

Dialkyl Phthalate Plasticizers

Efficiency vs. Molecular Weight and Architecture

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The solubility of a plasticizer in a polymer is governed by thermodynamic considerations well documented by numerous researchers.^{1,2,3} The effect of plasticizers on dynamic properties is less widely known. This paper tries to gain a better understanding of the dynamic mechanical properties as influenced by differences in plasticizer molecular weight and structure.

The majority of plasticizers used for polar elastomers are organic carboxylic acid esters. Among this category are dialkyl o-phthalate esters, a reaction product of a difunctional phthalic acid, and an alcohol. These plasticizers are available in both increasing molecular weight (see Fig. 2) and equivalent molecular weight (see Fig. 3). Seven plasticizers utilizing the alcohols listed in Table I were equivalently compounded at a thirty part (phr)

level in the model formula, Table II. Conventional static and the latest in dynamic testing were performed to delineate effects of increasing and equivalent molecular weights.

Experimental

The polar nature of o-phthalate ester plasticizers is imparted by the -COO- group identified in Figure 1. The increasing size of the nonpolar "R" group is a function of the specific alcohol utilized for the reaction. Since plasticization is predicated on thermodynamic miscibility phenomena, the solubility parameter for each plasticizer was calculated theoretically. Molar volumes were calculated using Fedors' group contribution technique." Because of the polar nature of the molecule, Van Krevelen's approach' was utilized in order to calculate the dispersion forces (δ_d), dipole forces (δ_p), and the H-bonding forces (δ_h), summarized in Table III.

The alcohols in the esterification reaction reduce to nonpolar alkyls rather

than polar alkoxy groups, as the alcohol -OH group condenses with the phthalic acid -H to give H₂O as a byproduct. Thus, the decreasing solubility parameter value δ is apparent as the molecular weight of the alcohol increases, indicating the molecule is becoming less polar. The fugitive nature of o-phthalate esters needs no further elaboration so the test conditions considered were relatively mild, i.e.: 70 hrs. at 100°C. These aging conditions were expected to show trends toward increasing volatility and extractability, which they did. The dynamic mechanical analysis was expected to develop the relevance of possible relationships between plasticizers of increasing and equivalent molecular weights.

Dynamic Mechanical Analysis

The DuPont 982 Dynamic Mechanical Analyzer⁶ works on the principle of a forced, resonant vibratory motion with a preselected fixed amplitude. The instrument senses the natural frequency (Ω_f), and supplies additional energy to compensate for the inherent elastomeric damping property.

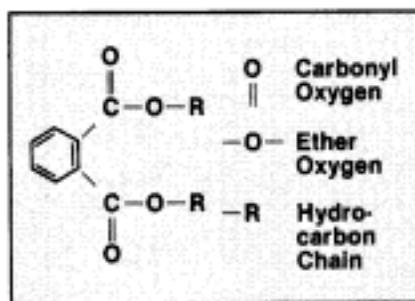


Fig. 1 — Model o-Phthalate Ester.

Generic Name	Structure	mw
DMP		194
DEP		222
DBP		278
DNOP		390

Fig. 2 — o-Phthalate Esters-Increasing Molecular Weight.

The frequency of oscillation is related to the modulus of the sample being tested. The low shear strain amplitude, approximately 0.1 percent at room temperature, gives a higher "apparent" modulus than what is typically reported using more conventional test procedures such as ASTM D1043 and 1053⁷. Similarly, the higher T_g values are what would be expected based on deformation (frequency) rate.⁸

The typical stress-strain cycle idealized in Fig. 4 is reported by the DMA instrument over a temperature range of -120°C to +20°C. The elastic stress, E' (tensile storage modulus), is in phase with the strain, the result of the individual rotational energy barriers in the polymer chain. The viscous stress, E'' (tensile loss modulus), is ninety degrees out of phase with the elastic stress, as viscous resistance depends on rate of deformation. This resistance is maximum when the strain is increasing most rapidly. The amplitude of the viscous stress cycle is related to the monomeric friction component. The total stress, E^* (complex dynamic tensile modulus), has an amplitude, A_f , equivalent to $(A_1^2 + A_2^2)^{1/2}$. The displacement between total stress E^* and elastic stress E' is the mechanical loss angle δ . $\tan \delta$ is the loss factor (A_2/A_1) and is an indication of the damping ability. We assumed $\tan \delta$ might be influenced by molecular weight and molecular architecture.

