

# **A DMA STUDY OF THE SUPPRESSION OF THE $\beta$ TRANSITION IN SLIGHTLY PLASTICIZED PVC BLENDS**

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## **Abstract**

A new criterion for evaluating different plasticizers the ability of suppression of the  $\beta$  transition in plasticized PVC blends. Accordingly, the  $\beta$  suppression ability is proportional to the PVC-plasticizer compatibility, expressed either by the critical solution temperature, CST, or by the interaction parameter related to the difference between the solubility parameters of the blend components. The criterion is, however, valid for low plasticizer contents (<5% w/w) only, as long as the  $\beta$  transitions are not overlapped by the  $\alpha$  transitions, shifted towards lower temperatures due to the effect of the plasticizer. For higher plasticizer contents the  $\alpha$  transition starts to overlap the  $\beta$  transition and the  $\beta$  suppression ability of the plasticizer depends increasingly on the efficiency of the plasticizer i.e. on the depression of the glass transition temperature of PVC (related to the  $T_g$  of the plasticizer). Accordingly, plasticizers with both good efficiency (low  $T_g$ ) and compatibility are more effective in the  $\beta$  suppression than plasticizers which have only a higher compatibility but also a high  $T_g$  (i.e. reduced efficiency).

**Keywords:** plasticizers, PVC blends,  $T_g$

## **Introduction**

One of the wide-spread polymers, poly(vinylchloride) – PVC –, being to brittle for most practical applications because of the enhanced glass temperature (81.2°C), has to be plasticized to improve both toughness and stiffness. Fortunately, PVC exhibits the ability of incorporating great amounts of plasticizers, resulting PVC-blends which show, depending on the concentration of plasticizer, dramatic changes of the physico-mechanical properties [1].

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Both the  $\alpha$  and the  $\beta$  transitions of PVC are markedly influenced by the plasticizers, which gradually diminish the intensity, mainly of the  $\beta$  transition, accompanied by a corresponding shift towards lower temperatures of both of the transitions. At the same time the width of the temperature ranges of the transitions changes too.

For 0–20% *w/w* plasticizer, the  $\beta$  transition of PVC flattens and finally disappears. At the same time the stiffness increases and the impact strength decreases [2]. This phenomenon is known as "antiplasticization" and has been attributed either to an increasing crystallinity [3–5] or to a decrease of the 'free volume' [6, 7], as well to PVC-plasticizer interactions [8–10]. According to the last two assumptions the plasticizer hinders local or cooperative motions of shorter segments of the PVC chain. Until today non unequivocal evidence in favour of one of these suppositions has been offered by the experimental methods used. Thus the origin of the antiplasticizing effect is still not established [11]. A second controversy refers to the correlation between the antiplasticizing ability and the plasticizing efficiency of plasticizers. In accordance with some earlier assumptions both properties exhibit similar trends [12], whereas in present most of the scientists adhere, however, to the explanation of Kinjo and Nakagawa [13] which assume opposite trends for the plasticizing efficiency and the antiplasticizing ability of plasticizers.

In the present paper we discuss some new data concerning the ability of suppression of the  $\beta$  transition in correlation with the PVC-plasticizer compatibility criteria (based on solubility parameters,  $\delta$ , and the critical solution temperatures, *CST*) and the efficiency criteria (related to the glass transition temperatures,  $T_g$ , of the plasticizer), respectively. The discussion of the effect of the plasticizers on the  $\alpha$  transition ( $T_g$ ) of PVC will be presented in a second paper.

## Experimental

For the preparation of the plasticized PVC-blends we used a PVC Fluka ( $K=69-71$ ) together with a series of 10 structurally different plasticizers supplied by various producers or synthesized in our laboratory (Table 1). Cd and Zn stearates were added as thermal stabilizers. Mixtures of different compositions comprising beside PVC and plasticizer a thermal stabilizer (in an amount of 2phr – *w/w* parts per hundred parts of resin) were dry-blended, roll-milled at 160°C and press-molded at 170°C into test pieces of 50×5×2 mm.

