

Influences of Contents and Molecular Weights of LDPE on DOP Plasticization of PVC

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ABSTRACT: Influences of contents and molecular weights of low-density polyethylene (LDPE) on dioctyl phthalate (DOP) plasticization in the poly(vinyl chloride) (PVC) plastisol (PVC/DOP/AO = 100/30/6.5) were investigated using DMA and DSC. The plasticization effects of DOP on the PVC plastisol were found to decrease with increasing LDPE content. A negligible plasticization effect of DOP on the PVC plastisol was found when the LDPE content was equal to or higher than 75 parts per 100 parts by weight of LDPE and PVC together. Based on thermal fractionation experiments, a favorable interaction between LDPE and DOP was developed during melt blending of LDPE and the PVC plastisol. The present interaction enabled the incorporation of DOP into LDPE and decreased the plasticization effects of DOP on the PVC plastisol. A further decrease in the plasticization effects of DOP on the PVC plastisol by the presence of LDPE was found with increasing LDPE molecular weights. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2548–2555, 2002

Key words: interaction; plasticization; poly(vinyl chloride); plastisol; polyethylene; phase segregation

INTRODUCTION

Dioctyl phthalate (DOP) is commonly used as a plasticizer in poly(vinyl chloride) (PVC) processing, to reduce processing temperature and prevent PVC from thermal degradation.¹ To reduce the significant shear force that may develop during extrusion compounding, potentially causing degradation of PVC, low molecular weight polyethylene (i.e., paraffin) is often added as a lubricant in PVC processing.^{2,3} To prevent the migration of DOP to the surface of the finished PVC products at elevated temperatures, thus leading

to deterioration in mechanical properties, a high molecular weight plasticizer is sometimes used to substitute completely or partially for the low molecular weight DOP. Chlorinated polyethylene (CPE) has been reported for this purpose and for improving the impact properties of PVC.^{4–9} The compatibility between CPE and PVC is dependent on the extent of chlorination of polyethylene and determines the efficacy of plasticization of CPE in PVC. Without chlorination, polyethylene (PE) is believed to show low compatibility with PVC because of significant differences in polarity and morphology, leading to phase separation and thus low plasticization effect of PE on PVC. Thus, it is important to know the plasticization effects of DOP on PVC in the presence of PE.

In molecular composition, PE is a hydrocarbon compound that is considered to be nonpolar. DOP has two polar ester linkages that are believed not to be compatible with nonpolar PE. DOP, on the

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other hand, has two hydrocarbon tails that are considered compatible with PE because of similar polarity. Each hydrocarbon tail of DOP is 8 carbons in length and possibly leads to a melt-miscible DOP/PE blend. However, PE is a crystallizable polymer and may involve phase segregation of the amorphous DOP diluent during cooling of the DOP/PE blends. PVC molecules are polar in nature and are believed to be compatible with the polar ester linkages of DOP, leading to its use as a plasticizer for PVC. The two nonpolar hydrocarbon tails of DOP are, however, believed to be in low compatibility with polar PVC, thus leading to migration of DOP to the surface of the finished PVC products. This outward migration of DOP from PVC molecules might be accelerated in the presence of PE because of the interaction between the hydrocarbon tails of DOP and PE. In addition, exclusion of PVC from the crystallizable PE is developed during cooling from the melt blending, leading to phase segregation from each other.

In the PE/PVC/DOP blend, segregation of the amorphous DOP and PVC in PE is natural, given that the driving force of crystallization of PE tends to separate them. For the PE/PVC/DOP blend, in thermodynamic essence, two entropic forces are developed during the melt blending and the subsequent cooling of the ternary blend. These include: (i) during the melt blending of the ternary blend, three constituents tend to incorporate into one another to reach the highest obtainable entropy, and (ii) during cooling of the ternary blend from the melt, PE crystallizes and tends to exclude the amorphous DOP and PVC molecules out of the PE crystals. On the other hand, five enthalpic forces are developed in the ternary blend, including (a) the favorable interaction between the hydrocarbon tails of DOP and the hydrocarbon chains of PE, (b) the unfavorable interaction between the polar ester linkages of DOP and the nonpolar hydrocarbon PE, (c) the favorable interaction between the polar ester linkages of DOP and the polar PVC, (d) the unfavorable interaction between the nonpolar hydrocarbon tails of DOP and the polar PVC, and (e) the unfavorable interaction between the nonpolar PE and the polar PVC. The enthalpic forces from the favorable interactions (i.e., a and c) and the entropic force (i) are against those from the unfavorable interactions (i.e., b, d, and e) and the entropic force (ii). The compatibility of the ternary blends and plasticization effects of DOP on PVC are consequently dependent on the respective magnitude of the above five enthalpic forces and two entropic

forces. All of these forces depend on composition, temperature, molecular weight, and cooling rate.

