

# Effect of Plasticizers on Mechanical, Electrical, Permanence, and Thermal Properties of Poly(vinyl chloride)

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**ABSTRACT:** Effects of three different plasticizers and their blends with dioctyl phthalate (DOP) on thermal stability, flammability, mechanical, electrical, and permanence properties of poly(vinyl chloride) (PVC) compound were studied. Various plasticizers used were DOP, butyl benzyl phthalate (BBP), isodecyl diphenyl phosphate (IDDP), and polybutylene adipate (PBA) at concentrations of up to 40 phr level. Studies showed that processability and softness were

improved by addition of BBP. An increase in the content of IDDP increased the electrical and flammability properties, whereas compositions with PBA exhibited the best permanence properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3278–3284, 2003

**Key words:** poly(vinyl chloride) (PVC); plasticizers; mechanical properties; thermal properties; permanence

## INTRODUCTION

Poly(vinyl chloride) (PVC), the second most widely consumed plastic material worldwide, is used in many demanding applications such as cable and wire jacketing, automotive, building and construction, and packaging, to cite just a few. A great number of additives can be compounded with PVC to give desired product properties ranging from flexible to rigid and translucent to opaque.

The use of plasticizers beyond the threshold limit of polymer results in increased softness. Plasticizers reduce the modulus as it weakens the bond holding the polymer molecules together, but it also facilitates processing. The effect of plasticizers on mechanical and electrical properties of PVC has been the focus of many investigations.<sup>1–9</sup>

Plasticizers improve processability by lowering the melting and softening points and viscosity of the melts. Plasticizers of high compatibility and solvency produce the fastest fusion during processing, thus shortening production cycles.<sup>10–12</sup> Ramos-de Valle and Gilbert<sup>11</sup> investigated the PVC/plasticizer compatibility on a Brabender Plasticorder. Xu and Guo<sup>12</sup> used the low molecular weight PVC prepared by vibromilling on PVC as the plasticizer of PVC and demonstrated that low molecular weight PVC greatly improved the processability, permanence, and mechani-

cal properties of PVC. It is obviously desirable that once the plasticizer is compounded with the PVC resin it should be permanently retained. Because plasticizers are not bound chemically to the polymer there is loss of plasticizer, to some extent, resulting from extraction and migration. Several researchers<sup>12–15</sup> have tried different methods to increase the extraction and migration resistance of plasticized PVC compounds.

Annakutty and Kishore<sup>16</sup> demonstrated that polyphosphate esters constitute efficient polymeric flame-retardant plasticizers for PVC in that they suppressed both combustion and ignition of polymer. They also showed that polymers are superior to non-polymeric additives in flame retarding the PVC. Minsker et al.<sup>17</sup> observed that the rate of PVC degradation increased with the use of alkyl and aryl-alkyl type plasticizers. On the contrary, Kovacic et al.<sup>18</sup> obtained results very different from those of Minsker. Djidjelli and coworkers<sup>19</sup> studied the effect of phosphate plasticizer (DIDP), DOP, and their mixture on the electrical properties of PVC compounds. It was concluded that electrical properties were dependent on the type and content of plasticizer and that the use of a plasticizer blend induces a synergetic effect.

Various investigators have studied different aspects of the effects of plasticizers on PVC, although various conflicting results were also observed. Migration and extraction of plasticizer mixtures were rarely studied. Moreover, the effect of blends of plasticizers on various properties of PVC remains to be extensively studied. Hence, the present investigation deals with the effects of three different plasticizers and their blends with dioctyl phthalate (DOP) on mechanical, electrical, thermal, and permanence (extraction and migration)

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TABLE I  
Formulation of PVC with DOP, IDDP, BBP, and PBA Plasticizers

Material (phr)	Sample notation												
	D <sub>4</sub>	I <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	I <sub>4</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100
TBLS	3	3	3	3	3	3	3	3	3	3	3	3	3
DBLS	2	2	2	2	2	2	2	2	2	2	2	2	2
DOP	40	30	20	10	—	30	20	10	—	30	20	10	—
IDDP	—	10	20	30	40	—	—	—	—	—	—	—	—
BBP	—	—	—	—	—	10	20	30	40	—	—	—	—
PBA	—	—	—	—	—	—	—	—	—	10	20	30	40

properties of PVC compounds. The effect on the stability of PVC was also investigated. All the results are compared with the PVC plasticized with DOP.