Original Properties

There were no dramatic original physical properties variations as indicated

Alcohol	Class	Carbons		mp (°C)	bp (°C)	mw
		Total	Chain			
Methanol	Primary	1	1	-97	64.5	32
Ethanol	Primary	2	2	-115	78.3	46
1-Butanol	Primary	4	4	-90	118	74
1-Octanol	Primary	8	8	-15	195	130
2-Ethyl-1 Hexanol	Primary (Branched)	8	6	-70	184	130
Isooctanol	Primary (Branched)	8	6	-95		130
2-Octanol	Secondary	8	7	-39	179	130

in Table IV. DIOP had both high elongation and the highest tensile stress values at 100, 200 and 300 percent extension. DBP showed evidence of being most soluble as indicated by lowest tensile strength and tensile stress at 100 percent.

Aging-Air, 70 Hrs. @ 100°C. - The air aging program was of sufficient duration to indicate trends of weight loss (see Table IV). Increasing molecular weight predictably shows decreasing weight loss. The data-point for DBP of -1.6 percent appears to be out of place and should be verified. Durometer change for DOP (+1) is surprisingly low compared to other equivalent weight plasticizers (+6 to +8).

Aging-Oil, 70 Hrs. @ 100°C. - The powerful extraction effect of ASTM #1 is also well illustrated in Table IV. The increasing negative volume change for increasing molecular weight is due to the increasing thermodynamic solubility of the nonpolar ASTM #1 oil with the longer nonpolar alkyl groups (see Fig. 3 and Table III). The methyl, ethyl and butyl o-phthalate esters have greater

polar δ_p , and δ_h components, Table III, indicating lesser solubility in the nonpolar ASTM #1 oil.

Dynamic Mechanical Analysis

Tensile Storage Modulus (E') or elastic stress for each of the seven samples is shown superimposed in Fig. 5. Fig. 5 is of interest because it grossly illustrates the variation of the glassy modulus strength. The increasing molecular weight series of plasticizers (see Fig. 2) have the highest (DEP) and lowest (DBP) E' values. For equivalent molecular weight plasticizers (see Fig. 3), which fall within the DBP-DEP limits, DOP is low and DIOP is high with a relatively narrow spread between. Assuming an interest of rubberlike properties, usable data would begin to occur at -40°C.

Tensile Loss Modulus (E'') or viscous stress is similarly displayed superimposed in Fig. 6. This is of interest since it illustrates alpha- α , beta- β , and gamma- γ transitions. Historically, glass transition temperature (T_g) has been mechanically (see Table VI) derived

