Mechanical and Thermal Properties of the Plasticized PVC-ESBO

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A B S T R A C T

The thermal and mechanical properties of plasticized PVC with epoxidized soya bean oil(PVC-ESBO) are studied. The repulsive interactions are used to explain the effect of epoxidization on the modulus of PVC with ESBO and plasticizer. The glass transition temperature of PVC is a linear function of the epoxidization of ESBO plasticizer. The activation energies of stabilized PVC/ESBO is also influenced by dehydrorochlorination reaction and HCl evolution. Addition of ESBO improves thermal behaviour of PVC. The higher activation energies of Ca-Zn, Ba-Zn stabilizers are responsible for the stability of PVC-ESBO. The epoxidization level of ESBO also improves the mechanical properties and thermal stability of PVC.

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INTRODUCTION

The low thermal stability of polyvinyl chloride (PVC) has limited the use of this polymer in industry. There has been many attempts to improve the thermal stability and mechanical properties of this polymer in recent years [1-3]. As polyvinyl chloride decomposes and loses HCl even at lower processing temperature, it is assumed that the active hydrogen is apparently replaced in PVC. It is possible to inhibit the eliminated HCl by organometallic salts, and stabilize

PVC or supress the catalytical effect of HCl in this reaction by epoxides [4]. We have earlier reported the effect of epoxidization of soya bean oil on the dynamic mechanical behaviour of DOP plasticized PVC. The storage modulus (E) and tan δ of the plasticized PVC-ESBO have been used to show the extent of homogeneity and stability of PVC [5]. Since the level of epoxidization improves the glass transition temperature (T_g), and the second phase order transition of PVC is a thermodynamic process we have studied the thermal effect of different levels of epoxidization of ESBO-PVC. In this paper we wish to report the stability of PVC with calcium, barium and zine stabilizers and show how these salts and the epoxidization level of SBO influence the decomposition time and temperature of PVC-ESBO.

EXPERIMENTAL

Materials and Equipment

Polyvinyl chloride is a pipe grade with K-value of 65 and density 0.580 g/cm^3. The plasticizer is DOP or epoxidized soya bean oil. PVC and dioctyl phthalate are manufactured by Iranian Petrochemicals. Soya bean oil (SBO) is form Pak Behshar, Iran. Percent unsaturation of oil is 8.6. The epoxidization of SBO is carried out with 30% H_2O_2 and acetic acid (4,5). Typical formulation consists of PVC and 10% epoxidized soya bean oil with 3, 5, 10.5, 14.5 and 20% epoxidization. The stabilizers are based on 2.5 wt% $BaCl_2$, $ZnSO_4$ or $CaCl_2$. Soya bean oil salts are prepared by addition of NaOH and precipitation of new salts from the solutions of $BaCl_2$, $ZnSO_4$ or $CaCl_2$. The mixing is carried out in a Haak Buchler Instrument, Model 750, torque rheometer. The storage modulus (E′) and glass transition temperature (T_g) are measured by dynamic mechanical thermal analyzer (DMTA). The thermal stability and weight loss of plastisols are measured by thermogravimetric analyzer (TGA). The tensile, impact resistance and hardness of samples are measured at 25ºC according to ASTM-D638, ASTM D256-88 and ASTM-D2240.

RESULTS AND DISCUSSION

Polyvinyl chloride exhibits a complex morphology with several hierarchies of particles and small degree of crystallinity. This means, the entanglements of the polymeric chain may have various levels [2]). Thermodynamically, the second order phase transition is a glassy like short-range order, but liquid like in long range disorder and solid. The glass transition state depends on $\overline{M}_n$ of polymer and hence one may assume that at the liquid-glass transition, the first derivative of free energy as volume, enthalpy and entropy are continuous quantities, but the second derivatives like the specific heat, compressibility or thermal expansion coefficient show jumps. Apart from some relations like WLF that expresses the viscoelastic behaviour of polymers with respect to their glass transitions, the nature of glass transition is not clear and new thermodynamic expressions are needed [6]. In this respect, we have utilize the additivity rule to develop useful equations that correlate the glass transition temperature of two component systems with certain thermodynamic parameter. In the past, there have been number of attempts to relate the glass transition temperature to the weight fractions [7, 8]. But these relations, do not express adequately the second phase transition order of the plasticized PVC with the epoxidized SBO.