## EXPERIMENTAL

### Materials and formulations

PVC, suspension-grade resin (Reon 6711, K-67, from Reliance Industries Ltd., India) was used in this investigation. Types of plasticizers used were as follows: di(2-ethylhexyl phthalate) (DOP; procured from local market), butyl benzyl phthalate (BBP; Santicizer 160, from Solutia, USA), isodecyl diphenyl phosphate (IDDP; Santicizer 148, from Solutia), and poly(butylene adipate) (PBA,  $M_n = 1200$ ; Santicizer 409A, polymeric plasticizer, from Solutia). Tribasic lead sulfate (TBLS) was used as a stabilizer and dibasic lead stearate (DBLS) (Fine Organics, India) was used as a secondary stabilizer/lubricant to TBLS (Fine Organics, India).

Table I shows the formulation of PVC with various plasticizers. The total plasticizer concentration was kept constant at 40 phr, whereas the concentration of DOP was varied from 40 to 0 phr.

### Processing

PVC, TBLS, DBLS, and plasticizer(s) were added according to the required concentrations and mixed thoroughly in a dry blender for 10 min at 80°C to obtain a compounded powder. The mixed powder was then processed in a Haake Rheocord 9000 (Bersdorff, Germany), using a Rheomix 600 batch mixer at 170°C and 70 rpm for 10 min. The batch mixed compound was molded into 2-mm-thick sheets by compression molding at 180°C and 150 kg/cm<sup>2</sup> pressure. The sheets were cut to desired test-specimen size for further testing. At least 10 specimens were prepared for each test and the average of 10 readings was taken.

### Testing

#### Mechanical properties

The ultimate tensile strength, Young's modulus, and percentage elongation at break were determined ac-

ording to ASTM D-638-58T using a Lloyd LR50K computerized machine with a 5-kN load cell and at test speed of 50 mm/min.

#### Electrical properties

The dielectric strength was determined by using a Zaran (India) apparatus according to ASTM D-149.

The volume resistivity was determined according to ASTM D-257 by using a high-resistance meter (Model No. 4339B; Agilent Technologies).

#### Permanence properties

Migration resistance was determined by placing a plasticized PVC disc of 50 mm diameter in a jar between two 30-mL layers of finely divided silica. The jar was placed at a constant room temperature for 1 to 7 days. After the specific period, discs were removed from jar and cleaned, after which the percentage plasticizer loss was calculated.

Extraction resistance was determined according to ASTM D-1239-92. The test was carried out in petrol and kerosene at room temperature for 24 h.

#### Thermogravimetric analysis (TGA)

Thermal stability was determined by using a Perkin-Elmer TGA-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The experiment was performed under N<sub>2</sub> atmosphere up to the final temperature of 600°C and at scanning rate of 10°C/min.

## RESULTS AND DISCUSSION

### Processability

To compare the processing characteristics of different plasticizers, equilibrium (final) torque and final melt temperature values after 10 min are plotted in Figures 1 and 2, respectively, as a function of DOP content. There is no significant difference in torque and temperature of compositions with 40 and 30 phr DOP, but with a further decrease in DOP content or with an increase in PBA and IDDP content the torque and

