Effect of Concentration and Type of Plasticizer on Some Physical Properties of Poly(vinyl Chloride)

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Synopsis

The effect of four different types and concentrations of plasticizers on some physical properties of poly(vinyl chloride) (PVC) has been studied. DOP, DOA, TTP, and Hex were used as plasticizers in concentration levels of up to 24% of PVC weight. The plasticized and unplasticized PVC were processed into sheets by compression molding. The sheets were tested for their vicat softening point, shore D hardness, flexural properties, and dynamic fatigue. It was found that the vicat softening point, shore D hardness, flexural yield strength, and flexural modulus decrease with increase in plasticizer concentration, though in some cases a threshold concentration must be passed before these effects can be observed. Close similarities were always found in the behavior of DOP and DOA and also between TTP and Hex. It was found in the study of flexural fatigue properties of PVC plasticized by DOP that an increase in plasticizer concentration led to a decrease in load bearing ability only at stress levels above 20 MPa.

INTRODUCTION

Plasticizers are compounded with poly(vinyl chloride) primarily to develop the desired physical properties. Two variables of concern are the kind of plasticizer used and its concentration. The temperature ranges in which the final product will be used, and also other environmental and processing factors, will also influence the choice and concentration of plasticizer.

In the usual range of concentrations, the addition of 20% plasticizer makes the resin more flexible, reduces the modulus and tensile strength, and gives greater elongation.

Plasticization may be achieved through the use of additive external plasticizers or through copolymerization, i.e., internal plasticization.

For most resin–plasticizer combinations at room temperature, a plasticizer threshold concentration must be passed before the normal plasticizer effects are observed on physical properties.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The composition shown in Table I was kept constant for all the experiments. In Table II the type and concentration of plasticizers used are given. The *k* value of this resin is 67–68. DOP [Bisoflex DOP, di(2-ethylhexyl phthalate) from B.P. Chemicals International], DOA [Uniflex di(2-ethylhexyl adipate) from Union Carbide Corporation], and TTP (tritolyl phosphate from Fredwhite and Son, Ltd.), and Hex (polypropylene adipate from ICI).

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TABLE I
Materials

Materials	%
PVC[a]	86.47
China clay	8.34
Calcium stearate	0.86
Tribasic lead sulphate	4.32

[a] PVC resin S 110/10 from B.P. Chemicals, Ltd.

Processing

The PVC, china clay, calcium stearate, and tribasic lead sulphate were mixed thoroughly in a ball mill for 8 h. The plasticizers were then added according to the required concentration, hand-mixed, and then mixed thoroughly in a ball mill for at least 1 h. The mixtures of the plasticizers and powders were gelled on a roll mill at 170°C and then compressed at 180°C and 14 MPa into a sheet of dimensions 150 × 150 × 6 mm. The sheets were cut to the approximate dimensions of the desired test specimens, and then machined to the exact dimensions using a routing machine.

Test Methods

The Vicat softening point was measured according to ASTM $D_{1525\text{-}16}$. The rate of heating used was 120° ± 12°C/h.

The shore D hardness was determined according to ASTM $D_{2240\text{-}75}$.

The flexural yield stress and flexural modulus were measured according to method I in ASTM $D_{790\text{-}71}$.

The flexural fatigue characteristics of the compounds were measured at 23°C in four-point bending, using a Macklow Smith fatigue machine. A frequency of 2 Hz was used.

EXPERIMENTAL RESULTS AND DISCUSSION

Vicat Softening Point

The Vicat softening point of the unplasticized and plasticized PVC with various types and concentrations of plasticizers is shown in Figure 1. It it clear that: As the concentration of plasticizer increases, the softening point decreases; the softening temperatures of PVC plasticized with 6% DOP or DOA are nearly the same and are higher than those given by TTP and Hex; the softening temperatures of PVC plasticized with DOP or TTP in concentrations higher than 12% are nearly the same and less than those given by DOA and Hex.

TABLE II
Type and Concentration of Plasticizers

Plasticizer type	Abbreviation	% (based on PVC wt)			
Di(2-ethylhexyl phthalate)	DOP	6.00	12.20	18.1	23.8
Di(2-ethylhexyl adipate)	DOA	6.00	12.00	18.1	24.1
Tritolyl phosphate	TTP	6.00	12.22	18.1	24.0
Polypropylene adipate (Hexaplas PPA)	Hex	6.00	12.00	18.1	24.1

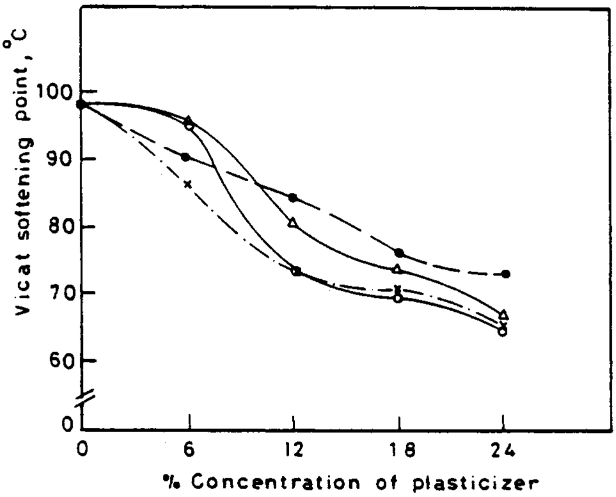

Fig. 1. Vicat softening point vs. % concentration of plasticizer: (O) DOP; (△) DOA; (×---×) TTP; (●---●) Hex.