The  $\beta$  transition of PVC-blends comprising respectively 0.5%, 10% and 13.5% *w/w* plasticizer was investigated by DMA (dynamic mechanical thermal analysis) with the Rheometrics RSA II visco-elastometer, equipped with the Dual-Cantilever device. Both strain and frequency (0.16 Hz) were kept constant during the selected temperature range (between –130 and +100°C) realized by using a heating rate of 2 K min<sup>-1</sup>.

Table 1 Characteristics of the plasticizers used

| Plasticizer                                     | Supplier  | Code   | $T_g/K$ | $\delta/(\text{cal/cc})^{1/2}$ | $CST/^\circ\text{C}$ |
|---|-----------|--------|---------|--------------------------------|----------------------|
| 2-ethylhexyl-diphenyl-phosphate                 | Monsanto  | S 141  | 188.0   | 9.32                           | 95                   |
| di-2-ethylhexyl-phthalate                       | Solventul | DEHP   | 188.3   | 8.95                           | 117                  |
| tri-2-ethylhexyl-trimellitate                   | Fluka     | TEHTM  | 197.5   | 8.84                           | 138                  |
| di-isodecyl-adipate                             | synthesis | DIDA   | 176.2   | 8.08                           | 156                  |
| benzyl-octyl-phthalate                          | Monsanto  | S 261  | 206.7   | 9.57                           | 108                  |
| di-butoxy-propyl-phthalate                      | synthesis | DBPP   | 183.2   | 9.35                           | 122                  |
| 2,2,4-trimethyl-1,3-pentane-diol-di-isobutirate | Ilechim   | KODA   | 172.6   | 8.14                           | 138                  |
| 2,2,4-trimethyl-1,3-pentane-diol-di-benzoate    | synthesis | KODADB | 228.7   | 9.34                           | 108                  |
| 2-ethyl-1,3-hexanediol-dibenzoate               | synthesis | EHDDB  | 223.7   | 9.51                           | 100                  |
| 1,3-butanediol-dibenzoate                       | synthesis | BDDB   | 219.2   | 10.01                          | 97                   |

The glass transition temperatures of the plasticizers were measured with the Perkin-Elmer DSC-7 using a heating rate of  $10 \text{ K min}^{-1}$ . As a general rule, the plasticizer efficiency increases with decreasing  $T_g$  of the plasticizer.

$CST$  was determined according to DIN 53 408, whereas the solubility parameters,  $\delta$ , were calculated by using the Coleman rule [14]. The PVC-plasticizer compatibility increases with both the decreasing  $CST$  and the decreasing difference between the solubility parameters of the blend components, which is related to the interaction parameter of the blends components [15].

$$B = (\delta_{\text{plastic}} - \delta_{\text{PVC}})^2$$

$$(\delta_{\text{PVC}} = 9.88 \text{ (cal/cm}^3)^{1/2}).$$

The respective characteristics of the plasticizers are shown in Table 1.

As shown in Fig. 1, the accordance between the compatibility tendencies of the plasticizers predicted by the interaction parameters,  $B$ , and the critical solution temperatures,  $CST$ , is satisfactory, i.e. small values of  $B$  are related to small values of  $CST$  and vice versa.

## Results and discussion

From the structural point of view, the plasticizers can be classified into three groups.

The first group comprises esters of very different structures: S 141, TEHTM, DEHP and DIDA. In this group the most common used plasticizer for PVC (DEHP) was associated with:

- the most compatible phosphate ester (S 141) [16]
- TEHTM, showing remarkable antifogging characteristics, due to its high stability [17]
- DIDA, very efficient because of its high molecular mobility, i.e. low  $T_g$  (like all aliphatic diesters) [18].

The structural differences are not that obvious in the two other groups. They show, however, important differences in compatibility and efficiency.