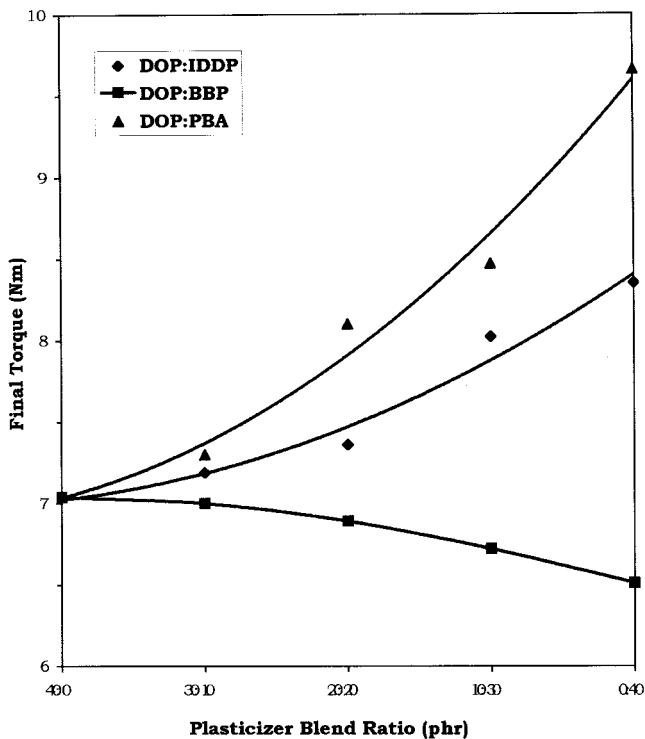


Figure 1 Effect on final torque with decrease in content of DOP.

temperature increases, indicating an increase in shear stress during processing, a result of the increase in viscosity of the molten compound. This may be attrib-

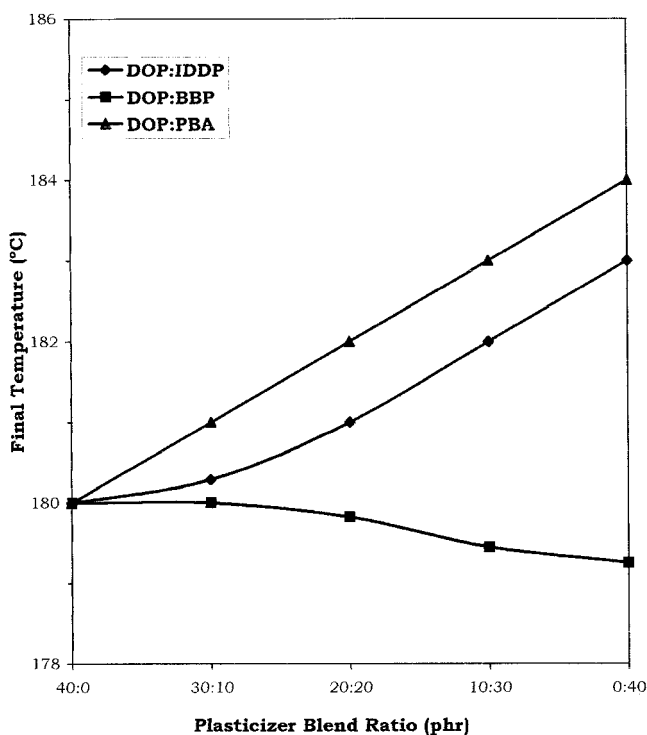


Figure 2 Effect on final melt temperature with decrease in content of DOP.

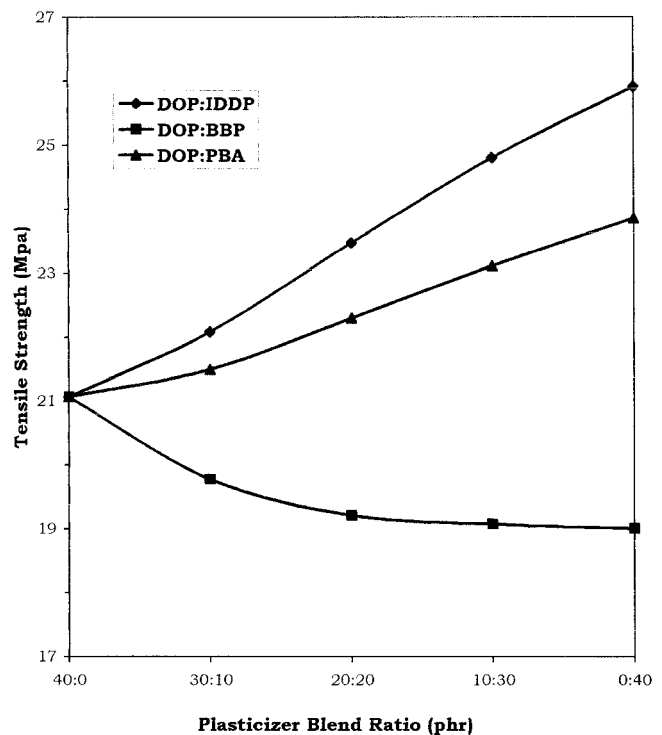


Figure 3 Effect on tensile strength with decrease in content of DOP.