Hardness

The shore D hardness of the unplasticized and plasticized PVC with various concentration and type of plasticizers is shown in Figure 2. It is clear that: The shore D hardness for the PVC plasticized by TTP and Hex are nearly constant, irrespective of the plasticizers concentration; the shore D hardnesses for PVC plasticized by DOP or DOA are nearly constant until 12%, and then start to decrease with increase in concentration.

Flexural Properties

The flexural yield strengths and flexural modulus of the various plasticized PVC compounds are given in Figures 3 and 4. The ultimate flexural strength of the materials was not measured as the specimens had failure strains greater than 5%.

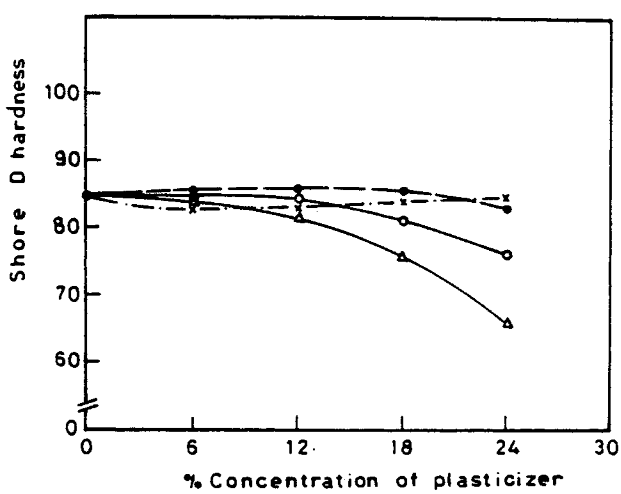

Fig. 2. Shore D hardness vs. % concentration of plasticizer: (O) DOP; (△) DOA; (×---×) TTP; (●---●) Hex.

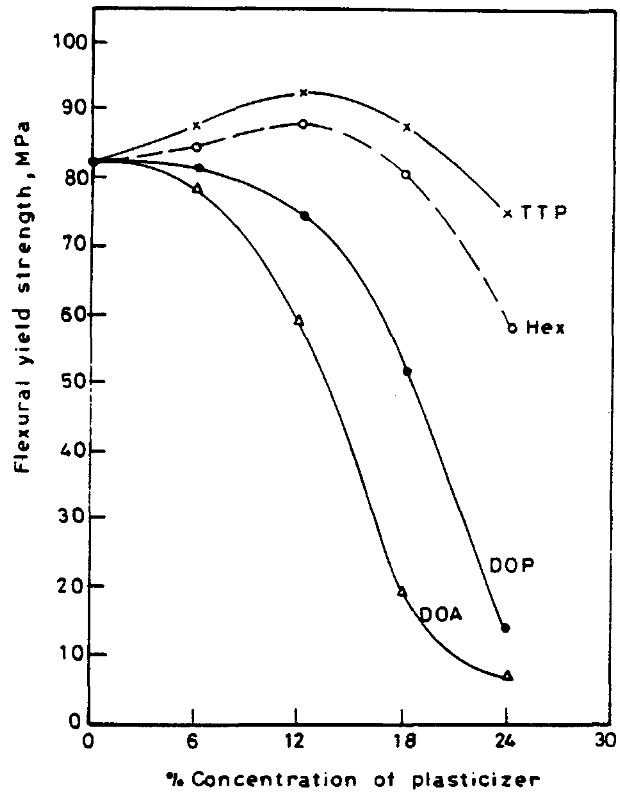

Fig. 3. Flexural yield strength vs. % concentration of plasticizer.

From Figure 3 it is clearly seen that: At all concentrations of plasticizer the flexural yield strength increases as we go in order from DOA to DOP to Hex to TTP, and the difference is small below 6% and increases with increase in concentration; with DOP and DOA the flexural yield strength decreases continuously with increase in concentration, but with TTP Hex it increases with increase in plasticizer concentration up to 12% and then decreases.

From Figure 4 it is clear that: At any concentration of plasticizer, the flexural modulus increases in order from DOA to DOP to Hex to TTP, and the difference is small below 6% and increases with increase in concentration; with DOP and DOA there is a slight increase in flexural modulus with increase in concentration to 6%, and then it decreases with further increase in concentration to 24% and 20% of DOP and DOA, respectively; above a concentration of 20% DOA it remains almost constant; in Hex and TTP the flexural modulus increases to 8% and 12% concentrations, respectively, and then it decreases with further increase in plasticizer concentration.