In this report, we intend to study the influences of the contents and molecular weights of LDPE on plasticization effects of DOP on the PVC plastisol. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used for this study.

EXPERIMENTAL

Materials and Sample Preparations

Three low-density polyethylenes (LDPEs) including LDPE1, LDPE2, and LDPE3 in different melt indices were used for this study. The melt indices of these three LDPEs are in the order of LDPE3 > LDPE2 > LDPE1. In other words, the molecular weights of these LDPEs are in the order of LDPE1 > LDPE2 > LDPE3. LDPE1 (product number, H0100; melt index, 0.5 g/10 min; density, 0.922 g/cm³) was received from Asia Polymer Corp. (Taipei, Taiwan). LDPE2 (product number, LE4074; melt index, 2.8 g/10 min; density, 0.917 g/cm³) was received from Borealis Corp. (Portugal). LDPE3 (product number, 7100; melt index, 7.3 g/10 min; density, 0.917 g/cm³) was received from Asia Polymer Corp. Melt indices were determined according to ASTM D1238 at 190°C and 2.16 kg of loading for all LDPEs. DOP was supplied by Union Petrochemical Corp. (Taipei, Taiwan). PVC (product number, S-65) was prepared by a suspension polymerization with a degree of polymerization of about 1000, and was supplied by Formosa Plastics Corp. (Taipei, Taiwan). The thermostabilizer (AO; product number, RP31M) is a mixture of mono-, di-, and tribasic lead compounds and was received from Taiwan Colors and Chemical Co.

The blends of LDPEs/PVC/DOP/AO = (100 - x)/x/0.3x/0.065x were prepared, where LDPEs included LDPE1, LDPE2, and LDPE3, and x was 0, 25, 50, 75, and 100 parts by weight, respectively. For preparations of the blends, the PVC plastisol (i.e., the PVC/DOP/AO blend) was first prepared by premixing the PVC/DOP/AO = 100/30/6.5 in a blender at 90°C for 30 min, followed by extrusion twice in a single-screw extruder (diameter, 30 mm; L/D, 19; compression ratio, 3.5) at 160°C in the feeding zone, 160°C in the compression zone, and 170°C in the metering zone. The prepared PVC plastisol was then mixed with LDPE (LDPE1, LDPE2, or LDPE3) powders, fol-

Table I Compositions of LDPEs/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ Blends (where x is 0, 25, 50, 75, and 100 parts by weight, respectively)

LDPEs	PVC	DOP	AO
0	100	30	6.5
25	75	22.5	4.9
50	50	15	3.3
75	25	7.5	1.6
100	0	0	0

LDPEs include LDPE1, LDPE2, and LDPE3.

lowed by extrusion twice in the single-screw extruder at the same conditions as above. Thus, compositions of the prepared blended samples are as listed in Table I. After extrusions, the pelletized samples were compression molded by a hot press at 150°C for 30 s to make 0.33-mm-thick film specimens for DMA measurements.

DMA Measurements

A dynamic mechanical analyzer (DMA 2980; TA Instruments, New Castle, DE) was used to analyze storage modulus, loss modulus, and $\tan \delta$ of film specimens [$25 \times 6 \times 0.33$ mm (length \times width \times thickness)]. DMA was measured in the tensile mode at a constant frequency of 50 Hz and a heating rate of 3°C/min from -150 to 100°C.

DSC Measurements

Crystallizations of the blend samples were performed on DSC (DSC 2010; TA Instruments) at a cooling rate of 20°C/min after the samples were heated to 150°C and held at this temperature for 3 min under nitrogen. For thermal fractionation, the samples were heated on the DSC at 10°C/min under nitrogen from 30 to 140°C, holding for 10 min, followed by cooling at a rate of 20°C/min to 110°C, holding for 30 min, and then the samples were successively cooled by 5°C at 20°C/min. The specimens were maintained at each temperature for 30 min. Thus, the specimens were kept at each of the following temperatures: 110, 105, 100, 95, 90, 85, and 80°C for 30 min, and then cooled to 30°C at 20°C/min. The samples were then heated again to 140°C at 10°C/min to obtain the endothermic thermograms, during which several peaks were obtained for each sample.

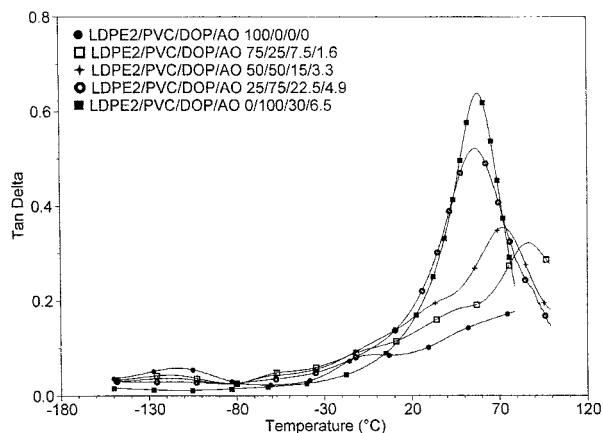


Figure 1 $\tan \delta$ curves of DMA as a function of temperature for the LDPE2/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively.

