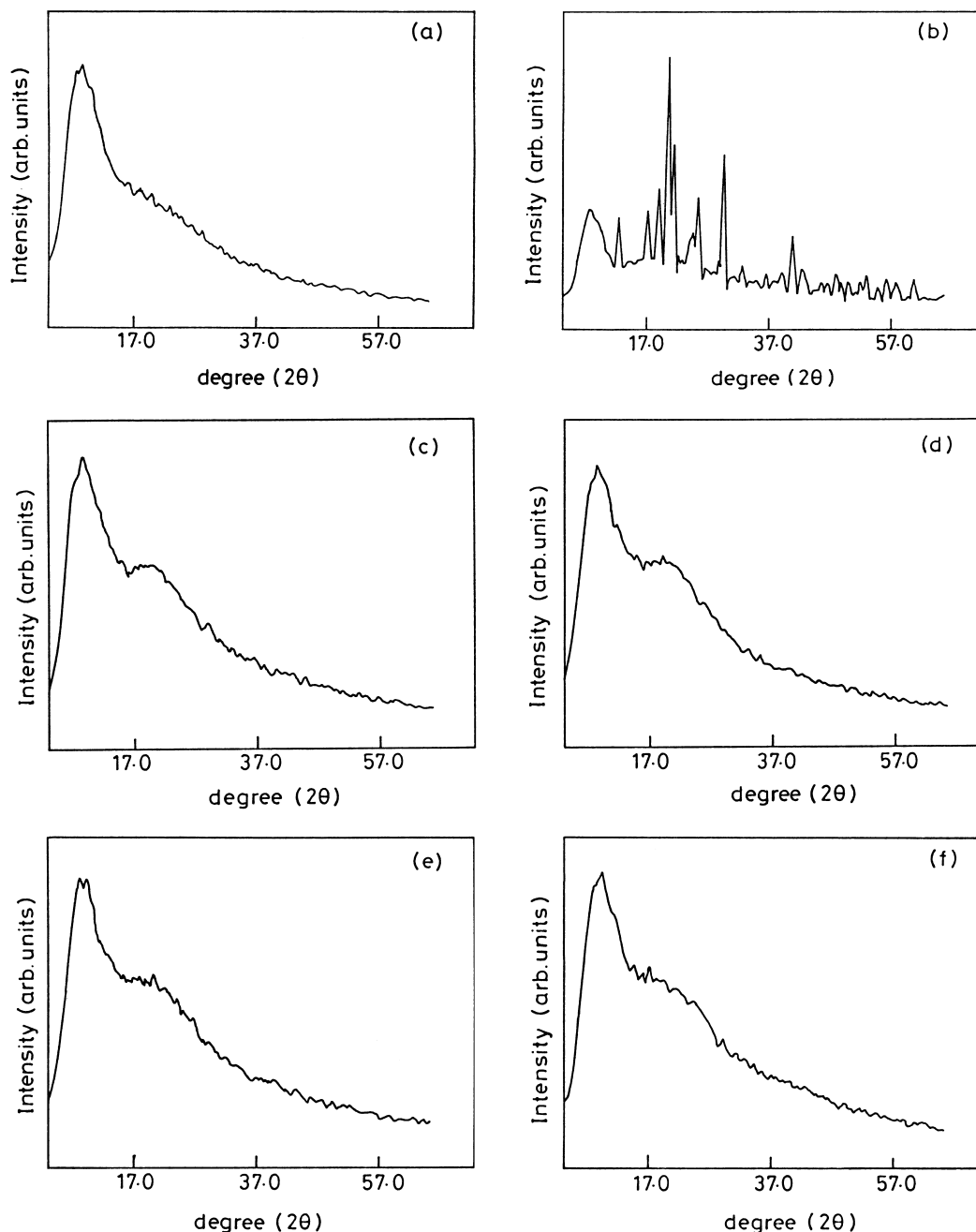


Fig. 1. XRD patterns for: (a) pure PVC; (b) pure LiAsF<sub>6</sub>; (c) PVC–LiAsF<sub>6</sub>–DBP (10:5:85 mol%); (d) PVC–LiAsF<sub>6</sub>–DBP (15:5:80 mol%); (e) PVC–LiAsF<sub>6</sub>–DBP (25:5:70 mol%); (f) PVC–LiAsF<sub>6</sub>–DBP (35:5:60 mol%).