uted to the significantly higher viscosity of PBA (2220 cP) and IDDP (570 cP) plasticizers than that of DOP (80 cP). The highest torque was shown by compositions containing 40 phr PBA because of its high viscosity. With an increase in BBP content, however, equilibrium torque and temperature decrease as a result of the decrease in viscosity. This may be a consequence of the high efficiency and low viscosity (75 cP) of BBP.

### Mechanical properties

Figures 3 and 4 show the effect of plasticizer composition on tensile strength and % elongation at break of PVC compound, respectively. The tensile strength increases gradually with the increase in content of IDDP and PBA, whereas the % elongation at break decreases with an increase in content of IDDP and PBA plasticizers. The compound with 40 phr IDDP gives the highest tensile strength. The increase in tensile strength and decrease in % elongation at break with IDDP plasticizer is attributed to the increased polarity of the plasticizer, which increases the cohesive energy density (intensity of intermolecular attractions), such that with a higher polarity, materials tend to hold themselves together more tightly. As a result the chain mobility and thus the flexibility of the compound are reduced, although the increase in tensile strength and decrease in % elongation at break with PBA plasticizer

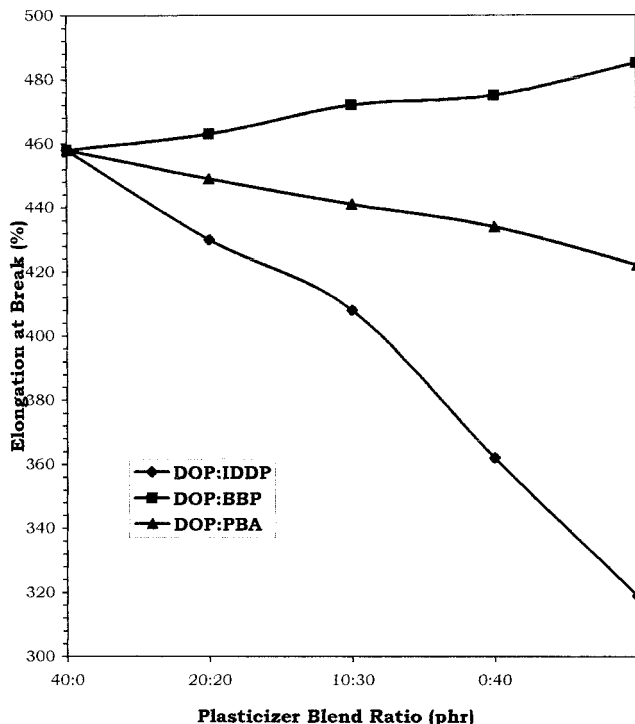


Figure 4 Effect on elongation at break with decrease in content of DOP.

may be attributed to its high molecular weight and viscosity. Reduction in tensile strength and increase in % elongation at break with an increase in BBP content possibly result from the low molecular weight and high plasticization efficiency compared to those of other plasticizers, which allows facile sliding of polymer chains past each other. Hence, the compound with 40 phr BBP gives the lowest tensile strength and high % elongation at break.

**Electrical properties**

The effect of decrease in DOP content on dielectric strength is shown in Figure 5. As the DOP content is decreased the dielectric strength gradually increases. The highest dielectric strength was given by samples plasticized with IDDP plasticizer. This characteristic of IDDP is useful in wire and cable coating applications apart from its flame retardancy. BBP gives the lowest dielectric strength because it not only lowers viscosity and the glass-transition temperature ( $T_g$ ) but also increases the mobility of ions.