RESULTS AND DISCUSSION

Influences of LDPE Contents on Plasticization Effects of DOP on the PVC Plastisol

In this study, the controlled plastisol sample has a composition of PVC/DOP/AO = 100/30/6.5. By incorporating polyethylene into the plastisol, the influences of the polyethylene content on the plasticization effects of DOP in the plastisol were evaluated by DMA measurements. Figures 1 and 2 show $\tan \delta$ and loss modulus curves of DMA, respectively, for LDPE2/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively. As can be

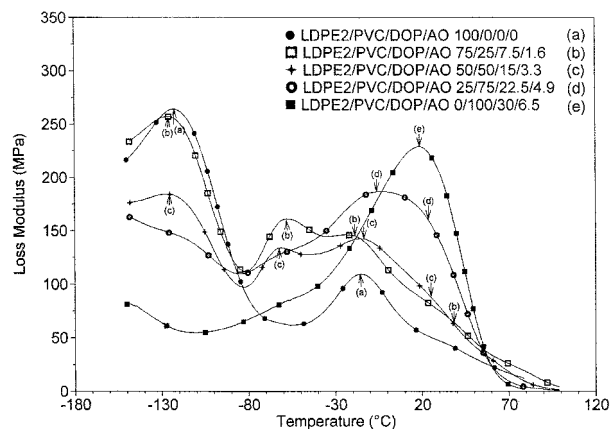


Figure 2 Loss modulus curves of DMA as a function of temperature for the LDPE2/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively.

seen in Figure 1, the LDPE2/PVC/DOP/AO = 0/100/30/6.5 blend exhibits a peak at near 56°C, corresponding to the glass-transition temperature (T_g) of the controlled PVC plastisol without the presence of polyethylene. The T_g of the PVC plastisol increases with increasing LDPE2 content. The plasticization effect of DOP in the PVC plastisol thus decreases with increasing LDPE2 content because of a migration of DOP from the PVC plastisol to LDPE2. The favorable interaction between the hydrocarbon tails of DOP and the hydrocarbon chains of LDPE2 apparently causes this migration of DOP. For the LDPE2/PVC/DOP/AO = 75/25/7.5/1.6 blend, the T_g is near 85°C. The T_g of this blend has a value close to that of the literature value, which is 83°C for pure PVC.¹⁰ Thus, negligible plasticization effect of DOP on the PVC plastisol in the presence of 75 or more parts by weight of LDPE2 is demonstrated.

As can be seen from the loss modulus curves in Figure 2 for the LDPE2/PVC/DOP/AO = 0/100/30/6.5 blend, the peak is narrow and the peak temperature is near 20°C. With increasing LDPE2 content in the blend, the peak breadth increases. These broadened peaks seemingly result from two overlapped peaks, with peak values as shown in Figure 2 by the small downward arrow symbols. These two overlapped peaks, consisting of one at a lower temperature and the other at a higher temperature, correspond to relaxations of two separated PVC plastisol phases having a higher DOP and a lower DOP content, respectively. The PVC plastisol phase with the lower DOP content is apparently the result of a loss of DOP arising from extraction by LDPE2.

DOP was previously found in our laboratories¹¹ to be able to incorporate into the amorphous domain of LDPE2, despite the fact that LDPE2 is crystalline. Figure 3 shows loss modulus curves for LDPE2/DOP = 100/0, 75/7.5, and 50/15 blends. As can be seen in Figure 3 for pure LDPE2, two peaks are found at -15 and -120°C. By addition of 10 phr DOP, the blend gives a new peak at near -50°C and the present peaks for pure LDPE2 decreasingly shift to -20 and -123°C, respectively. After the addition of DOP, three transition temperatures all decrease with increasing DOP content, which demonstrates that the plasticization of LDPE2 can be achieved by the addition of DOP. The plasticization effect of DOP on LDPE2 can also be seen in Figure 2 from the small upward arrows. For pure LDPE2 (i.e., the LDPE2/PVC/DOP/AO = 100/0/0/0