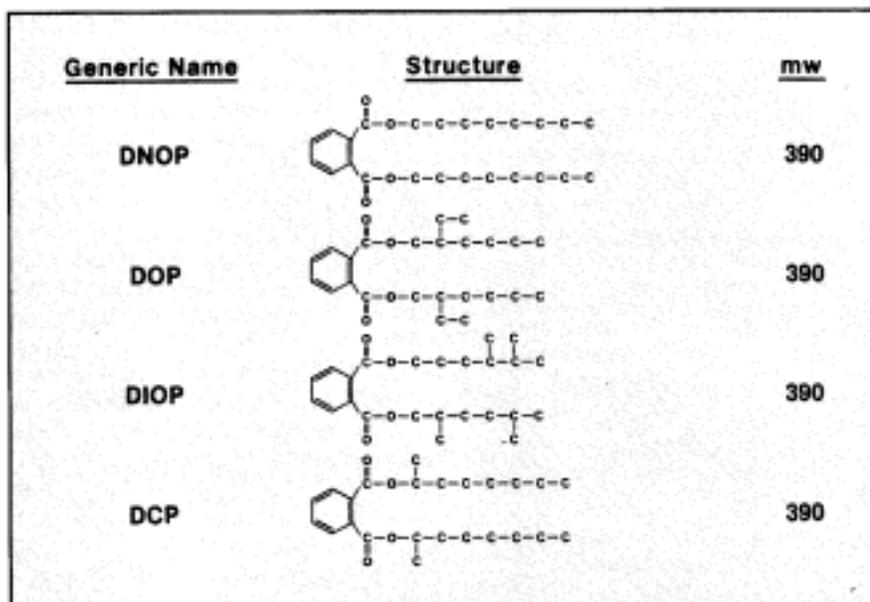


Fig. 3 — o-Phthalate Esters-Equivalent Molecular Weight.

	PHP	Wt. %
Nitrile Rubber-34% ACN(1)	100.0	46.4
Sulfur	1.5	0.7
MBTS	1.5	0.7
Zinc Oxide	5.0	2.3
Stearic Acid	1.0	0.5
Agerite Stalite-S(2)	1.5	0.7
N550 Black	75.0	34.8
Plasticizer	30.0	13.9
	215.5	100.0%

(1) Polysar Krynac 34.80
(2) R.T. Vanderbilt

Cure Conditions: 15' @ 330° (test specimens)
30' @ 330° (DMA specimens)

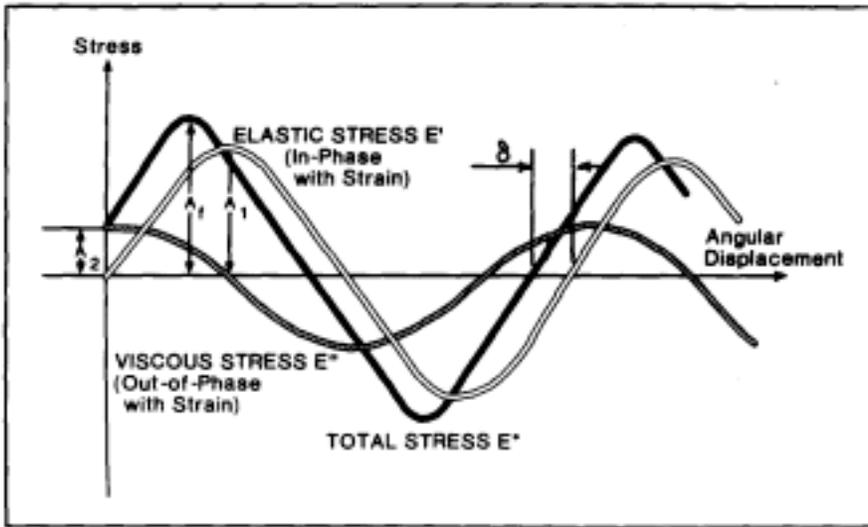


Fig. 4 — Stress vs. Sinusoidal Strain.

from $\tan \delta$ values. Heijboer⁹ points out α -transitions (in most cases, T_g) are main chain segmental motions. At T_g , it is assumed that main polymer chains are sufficiently confined due to reduced space considerations so that glassy fracture failure can occur. As previously noted, the α -transitions are the resultant of major segments of the polymer

chain being frozen in. Heijboer notes two additional motions occurring with polymers below their T_g : Local main-chain motion and side group motion with some cooperation of the main chain. In Fig. 6 increasing molecular weight plasticizers, DMP, DEP and DBP, have α -transitions only. Equivalent molecular plasticizers have a different response.