If we assume that fractional free volume increases linearly with temperature even at $T > T_g$, and the increment of expansion coefficient at T_g remains constant; then one can express the epoxidization level with, a similar thermodynamic relation:

$$T_g = \frac{(W_1 + KW_2)T_{g_1} T_{g_2}}{T_g W_2 + KW_2 T_{g_1}} \qquad (1)$$

In eqn (1), K is defined as:

$$K = (\frac{d_1}{d_2})(\frac{T_{g_1}}{T_{g_2}}) \qquad (2)$$

Where W_1 and W_2 are weight fractions of the first and second components of PVC but with two different levels of epoxidizations and (d_1/d_2) is the density ratio (K ~ 1.0). The glass transition temperature of α-transition from dynamic mechanical analysis, is used to show the linear relation of ESBO with respect to epoxidization. The elastic modulus (E) of PVC/plasticizer (90/10 wt%) at different levels of epoxidization temperatures (25, 70 and 100ºC) are shown in Figures 1-3. These
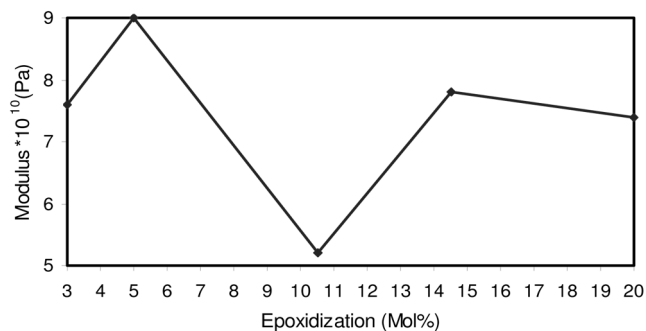
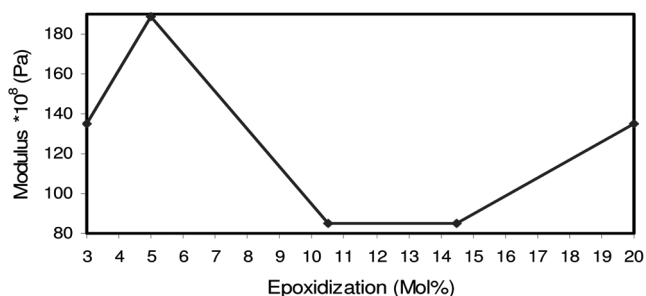**Figure 1.** The effect of epoxidization level on the elastic modulus of PVC/ESBO plasticizer at 25°C.

Figure 2. The effect of epoxidization level on the elastic modulus of PVC/ESBO plasticizer at 75°C.
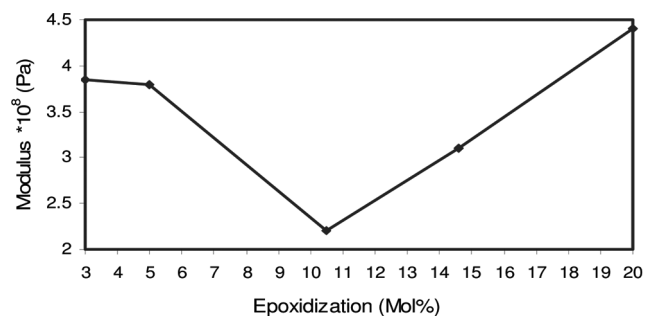

Figure 3. The effect of epoxidization level on the elastic modulus of PVC/ESBO plasticizer at 110°C.

Figure 4. The effect of weight percent of (10.5% mole) ESBO on the impact strength of PVC.

Figure 5. The effect weight percent of (10.5% mole) ESBO on the hardness of PVC.