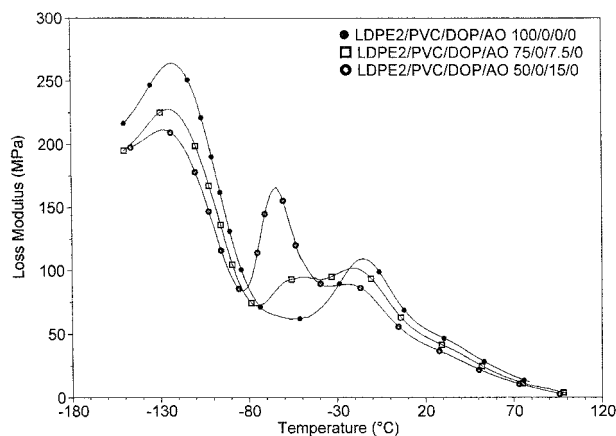


Figure 3 Loss modulus curves of DMA as a function of temperature for the LDPE2/PVC/DOP/AO = 100/0/0, 75/0/7.5/0, and 50/0/15/0 blends.

blend), two transitions at near -15 and -120°C are observed. For both LDPE2/PVC/DOP/AO = 75/25/7.5/1.6 and 50/50/15/3.3 blends, a new peak given in the range of -55 to -65°C is observed, attributed to the DOP plasticization in interfibrillar region in LDPE2.¹¹ The LDPE2/PVC/DOP/AO = 50/50/15/3.3 blend has a higher DOP plasticization on LDPE2 than the LDPE2/PVC/DOP/AO = 75/25/7.5/1.6 blend, because the former blend has a higher DOP content in LDPE2 and exhibits transition peaks at lower temperatures (see small upward arrows) than those of the latter blend. The peak corresponding to the amorphous component of pure LDPE2 at near -120°C was found to be shifted to lower temperatures as the DOP content increases as a result of increasing DOP plasticization compared to that among the LDPE2/PVC/DOP/AO = 100/0/0/0, 75/25/7.5/1.6, and 50/50/15/3.3 blends. The peak at near -120°C disappears, however, for the LDPE2/PVC/DOP/AO = 25/75/22.5/4.9 blend because of the formation of one homogeneous system.

The incorporation ability of DOP into LDPE2 can also be demonstrated by DSC thermograms of cooling scans of LDPE2 and its blends with PVC and DOP, as shown in Figure 4. As can be seen in Figure 4 for pure LDPE2, the crystallization temperature is near 93°C. For LDPE2 in the blends, the crystallization temperatures decrease by 3°C for all blends, suggesting that the incorporation of DOP into LDPE2 reaches the highest amount that LDPE2 can hold for even the lowest DOP-containing blend, and that the LDPE2 phase is completely separated from the PVC phase. In other words, although the favorable interaction

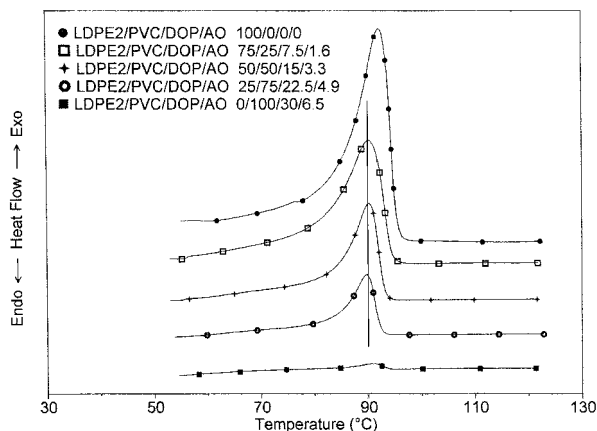


Figure 4 DSC thermograms of first-cooling scans for the LDPE2/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively.

between LDPE2 and the hydrocarbon tails of DOP can cause migration of DOP out of the PVC plastisol, the unfavorable interaction between LDPE2 and the polar ester linkages of DOP and the unfavorable interaction between nonpolar LDPE2 and polar PVC result in only a small amount of DOP incorporation into LDPE2 and phase separation between LDPE2 and PVC. Because of the phase separation, PVC exerts no effect on the crystallization of LDPE2.

LDPE2 is heterogeneous in molecular structure and gives multiple melting endotherms after being thermally fractionated.¹²⁻¹⁵ Thermal fractionation was performed on the blends to investigate the effects of the interactions in the blends on the crystallization of LDPE2 in the presence of DOP and PVC. Figures 5 and 6 show DSC heating thermograms for LDPE2/DOP and LDPE2/PVC/DOP/AO blends that were thermally fractionated on DSC. As can be seen in Figure 5, multiple endothermic peaks are found for pure LDPE2 and its blends with various amounts of DOP. These multiple endothermic peaks correspond to different sizes or perfection of crystals resulting from the structural heterogeneity of LDPE2. The strongest peak for pure LDPE2 at 110°C corresponds to the melting of crystals formed from the most structurally regular segments of LDPE2 molecules. By addition of DOP, the peak at 110°C decreases in intensity with increasing DOP content. This suggests that the crystallization from the most structurally regular segments of LDPE2 molecules is obstructed by DOP and that DOP is able to enter into the LDPE2 crystals. A compar-