The volume resistivity is the measure of conductivity of the compound. The effect on volume resistivity of plasticizers and filler in PVC is shown in Figure 6. The volume resistivity increases with an increase in IDDP content and decreases with increases in the contents of PBA and BBP. The increase in conductivity

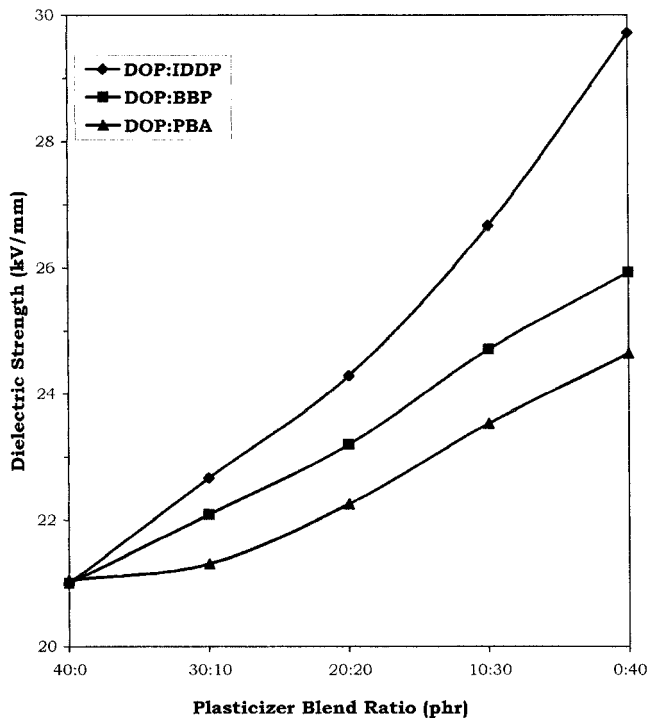


Figure 5 Effect on dielectric strength with decrease in content of DOP.

with increase in content of BBP is perhaps attributable to its high plasticizing efficiency, which facilitates the mobility of ions. The increase in conductivity by PBA

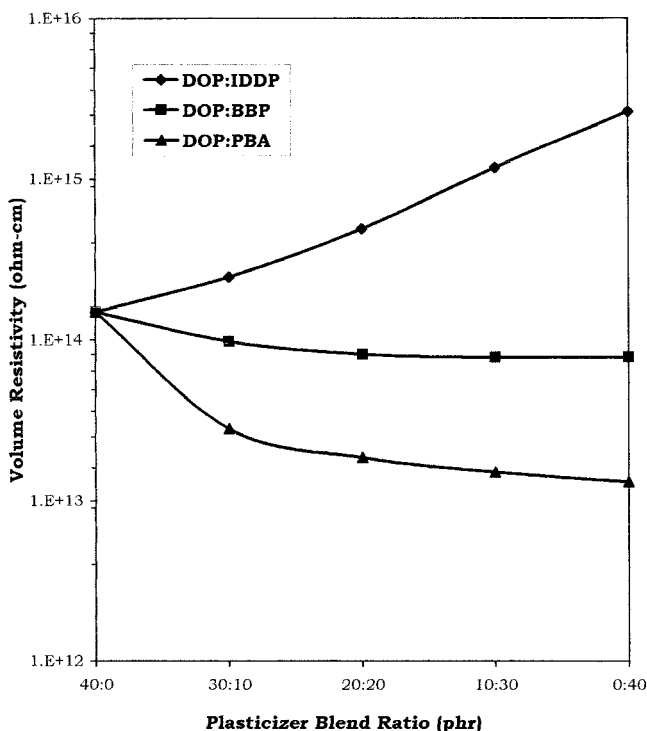
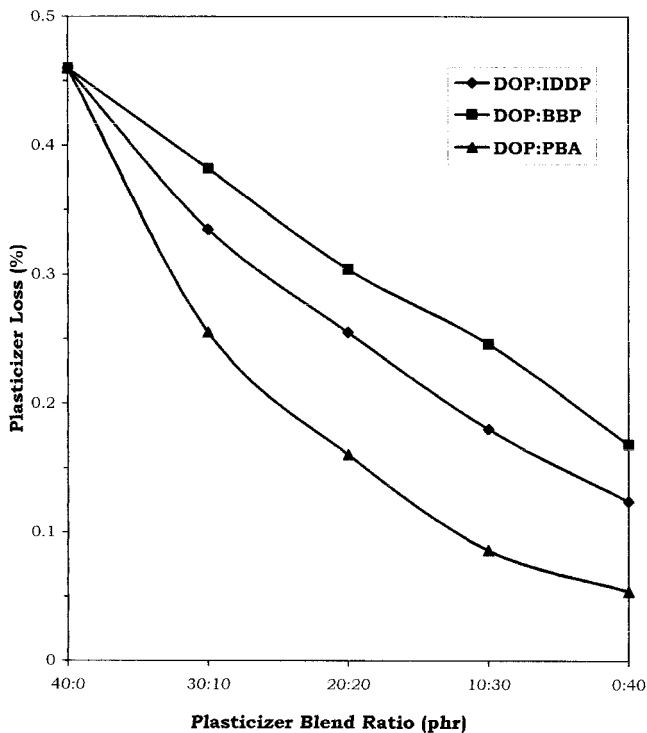