results show that at 10.5% of epoxidization, the storage modulus drops. This behaviour is best explained by the repulsive interactions between the PVC and the epoxidized groups in ESBO. Since the epoxy group enhances the polarity and interaction of the oil with PVC, it is expected that at a higher epoxidization level, the miscibility and homogeneity of PVC-EPSBO also increases, thi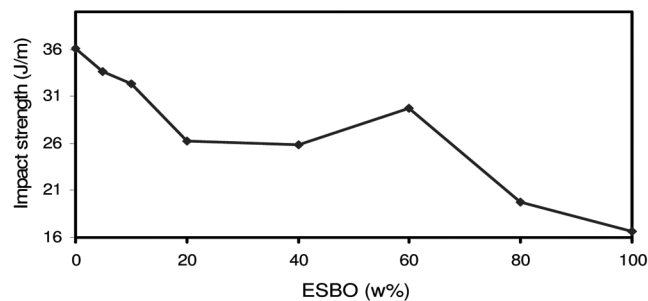s explains the behaviour of the elastic modulus of the plastisol at higher levels of epoxidization. At the lower level of epoxidization, the interactions are not sufficient to bring about the necessary homogeneity or the miscibility of ESBO plasticizer. Similar behaviour has been reported for the viscosities of the epoxidized liquid natural rubber and PVC (8). The transformation of PVC-ESBO phases into a single homogeneous phase controls the elastic modulus [5]. Apparently tensile and other mechanical properties of PVC-EPSBO at 25°C are controlled by the same effect and the homogeneity of the phases involved can improve the mechanical properties of PVC-DOP/ESBO shown in Figures 4-5.

Plasticization of PVC with DOP and ESBO

The effect of DOP on the mechanical properties of PVC/plasticizer (90/10), with the plasticizer made up of (DOP/ESBO) is studied on 95/5, 90/10, 80/20, 60/40, 40/60 and 20/80 weight ratios of DOP/ESBO. Since DOP with 10.5 mole percent ESBO linearly reduces the glass transition temperature of PVC in Figure 6, it is concluded that, at this level of epoxidization, the ester groups from DOP act like the epoxy groups in ESBO
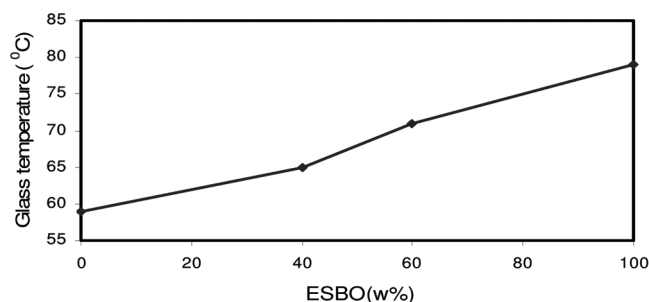
Figure 6. The effect of weight percent ESBO (10.5% mole) on the glass transition temperature of PVC.

and improve the miscibility of the plasticizer, and reduce the second order phase transition temperature (T_g).

The mechanical properties of PVC/DOP/ESBO in Table 1 show the same effect and addition of DOP increases the elongation and impact resistance of PVC, but decreases the tensile modulus and hardness of the plasticized PVC.

Thermal Stability of PVC

Heat and oxygen are the main causes of the degradation. Thermogravimetric (TGA) studies are used to study the thermal stability and thermal behaviour of PVC. The thermal behaviour of PVC and stabilized PVC with Ba-Zn and Ca-Zn stabilizers are shown in Figures 7-9. These results show that under oxygen; mass increase of PVC/stabilizer (95/5) is most likely related to the cross-linking followed by decomposition (T_{dec}) process (above 200°C), and the recorded exothermic temperature is related to the oxidization of

the polymer and it is usually accompanied by an oxidative induction time (OIT). If the partial pressure of oxygen under these conditions is assumed constant, the consumption of the stabilizer during the induction time becomes almost independent of the concentration of Ba-Zn stabilizer and the increased weight percent of Zn stabilizer with respect to time approaches 1.16. But with lower weight ratio of a PVC/stabilizer (95/5) decomposition peak after 39.40 s is 242.18°C. This time Length is shorter for Ca-Za stabilizers and the decomposition temperature for PVC/Ca-Zn with the weight ratio of (95/ 5) is 236°C. PVC/Ca-Zn with 60/40 weight ratio shows the same thermal behaviour after 22.80 s.
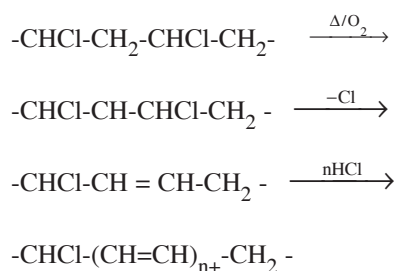
However, further addition of Zn stabilizer does not improve the decomposition time or temperature. Since epoxides are considered as additional source of stability, it is expected that the salt, or the salt of ESBO impart certain degrees of stability. The thermal stability of PVC is best explained by the activation energies involved in this process. If we use (WFL) equation to calculate the activation energy of PVC within the temperature range of $T_g + 186K$ (Eqn 3):

$$\log a_T = \frac{E_a}{R(T - T_r)} \tag{3}$$

The calculated E_a may be used for this purpose. The decomposition time and temperature of these systems with their activation energies are shown in Table 2. These results show that, the low activation energy of the primary stabilizers like Ba-Zn or Ca-Zn do not pre-