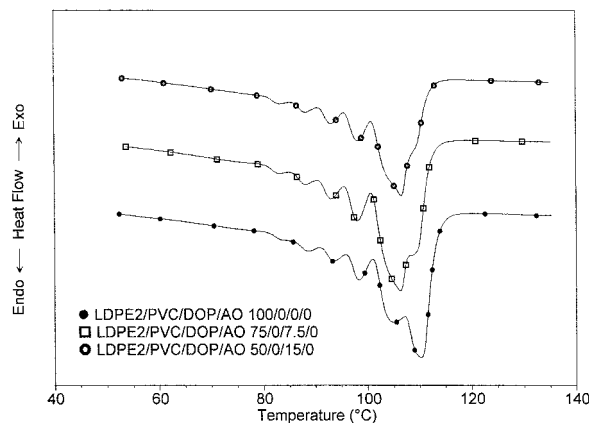


Figure 5 DSC thermograms of heating scans for the LDPE2/PVC/DOP/AO = 100/0/0/0, 75/0/7.5/0, and 50/0/15/0 blends. Prior to the heating scans, the blends were thermally fractionated on DSC.

ison of the LDPE2/DOP = 100/0, 75/7.5, and 50/15 blends in Figure 5 and the LDPE2/PVC/DOP/AO = 100/0/0/0, 75/25/7.5/1.63, and 50/50/15/3.25 blends in Figure 6, having the same LDPE2/DOP ratios but having different PVC contents, shows a negligible change in these multiple endothermic peaks. This indicates that PVC does not affect the crystallization of LDPE2 in the blends. In other words, PVC does not affect the interactions between LDPE2 and DOP.

Influences of Molecular Weights of LDPE on Plasticization Effects of DOP on the PVC Plastisol

Figure 7 shows $\tan \delta$ curves of DMA for LDPE3/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends,

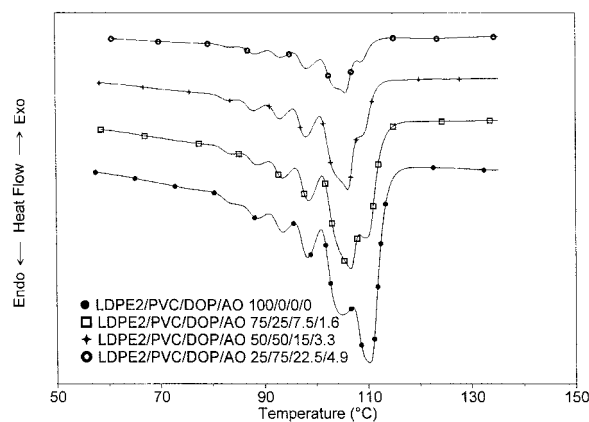


Figure 6 DSC thermograms of heating scans for the LDPE2/PVC/DOP/AO = $(100 - x)/x/0.3x/0.065x$ blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively. Prior to the heating scans, the blends were thermally fractionated on DSC.

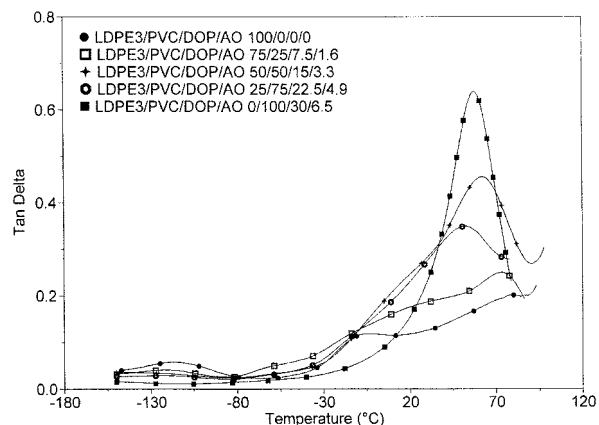


Figure 7 Tan δ curves of DMA as a function of temperature for the LDPE3/PVC/DOP/AO = (100 - x)/ x /0.3 x /0.065 x blends, where x is 0, 25, 50, 75, and 100 parts by weight, respectively.

where x is 0, 25, 50, 75, and 100 parts by weight, respectively. As can be seen in Figure 7, the T_g of the PVC plastisol also increases with increasing LDPE3 content in the blends. This finding from Figure 7 is thus similar to the finding from Figure 1, except for the LDPE3/PVC/DOP/AO = 25/75/22.5/4.9 blend for which the T_g is decreasing (less than 56°C). In other words, the plasticization effect of DOP on the PVC plastisol decreases with increasing either LDPE3 or LDPE2 content, except for the low LDPE3-containing blend. Apparently, the low molecular weight LDPE3 in a low content in the blend is unable to effectively extract DOP from the PVC plastisol to lead to an increase in its T_g . Consequently, polyethylene in a