The
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Table III o-Phthalate Esters Solubility Parameters (SP) δ
 $\delta(\text{SP}) = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$

	DMP	DEP	DBP	DNOP	DOP	DIOP	DCP
δ_d^1	18.6	18.3	17.9	17.5	17.3	17.0	17.3
δ_p^2	8.4	5.3	3.9	2.8	2.8	2.6	2.6
δ_h^3	9.5	8.6	7.5	6.1	6.1	6.1	6.1
δ^4	21.8	20.9	19.8	18.7	18.5	18.3	18.5

¹Dispersion Forces
²Dipole Forces
³H-Bonding Forces
⁴J²/cm³

Table IV Physical Properties

	DMP	DEP	DBP	DNOP	DOP	DIOP	DCP
Main Chain Carbons	1	2	4	8	6	6	7
Original Properties:							
Durometer-Shore A	65/62	65/62	63/60	60/57	66/63	63/60	63/60
Tensile (MPa)	15.17	15.17	13.79	14.48	16.55	15.17	14.48
Elongation (%)	475	490	550	600	550	600	580
M-100	2.38	2.21	1.84	2.02	2.54	5.26	2.21
M-200	8.35	8.26	5.33	4.97	6.35	10.17	4.97
M-300	10.52	10.30	8.46	7.91	10.71	14.52	8.46
Air Aged: 70 hrs. @ 100°C							
Durometer Change	+5	+5	+5	+8	+1	+8	+6
Tensile Change (%)	+17	+7	+20	+12	+2	+16	+14
Elongation Change (%)	-33	-35	-36	-42	-36	-42	-40
Weight Loss (%)	-3.2	-0.7	-1.6	-0.2	-0.26	-0.14	-0.08
Oil Aged: 70 hrs. @ 100°C							
ASTM #1							
Durometer Change	+9	+10	+11	+16	+13	+10	+15
Tensile Change (%)	+11	+16	+28	+26	+8	+20	+29
Elongation Change (%)	-21	-22	-27	-25	-18	-25	-22
Volume Change (%)	-8.6	-9.9	-11.7	-14.7	-15.4	-13.4	-15.2

DNOP and DCP show strong β -transitions at -120 and -75°C respectively. DIOP shows both a β -transition at -40° and a γ -transition at -88°C. DOP has only an α -transition at -19°C. The low E'' values at 20°C indicate high resiliency (low damping) of all seven plasticizers at this temperature.

Transitions α, β & γ . The very interesting pattern of low temperature transitions in E'' , Fig. 6, is worthy of additional investigation. DMP, DEP, DBP and DOP do not exhibit β or γ transitions. This could be easily rationalized in terms of thermodynamic solubility for DMP, DEP and DBP ("R" equivalent to C_1, C_2 and C_4 chains). DOP, however, is a C_6 chain along with DIOP, which has both a β and γ transition temperature. Sperati and coworkers¹⁰ point out that polyethylene properties are controlled by short chain and long chain branching. Their work notes that an ethyl (C_2) branch interrupts main chain crystallization for about 6-8 carbons on either side of the ethyl branch. A methyl (C_1) group (DIOP has 2) is not as effective as ethyl. The β and γ transitions could easily be a manifestation of Heijboer's description of β and γ transitions noted earlier. This would be in agreement with Matsuoka and Kwei's descriptions¹¹ for the same event.

DNOP and DCP (C_2 and C_8 chains) appear to be another case. Apparently the longer chains are too long to be

thermodynamically soluble and are mechanically folding back on themselves, thus creating the β transitions. Alcohols referred to in Table I and Increasing MW o-Phthalate Esters, referred to in

Fig. 3 probably give the clues for these various transitions. The rationalization I leave to those more knowledgeable in field.

Complex Dynamic Modulus (E^*) or total stress has been calculated by the equation $(E' + E''^2)^{1/2}$ and is summarized over the temperature range of -120° to $+20^\circ\text{C}$ in Table V. DBP stands out with relatively flat values over the range of -10° to $+20^\circ\text{C}$.

Mechanical Loss Angle-Tan β is the ratio of lost to stored energy. Fig. 7, a superimposition of DuPont data, is revealing. At -120° , the low Tan δ values are characteristic of a typical high modulus linearly elastic solid. This is understandable by noting the E^* values (see Table V) with modulus ranging from 3.44 GPa to 5.25 GPa (500,000 to 750,000 psi). Fig. 7, along with indicating maximum damping temperature, also illustrates response to increasing temperature. DBP is the quickest to recover rubbery properties while DOP is the slowest.