Table 1. Mechanical properties of PVC/plasticizer (90/10): Plasticizer is DOP/ESBO and the epoxidization level is 10.5 mol%.

No	Weight ratio of DOP/ESBO	Impact strength (J/m)	Average hardness (lbf/in)	Average force (lbf)	Elastic modulus (N/m^2)	Percentage elongation
1	100:00	36.09	75.4	33.55	1214.2	163.77
2	95:5	33.61	76.6	34.05	1131.7	115.7
3	90:10	32.37	77.37	34.39	---	---
4	80:20	26.19	78.25	34.28	1269	107
5	60:40	25.86	79.50	36.34	1145	16.4
6	40:60	29.72	80.0	35.56	1731	19.58
7	20:80	19.79	80.70	35.87	1168.45	12.57
8	0:100	16.33	81.40	36.18	---	2.47

-CHCl-CH$_2$-CHCl-CH$_2$- $\xrightarrow{\Delta/O_2}$

-CHCl-CH-CHCl-CH$_2$ - $\xrightarrow{-Cl}$

-CHCl-CH = CH-CH$_2$ - $\xrightarrow{nHCl}$

-CHCl-(CH=CH)$_{n+}$-CH$_2$ -

Scheme I

vent the dehydrochlorination reaction or the effects of HCl evolution as shown in the PVC degradation Scheme I. But the addition of ESBO as a secondary stabilizer can greatly improve the thermal stability, and as the activation energy rises; the effect of stabilization is more pronounced. The lower electronegativity of barium, and its higher activity compared to calcium, or the relative alkalinity of CaCl$_2$, makes Ca-Zn stabilizer less effective. Therefore, Ba-Zn stabilizer shows its effect within a shorter thermal range or $\Delta T \sim 7^{o}C$. Addition of ESBO can improve this range by increasing the internal mobilityof the polymer. The higher activation energy $\Delta E_a \sim 18.11$ cal/mol K involved during the heating improves the stabilization of PVC/ESBO. This effect reaches its maximum, for the ionic form of Ba-Zn (ESBO), where Ba-Zn forms an ionic complex with PVC/plasticizer. As shown in Table 2, the activation energy of the polymer-stabilizer complex increases further to Ea~34.8138 cal/mol K, and thermal stability of PVC also improves to a higher range of T~18.07^{o}C. The higher activity of Ba-Zn stabilizer fascilitates the stabilization of PVC and formation of the complex with polymer. This process can inhibit further, the elimination of HCl and degredation of PVC. In this case the higher ionization potential of calcium and its capabili-

Table 2. The effect of Ba-Zn and Zn-Ca stabilizers, the epoxid salts and ESBO on the thermal range and activation energy of PVC/ESBO.

No	Stabilizer	ΔT (°C)	Log a$_T$	ΔE_a cal/mol K
1	Ba-Zn	-13.28	1.7814	13.28
2	Zn-Ca	-7.6	0.4788	7.204
3	Ba-Zn+ESBO	-17.61	0.955952	33.331
4	Ca-Zn+ESBO	-9.4	0.91312	18.11
5	Ca-Zn(ESBO)	-18.07	0.973035	34.8138

ty in complex formation with polyene involved during the degredation is possibly responsible for the higher stability of PVC [9].

CONCLUSION

The stabilization of PVC with Ba-Zn stabilizer is longdr than Ca-Zn stabilizer. The addition of excess Zn stabilizer does not improve the decomposition time or temperature. The activation energy of stabilized PVC with ESBO depends on the lower electornegativity of barium as compared to calcium. The ESBO improves the internal mobility of the system and the higher activation energy of Ba-Zn improves its stability and hardness.

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