Figure 6 Effect on volume resistivity with decrease in content of DOP.



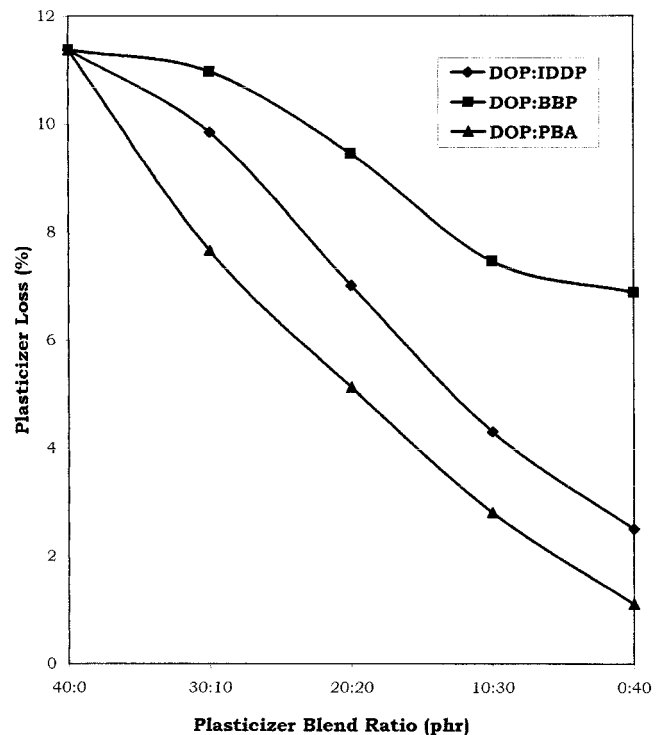
**Figure 7** Effect on migration resistance with decrease in content of DOP.

may be attributed to some ionizable impurities (e.g., catalyst residue) present in the plasticizer.

### Permanence properties

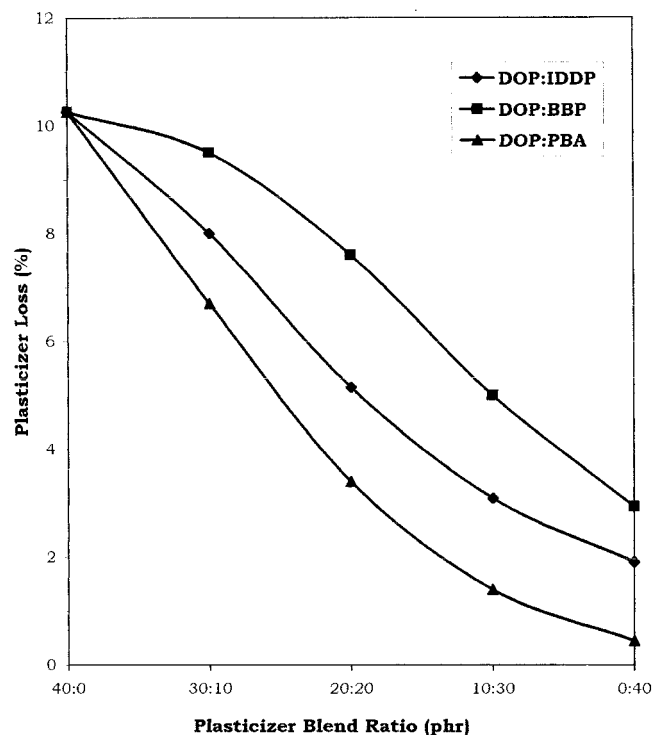
Figure 7 shows the % plasticizer loss after 7 days by migration to silica gel with respect to plasticizer composition. The loss of plasticizer decreases as the DOP is replaced by BBP, IDDP, and PBA. Plasticizer loss is highest in DOP followed by BBP, IDDP, and PBA. The high migration resistance in PBA is attributed to its high molecular weight compared with that of other plasticizers, which reduces the migration of plasticizer on the surface.