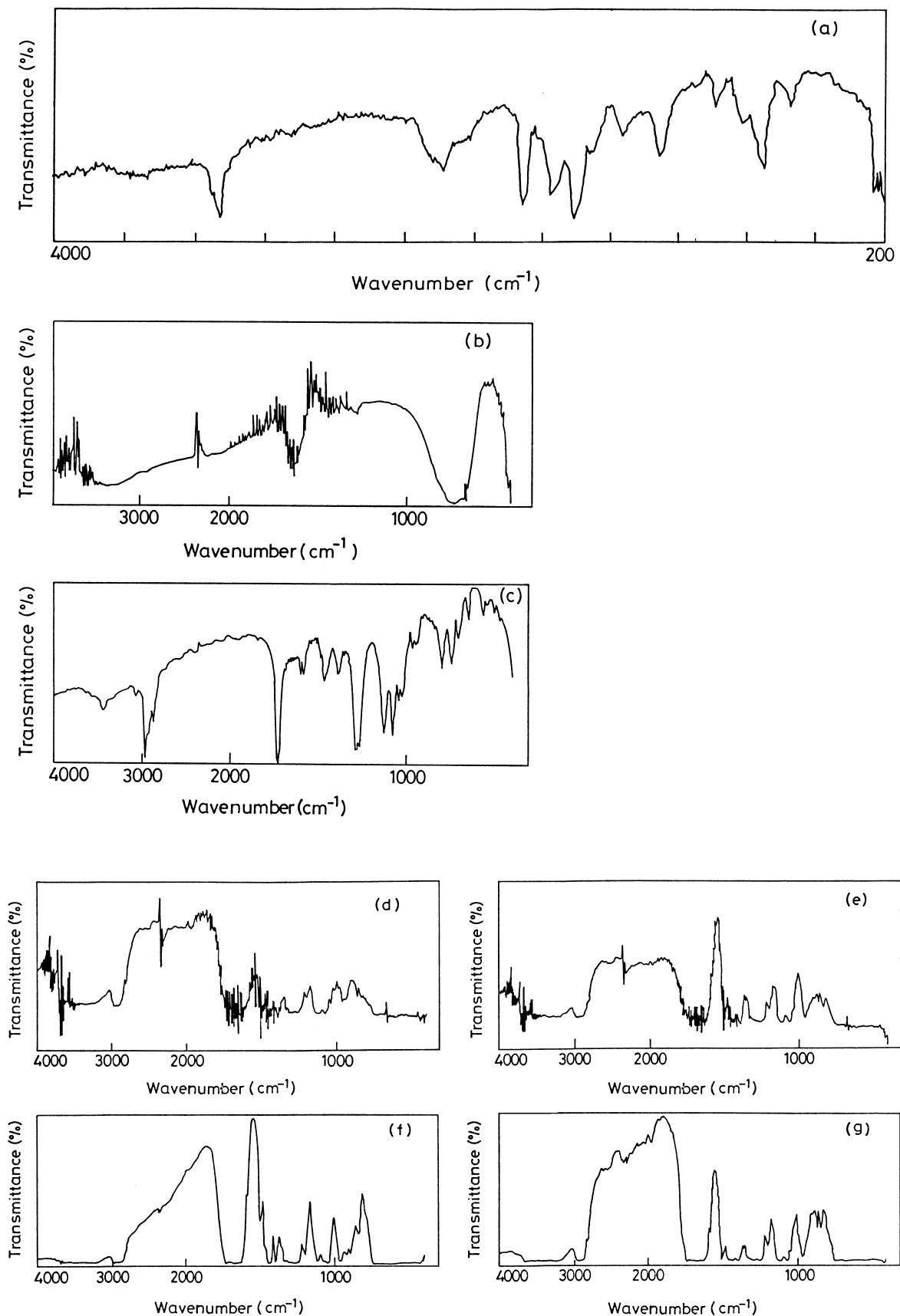


Fig. 2. FTIR plots for: (a) pure PVC; (b) pure  $\text{LiAsF}_6$ ; (c) DBP; (d) PVC- $\text{LiAsF}_6$ -DBP (10:5:85 mol%); (e) PVC- $\text{LiAsF}_6$ -DBP (15:5:80 mol%); (f) PVC- $\text{LiAsF}_6$ -DBP (25:5:70 mol%); (g) PVC- $\text{LiAsF}_6$ -DBP (35:5:60 mol%).

patterns of pure PVC and complexed PVC indicate low crystallinity. By contrast,  $\text{LiAsF}_6$  is found to be crystalline. No peaks corresponding to  $\text{LiAsF}_6$  are observed in complexed PVC, which indicates the absence of excess salt (uncomplexed) in the material.