Table II Peak Temperatures (T_g 's) of DMA tan δ for LDPEs/PVC/DOP/AO = (100 - x)/ x /0.3 x /0.065 x Blends (where LDPEs include LDPE1, LDPE2, and LDPE3, and x is 75, 50, and 25 parts by weight, respectively)

Blend Composition	T_g (°C)
Control (PVC/DOP/AO = 100/30/6.5)	56
LDPE1/PVC/DOP/AO = 25/75/22.5/4.9	56
LDPE2/PVC/DOP/AO = 25/75/22.5/4.9	54
LDPE3/PVC/DOP/AO = 25/75/22.5/4.9	50
LDPE1/PVC/DOP/AO = 50/50/15/3.3	75
LDPE2/PVC/DOP/AO = 50/50/15/3.3	70
LDPE3/PVC/DOP/AO = 50/50/15/3.3	61
LDPE1/PVC/DOP/AO = 75/25/7.5/1.6	83
LDPE2/PVC/DOP/AO = 75/25/7.5/1.6	85
LDPE3/PVC/DOP/AO = 75/25/7.5/1.6	72

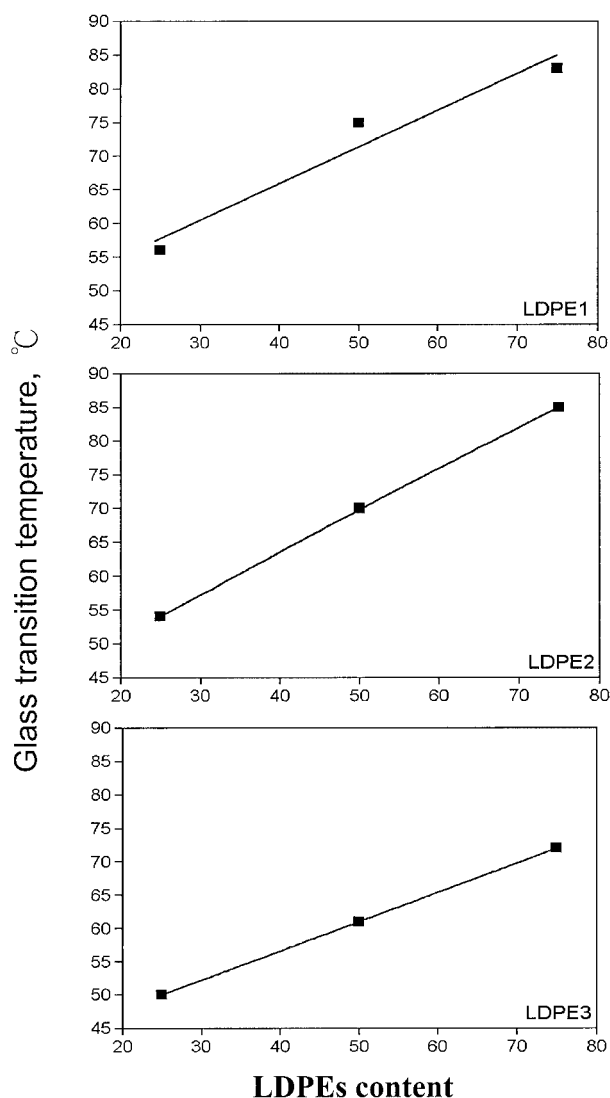


Figure 8 Effects of molecular weights of LDPEs on the plots of glass-transition temperatures of the PVC plastisol versus LDPEs contents. The measurements were conducted by using DMA on LDPEs/PVC/DOP/AO = (100 - x)/ x /0.3 x /0.065 x blends, where LDPEs include LDPE1, LDPE2, and LDPE3, and x is 25, 50, and 75 parts by weight, respectively. T_g of the PVC plastisol is 56°C, as can be seen from Figures 1 and 7.

higher molecular weight, that is, in higher chain entanglements, is more capable of preserving the extracted DOP from the PVC plastisol by the favorable interaction between hydrocarbon chains of polyethylene molecules and hydrocarbon tails of DOP developed during the melt blending of the blends.

More evidence that the higher the molecular weight of polyethylene, the higher the extent of DOP extraction from the PVC plastisol, can be

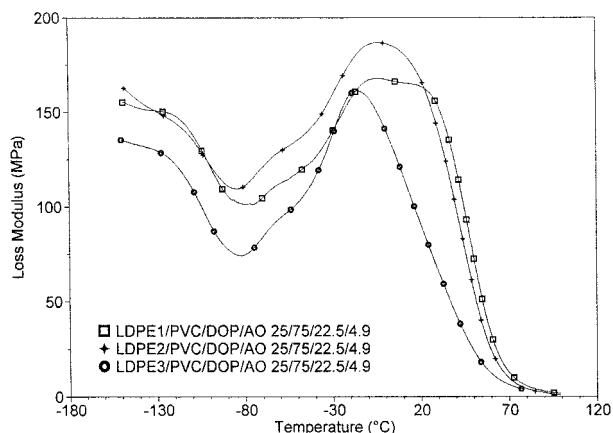


Figure 9 Loss modulus curves of DMA as a function of temperature for the LDPEs/PVC/DOP/AO = 25/75/22.5/4.9 blends, where LDPEs include LDPE1, LDPE2, and LDPE3.