Four-Point Bending Dynamic Fatigue

Rectangular samples were prepared with dimensions of approximately 130 × 12 × 6 mm. It was found necessary to drill a hole in the middle of the specimen to introduce stress concentration to prevent failure at the specimen loading clamps. The hole diameter was 1.59 mm, which introduces a stress concentration of 2.5.[1]

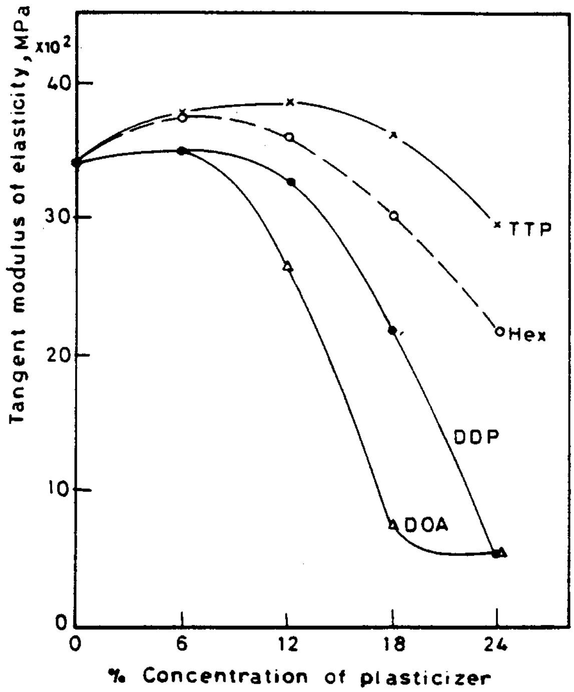

Fig. 4. Tangent modulus of elasticity vs. % concentration of plasticizer.

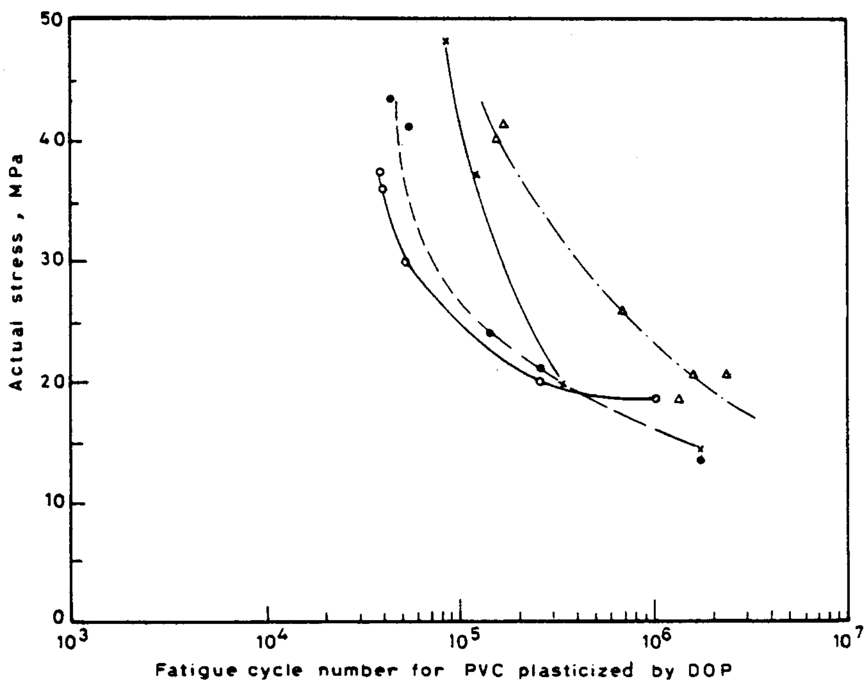

Fig. 5. Actual stress against fatigue cycles number for PVC plasticized by DOP.

Figure 5 shows the fatigue performance of the various DOP compositions. It is clearly seen that:

1. At a given level of concentration of DOP, as the applied stress decreases, the number of cycles to failure increases.

2. At stress levels above 20 MPa, the fatigue life is reduced as the concentration of plasticizers increases. Below 20 MPa, however, increasing plasticizers leads to an increase in fatigue life at a given stress level.

CONCLUSIONS

From this study of the effect of type and concentration of plasticizer on some physical and mechanical properties of poly(vinyl chloride), the following conclusions may be drawn:

1. The Vicat softening point, shore D hardness, flexural yield strength, and flexural modulus decrease with increase in plasticizer concentration, though in some cases a threshold concentration must be passed before these effects can be observed.

2. Close similarities are always found in the behavior of DOP and DOA; this may be due to the fact that they are both esters of the same long chain alcohol. There are also close similarities in the effects of TTP and Hex.

3. In the study of the flexural fatigue properties of poly(vinyl chloride) plasticized by DOP, it was found that an increase in plasticizer concentration led to a decrease in load bearing ability only at stress levels above 20 MPa.

References

1. R. E. Peterson, *Stress Concentration Factors*, Wiley, New York, 1974.

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