Extraction is strictly a process in which the liquid is introduced into the PVC and draws out the plasticizer. The effect of petrol as an extractant on the extraction resistance of a plasticized PVC sample with respect to decrease in content of DOP is shown in Figure 8. As the DOP was replaced with BBP, IDDP, and PBA, the extraction resistance continues to gradually rise; the polymeric plasticizer PBA gives maximum extraction resistance followed by IDDP and BBP. The good extraction resistance with PBA is attributed to its high molecular weight compared to that of other monomeric plasticizers. The increase in extraction resistance by BBP compared to DOP is mainly because of its higher compatibility with PVC resin. Although for



**Figure 8** Effect on extraction resistance with decrease in content of DOP (petrol extractant).

IDDP polarity plays a role against the DOP in increasing its extraction resistance, increased polarity leads to an increase in compatibility with PVC.



**Figure 9** Effect on extraction resistance with decrease in content of DOP (kerosene extractant).

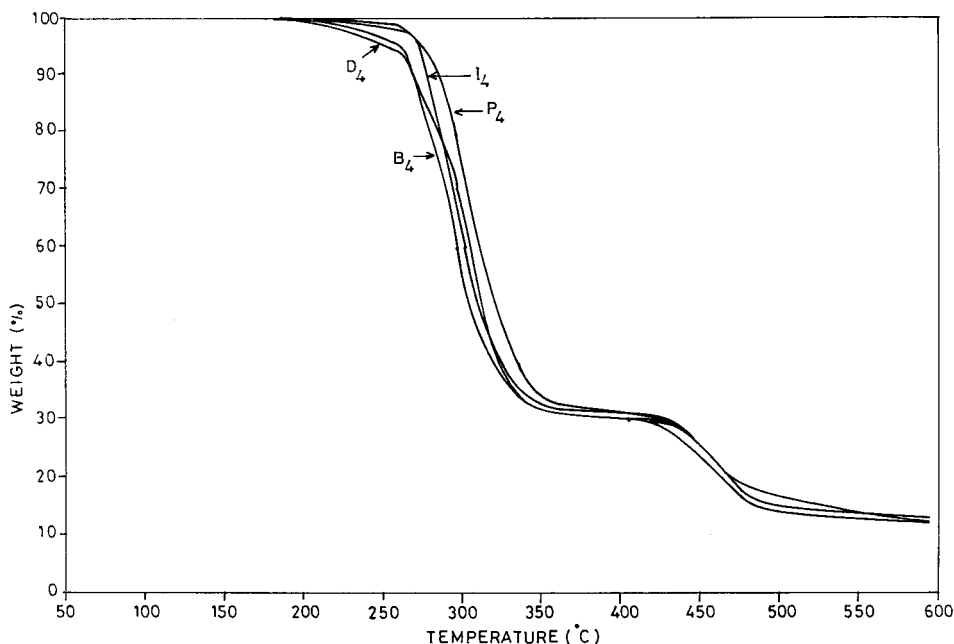


Figure 10 Thermograms of different samples as a function of type of plasticizer.

Figure 9 shows the effect on extraction resistance by change in type and ratio of plasticizer with kerosene as an extractant. With petrol as an extractant, trends similar to those of extraction resistance were observed. The samples with PBA are the most resistant to extraction followed by IDDP and BBP.

#### Thermogravimetric analysis

Figure 10 illustrates the effect of plasticizer type on the sample mass loss. The curves have similar shape for all formulations and each one presents two distinct stability stages. Mass loss starts at 210–220°C and accelerates sharply at 270°C. Upon heating over 500°C, the remaining residue stays more or less stable.