obtained from loss tangent ($\tan \delta$) measurements of LDPEs/PVC/DOP/AO = 25/75/22.5/4.9, 50/50/15/3.3, and 75/25/7.5/1.6 blends. The peak temperatures (i.e., T_g 's) of the $\tan \delta$ curves are listed in Table II. LDPEs include LDPE1, LDPE2, and LDPE3 having molecular weights in the order of LDPE1 > LDPE2 > LDPE3. As can be seen in Table II, the T_g 's of the PVC plastisol in the blends are in the range of 50–85°C and increase with increasing molecular weight of LDPEs. Figure 8 shows the effect of LDPEs' molecular weights on the plots of glass-transition temperatures of the PVC plastisol versus LDPEs content. The glass-transition temperatures are found to

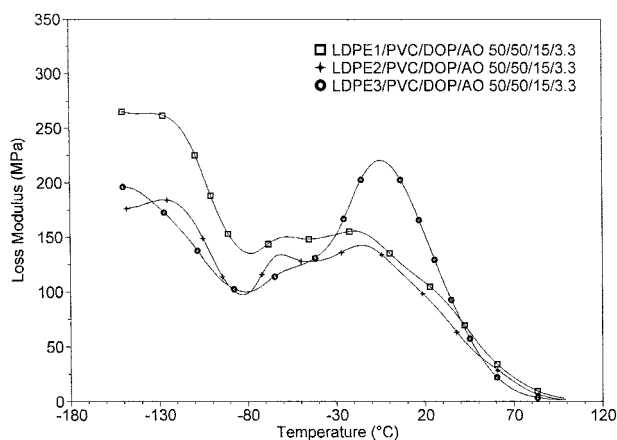


Figure 10 Loss modulus curves of DMA as a function of temperature for the LDPEs/PVC/DOP/AO = 50/50/15/3.3 blends, where LDPEs include LDPE1, LDPE2, and LDPE3.

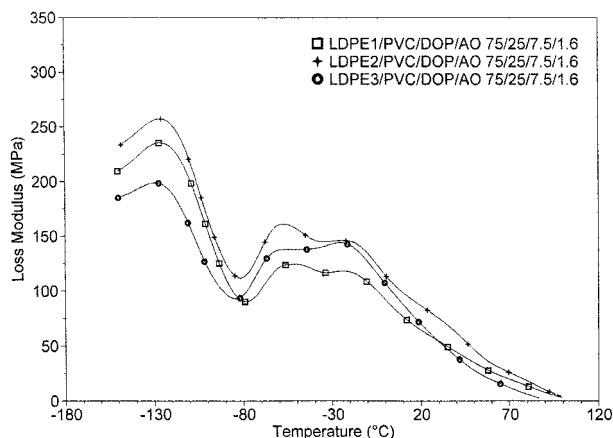


Figure 11 Loss modulus curves of DMA as a function of temperature for the LDPEs/PVC/DOP/AO = 75/25/7.5/1.6 blends, where LDPEs include LDPE1, LDPE2, and LDPE3.

increase with increasing LDPEs content, as also previously found. The effects of LDPEs contents on glass-transition temperatures of the PVC plastisol are decreased with decreasing molecular weights of LDPEs present in the blends. This is, again, the result of lower DOP extraction ability for lower molecular weight LDPEs.

Influences of molecular weights of LDPEs on the extent of DOP extraction from the PVC plastisol in the blends can be also seen in Figures 9–11, where loss modulus curves of DMA for LDPEs/PVC/DOP/AO = 25/75/22.5/4.9, 50/50/15/3.3, and 75/25/7.5/1.6 blends are shown, respectively. Figure 12 shows loss modulus curves of DMA for three pure LDPEs. As can be seen in Figure 12, two loss maxima corresponding to α -

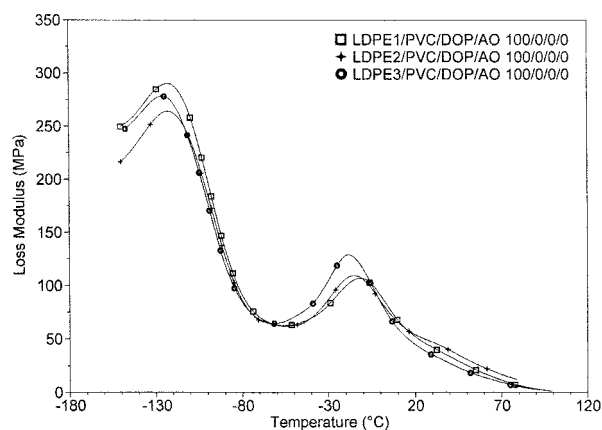


Figure 12 Loss modulus curves of DMA as a function of temperature for LDPE1, LDPE2, and LDPE3.