Conclusions

The predictability of plasticizing events for the methyl, ethyl, and butyl o-phthalate esters has long been well known. The effects of the longer chain "R" groups are more complex due to their nonpolar aspect. This could be a critical factor in developing two-phase networks where the secondary network might be a multifunctional monomer with reactive terminal groups.

Editor's Note: For readers interested in the actual DuPont DMA data on which this paper is based, see "Practical Plasticization and Plasticizer Theory," Educational Symposium No. 10, John H.

Gifford Library & Information Center, The University of Akron, Akron, OH 44325

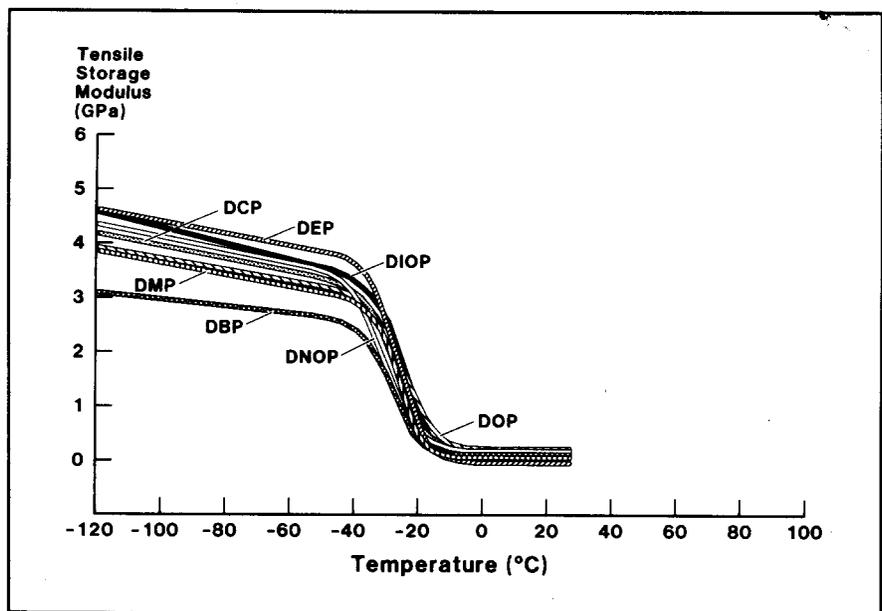


Fig. 5 — Tensile Storage Modulus (E').

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Table V Complex Dynamic Modulus- E^* , o-Phthalate Esters (MPa)

O°C	DMP	DEP	DBP	DNOP	DOP	DIOP	DCP
-120	4440	5250	3441	4523	3881	4662	4311
-110	4340	5151	3361	4402	3821	4522	4171
-100	4220	5031	3271	4311	3761	4382	4051
-90	4090	4911	3190	4201	3680	4213	3931
-80	3950	4781	3110	4101	3590	4032	3811
-70	3820	4821	3020	3981	3481	3881	3661
-60	3690	4421	2930	3841	3351	3771	3561
-50	3550	4221	2811	3671	3191	3631	3441
-40	3350	3982	2553	3303	3001	3374	3201
-30	2590	3024	1678	2234	2508	2802	2436
-20	750	1008	378	729	1268	1390	884
-10	138	157	64	154	270	254	136
0	43	42	13	41	56	61	38
+10	20	19	14	18	24	21	15
+20	19	13	13	18	14	20	14

Table VI Glass Transitions (T_g) (°C)

	E' (ref.)	Tan δ (ref.)	Differential
DMP	-22	-18	4
DEP	-22	-18	4
DBP	-23	-19	4
DNOP	-22	-18	4
DOP	-19	-10	9
DIOP	-20	-12	8
DCP	-22	-17	5
E' Transitions			
	α	β	γ
DMP	-22		
DEP	-22		
DBP	-23		
DNOP	-22	-120	
DOP	-19		
DIOP	-20	-40	-88
DCP	-22	-75	