The first stage corresponds to the plasticizer migration and the step-by step elimination of HCl with some benzene traces. The second stage corresponds to formation of conjugated unsaturation that results from elimination of HCl from adjacent carbon atoms; this resembles polyacetylene structure that gradually reticulates and become more stable than PVC.<sup>1</sup> From 400°C, a mass loss is observed and is attributed to the polyacetylene cracking.

The polymeric plasticizer shows the highest onset temperature, subsequently followed by IDDP, DOP, and BBP. This result is attributed to the difference in fire point of the plasticizers, with PBA having the highest followed by the order of stability. The plasticizer with high polarity surrounds the PVC molecule such that the electrons in the polymer are shared to some extent with the plasticizer. This pulls on and weakens the C—H and C—Cl bonds, with

the result that they can dissociate at relatively lower temperatures and recombine as HCl and  $-C=C-$ . Therefore the more polar the plasticizer, the less

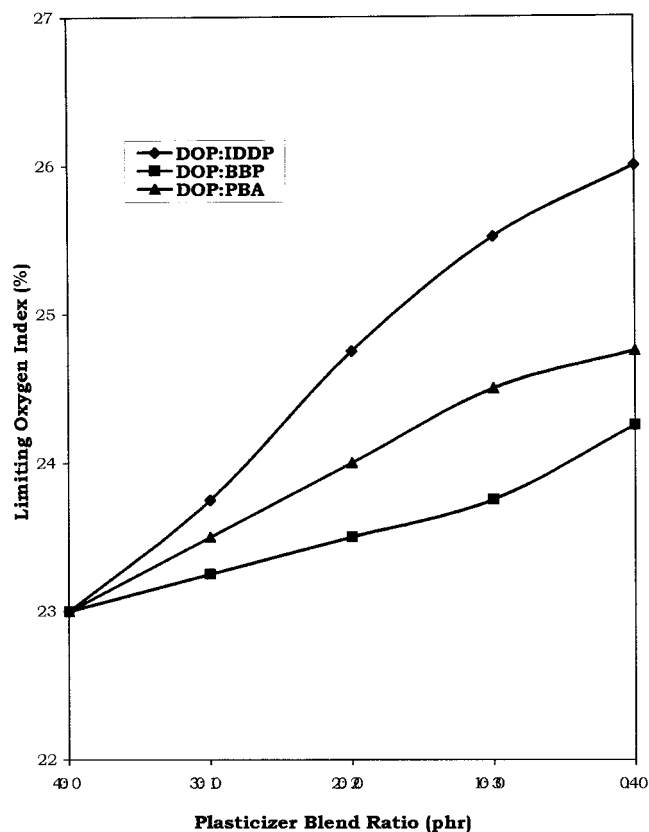


Figure 11 Effect on limiting oxygen index with increase in content of IDDP.

stable the PVC will be in its presence. That is why the onset temperature of the sample with IDDP plasticizer is higher than that of than DOP but its rate of mass loss (degradation) is also higher than that of DOP.

#### Flammability (limiting oxygen index)

Figure 11 shows the effect on limiting oxygen index (LOI) with decreasing content of DOP. The highest LOI is shown by sample I<sub>4</sub>, whereas the lowest is shown by D<sub>4</sub>. As the content of DOP is decreased with the increase in content of IDDP, PBA, and BBP, the percentage oxygen required to burn the compound is also increased. The high LOI shown by the samples with IDDP is attributed to its content of phosphate, which is a flame retardant.

#### CONCLUSIONS

From the preceding results it can be concluded that the processability of plasticized PVC compound is improved by butyl benzyl phthalate, which also reduces the fusion time. BBP also increases the elongation at break and softness. This is attributed to the high plasticizer efficiency and low viscosity of BBP. The best mechanical and electrical properties, and flammability are given by the compound plasticized by IDDP because of its compatibility with PVC and its phosphate content. PBA gives the best migration and extraction resistance. It also increases the onset degradation temperature of the PVC compound. This is probably because of its high molecular weight, the

highest among all plasticizers. It can thus be concluded that properties of plasticized PVC compound are dependent on plasticizer type, content, and molecular weight.

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