The second group includes diesters of the orto-phthalic acid with different monohydroxy alcohols: beside DEHP (belonging to the first group too), it comprises the more compatible (due to the high aromaticity) but less efficient phthalate S 261 and the both more compatible and, due to the remarkable mobility of the etheric bond, the more efficient DBPP [19].

The third group comprises diesters of differently branched 1,3-diols with isobutiric, KODA (characterized by both very low  $T_g$  and low compatibility) and respective benzoic acid, BDDB, EHDDB and KODADB (which show the high-

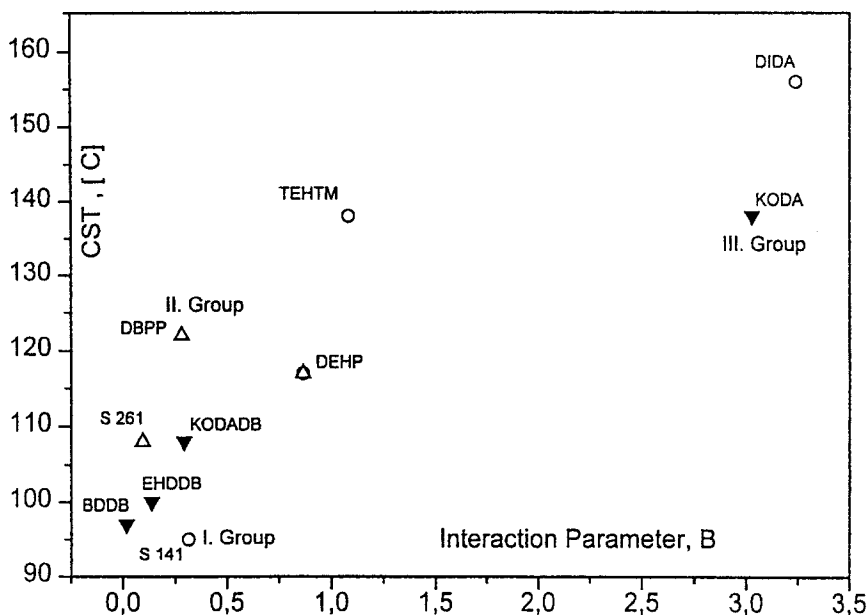


Fig. 1 Correlation between the compatibility criteria for the PVC-plasticizer blends, Critical Solution Temperature,  $CST$ , and Interaction Parameter,  $B$

est compatibility but also high  $T_g$ 's). For correlations concerning the efficiency (expressed by  $T_g$ ) and the compatibility (expressed by both  $B$  and  $CST$ ) see Fig. 2.

While the first group includes well known and intensively studied plasticizers of PVC, the plasticizers incorporated in the two other groups are tested for the first time for PVC plastification.

The results of the DMA analysis of the plasticized PVC blends presented in Figs 3–5 clearly illustrate the flattening of the loss factor,  $\tan\delta$ , accompanied by a shift towards lower temperatures of the  $\beta$  transition. The intensities of these effects depend on both the structure and concentration of the plasticizer used. Beginning with 10%  $w/w$  content of plasticizer, it becomes obvious that the right, high temperature branch of the  $\beta$  peak is changing due to an increased overlapping by the  $\alpha$  transition ( $T_g$ ) shifted to lower temperatures. In the PVC plasticized with the most compatible and also effective (low  $T_g$ ) S 141 the  $\beta$  transition is already suppressed for a 10%  $w/w$  plasticizer content. In the PVC blends with 10%  $w/w$  DEHP, DBPP and DIDA the  $\beta$  peaks appear sooner as a low temperature shoulder of the  $\alpha$  transition shifted to lower temperatures. This shoulder disappears finally as soon as the plasticizer content reaches 13.5%  $w/w$ . All other studied plasticizers do not result in an entirely suppression of the  $\beta$  transition even at the highest studied content of 13.5%  $w/w$ .