The IR spectra were recorded in the range 200 to 4000  $\text{cm}^{-1}$  in the transmittance mode. The spectra for pure PVC, pure  $\text{LiAsF}_6$ , DBP and PVC– $\text{LiAsF}_6$ –DBP complexes are shown in Fig. 2a,b,c and d–g, respectively. The peak at 1240  $\text{cm}^{-1}$  is assigned to the CH-rocking vibration in pure PVC which is shifted to 1257  $\text{cm}^{-1}$  in the complex. This suggests that the Li ion may be located on the vinyl chloride of the polymer chain  $-\text{[CH}_2\text{-CHCl-]}_n$ . The peak at 950  $\text{cm}^{-1}$  in pure PVC is shifted to 956  $\text{cm}^{-1}$  in the polymer complex.

A comparison indicates that some additional peaks appear in complexed PVC (Fig. 2d) at 1731, 1681, 1556 and 1454  $\text{cm}^{-1}$ . These peaks are not associated with pure

PVC,  $\text{LiAsF}_6$  or DBP. In addition to this, the disappearance of pure PVC bands at 895, 1315, 1240, 760, 660 and 595  $\text{cm}^{-1}$  in the complexes suggests the co-ordination or complexation of  $\text{Li}^+$  ions to the chlorine of PVC. The disappearance of some of the peaks observed for pure  $\text{LiAsF}_6$  (3850, 3830, 3813 and 3793  $\text{cm}^{-1}$ , etc.) in polymer complexes may be due to the fact that the  $\text{AsF}_6^-$  ion is in different surroundings in the polymer complexes compared with those in the pure  $\text{LiAsF}_6$  salt. In summary, these observations confirm the complexation of  $\text{LiAsF}_6$  with PVC.

### 3.2. Electrical conductivity

A typical complex impedance diagram for the cell SS/PVC– $\text{LiAsF}_6$ –DBP/SS is shown in Fig. 3. In the high frequency region, the bulk impedance of the system is