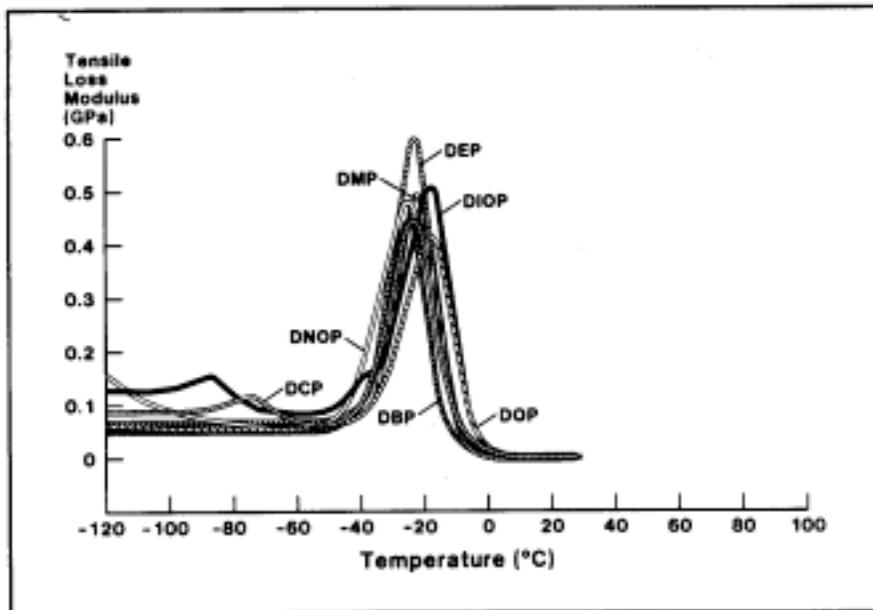


Fig. 6 — Tensile Loss Modulus (E'').

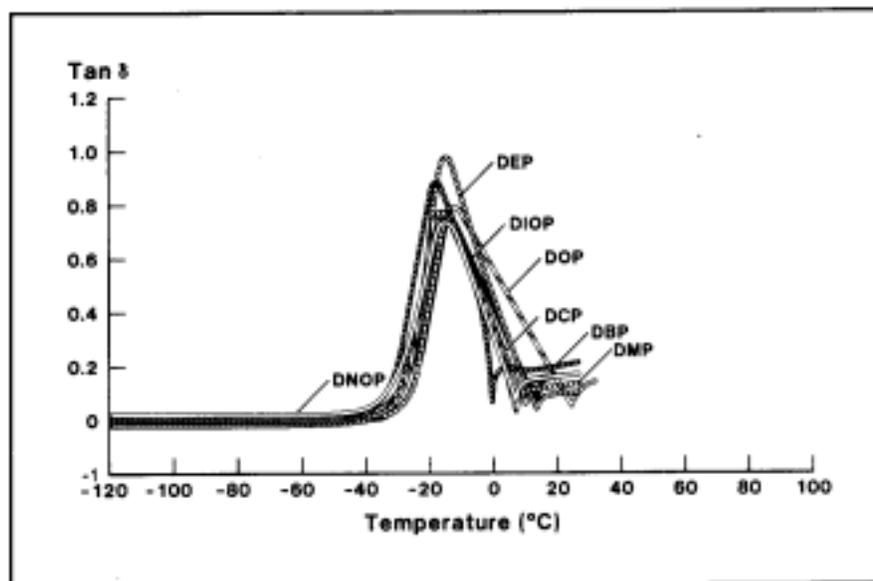


Fig. 7 — Tan δ .

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Table VII Chemical Names			
Abbreviation	Common Name	CAS No.	Source
DMP	Dimethyl Phthalate	131-11-3	Eastman Chemical Co.
DEP	Diethyl Phthalate	84-86-2	Eastman Chemical Co.
DBP	Dibutyl Phthalate	84-74-2	Eastman Chemical Co.
DNOP	Di-n-octyl Phthalate	117-84-0	C.P. Hall
DOP	Di-2-ethylhexyl Phthalate	117-81-7	Eastman Chemical Co.
DIOP	Diisooctyl Phthalate	27554-26-3	C.P. Hall
DCP	Dicapryl Phthalate	84-77-5	Union Camp