and γ -relaxation transitions¹¹ are found, including one at near -20°C and the other at near -120°C . These two loss maxima are found to shift to lower temperatures with decreasing molecular weights of LDPEs. As demonstrated previously in Figure 3, a loss maximum assigned to β -relaxation transition¹¹ is found at near -60°C by addition of DOP into LDPE2. From Figure 11, three loss maxima corresponding to α -, β -, and γ -relaxation transitions at near -20 , -60 , and -120°C , respectively, are clearly seen for LDPEs in the LDPEs/PVC/DOP/AO = 75/25/7.5/1.6 blends, although no loss maximum in the high temperature range is clearly seen for the PVC plastisol.

The present three loss maxima for LDPEs are found to shift to lower temperatures with decreasing molecular weights of LDPEs. From Figure 10, a strong peak at near -5°C is found for the LDPE3/PVC/DOP/AO = 50/50/15/3.3 blend and should correspond to a transition of the PVC plastisol in the blend. This transition for the PVC plastisol is not apparent for the blends containing LDPE1 and LDPE2. Two bumps on the curves of both LDPE1/PVC/DOP/AO and LDPE2/PVC/DOP/AO blends, however, appear to be at near -15 and 35°C , corresponding to the PVC plastisol containing a higher DOP and a lower DOP content, respectively. The separation of the PVC plastisol into two phases, as discussed previously, results from the extraction of DOP from the PVC plastisol in the blend. It is thus demonstrated that higher molecular weights of LDPE can lead to higher extent of DOP extraction from the PVC plastisol in the blend. From Figure 9, influences of molecular weights of LDPEs on the extent of DOP extraction from the PVC plastisol in the blend containing a low amount of LDPEs is more obvious. As seen in Figure 9, the peak width in the temperature range -20 to 40°C increases with increasing molecular weights of LDPEs, indicating that higher molecular weights of LDPE can indeed lead to a greater extent of extraction of DOP from the PVC plastisol, greater phase separation of the PVC plastisol, and a broader transition peak of the PVC plastisol.

CONCLUSIONS

This work investigated the plasticization effects of DOP on a PVC plastisol, with a composition of

PVC/DOP/AO = 100/30/6.5, by the presence of polyethylene using DMA and DSC. Influences of contents and molecular weights of LDPE on plasticization effects of DOP in the PVC plastisol were the main focus of the investigation. The plasticization effects of DOP in the PVC plastisol were found to decrease with increasing LDPE incorporations up to 75 parts per 100 parts by weight of LDPE and PVC together. The DOP plasticization in the PVC plastisol was found to decrease with LDPE molecular weights, except for those blends having LDPE in low contents and low molecular weights.

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REFERENCES

1. Mark, H. Encyclopedia of Polymer Science and Engineering, Vol. 17, 2nd ed.; Wiley: New York, 1989.
2. Mondragon, M.; Flores, A. C. *J Vinyl Technol* 1993, 15, 46.
3. Falter, J. A.; Geick, K. S. *J Vinyl Technol* 1994, 16, 112.
4. Brydson, J. A. *Plastics Materials*, 6th ed.; Butterworth-Heinemann: Oxford, 1995.
5. Xu, X.; Meng, X.; Chen, K. *Polym Eng Sci* 1986, 27, 391.
6. Yang, W.; Wu, Q.; Zhou, L.; Wang, S. *J Appl Polym Sci* 1997, 66, 1455.
7. Gerlach, D. *Kunstst Plast Eur* 1998, 88, 47.
8. Tse, A.; Laakso, R.; Baer, E.; Hiltner, A. *J Appl Polym Sci* 1991, 42, 1205.
9. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. *J Appl Polym Sci* 1995, 58, 1087.
10. Nielsen, L. E. *Mechanical Properties of Polymers*; Reinhold: New York, 1962.
11. Shieh, Y. T.; Liu, C. M. *J Appl Polym Sci* 2001, 82, 3591.
12. Adisson, E.; Ribeiro, M.; Deffieux, A.; Fontanille, M. *Polymer* 1992, 33, 4337.
13. Keating, M. Y.; McCord, E. F. *Thermochim Acta* 1994, 243, 129.
14. Wolf, B.; Kenig, S.; Klopstock, J.; Miltz, J. *J Appl Polym Sci* 1996, 62, 1339.
15. Shieh, Y. T.; Chen, J. S.; Lin, C. C. *J Appl Polym Sci* 2001, 81, 591.