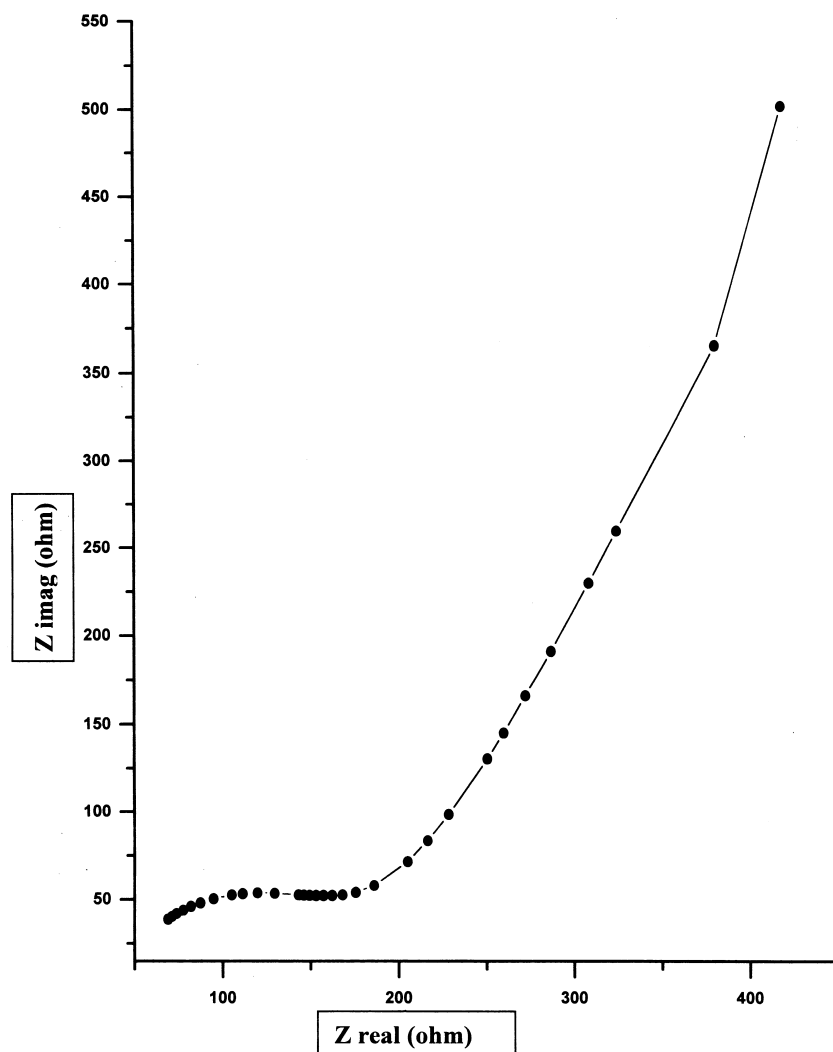


Fig. 3. Impedance diagram for PVC– $\text{LiAsF}_6$ –DBP (10:5:85 mol%) at room temperature (304 K).

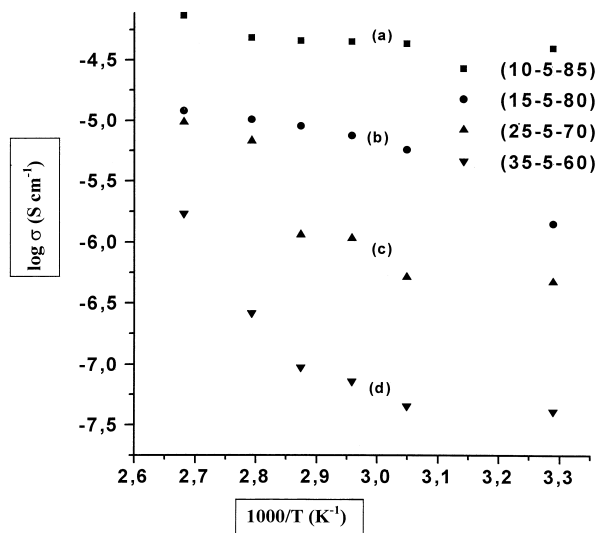


Fig. 4. Arrhenius plot of log conductivity against reciprocal temperature of: (a) PVC–LiAsF<sub>6</sub>–DBP (10:5:85 mol%); (b) PVC–LiAsF<sub>6</sub>–DBP (15:5:80 mol%); (c) PVC–LiAsF<sub>6</sub>–DBP (25:5:70 mol%); (d) PVC–LiAsF<sub>6</sub>–DBP (35:5:60 mol%).

estimated to be 179.7  $\Omega$ . The low frequency spur in Fig. 3 shows the ion blocking nature of the SS electrode.

The variation of the logarithm of electrical conductivity ( $\log \sigma$ ) with inverse absolute temperature for various complexes is presented in Fig. 4. There is a linear relationship which can be described as ‘apparently Arrhenius’ and is given by  $\sigma = \sigma_0 \exp[-E_a/KT]$  where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy, and  $K$  is the Boltzmann’s constant. The conductivity values and activation energies of the four polymer complexes are listed in Table 1.

The conductivity decreases markedly, from  $10^{-5}$  to  $10^{-8}$  S cm<sup>-1</sup>, as the mole fraction of PVC is increased from 10 to 35 and the logarithm of the conductivity decreases almost proportionally with increase in the PVC mole fraction. The decrease in conductivity is mainly due to the decrease in mobility. Although it has been found

Table 1

Conductivity values and activation energies of PVC–LiAsF<sub>6</sub>–DBP polymer complexes

Polymer complex	$\sigma (\times 10^{-5} \text{ S cm}^{-1})$			Activation energy $E_a$ (eV)
	304 K	338 K	373 K	
PVC–LiAsF <sub>6</sub> –DBP [10:5:85]	3.938	4.479	7.540	0.152
PVC–LiAsF <sub>6</sub> –DBP [15:5:80]	0.141	0.739	1.204	0.607
PVC–LiAsF <sub>6</sub> –DBP [25:5:70]	0.046	0.106	0.957	0.926
PVC–LiAsF <sub>6</sub> –DBP [35:5:60]	0.004	0.007	0.169	0.975

[11] that the addition of PVC facilitates ionic dissociation in a solution of NaBPh<sub>4</sub> in a PVC membrane plasticized by dioctyl sebacate, the addition of PVC to the present ionic system seems to reduce the ionic mobility and the degree of dissociation does not seem to be enhanced by the PVC addition.

Finally, the ionic conductivity increases with temperature, in agreement with theoretical considerations. It was found that the ionic conductivity increases as the concentration of plasticizer increases. This may be due to the lowering of viscosity with increasing plasticizer concentration.

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