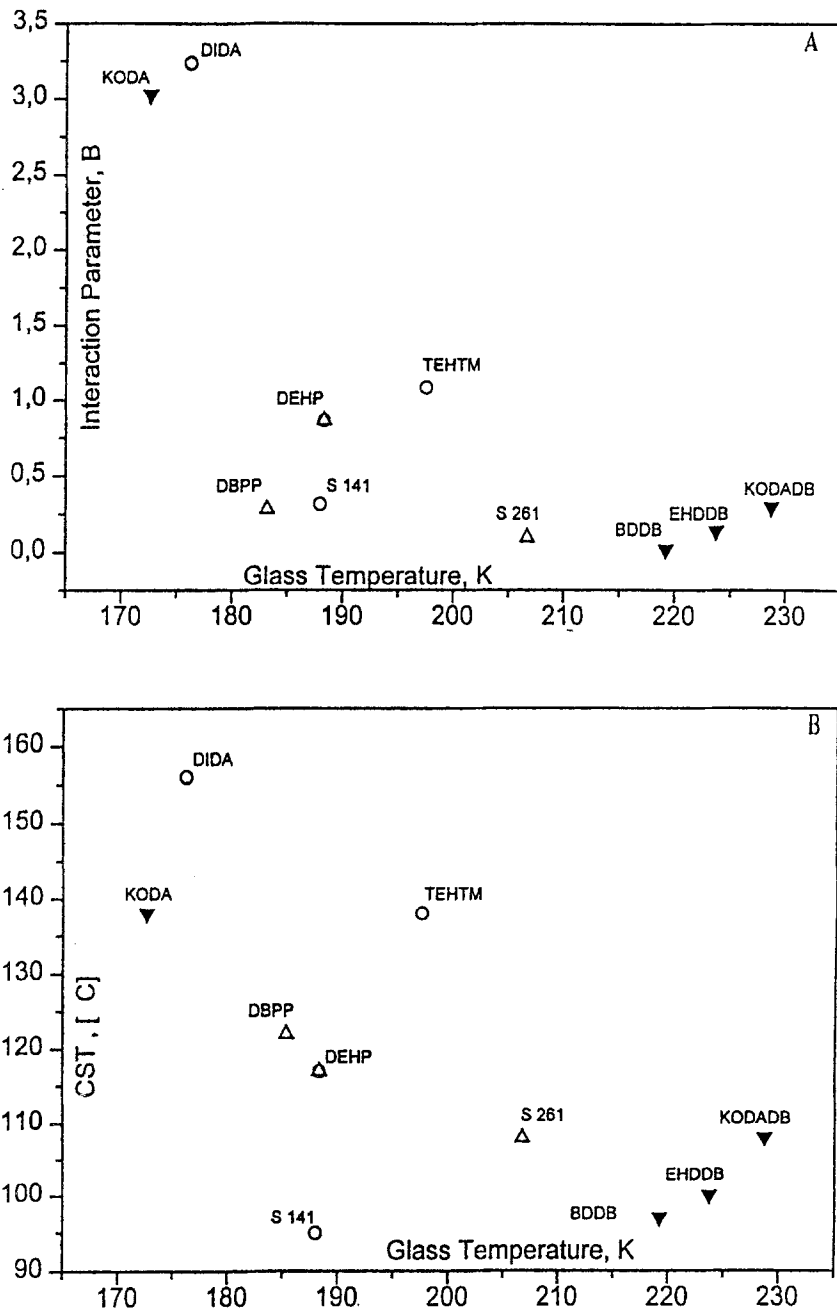


Fig. 2 Correlation between the compatibility criteria and the efficiency of plasticizers, expressed by the glass transition temperature; a) interaction parameter,  $B$ , vs. glass transition temperature,  $T_g$ , b) critical solution temperature,  $CST$ , vs. glass transition temperature,  $T_g$

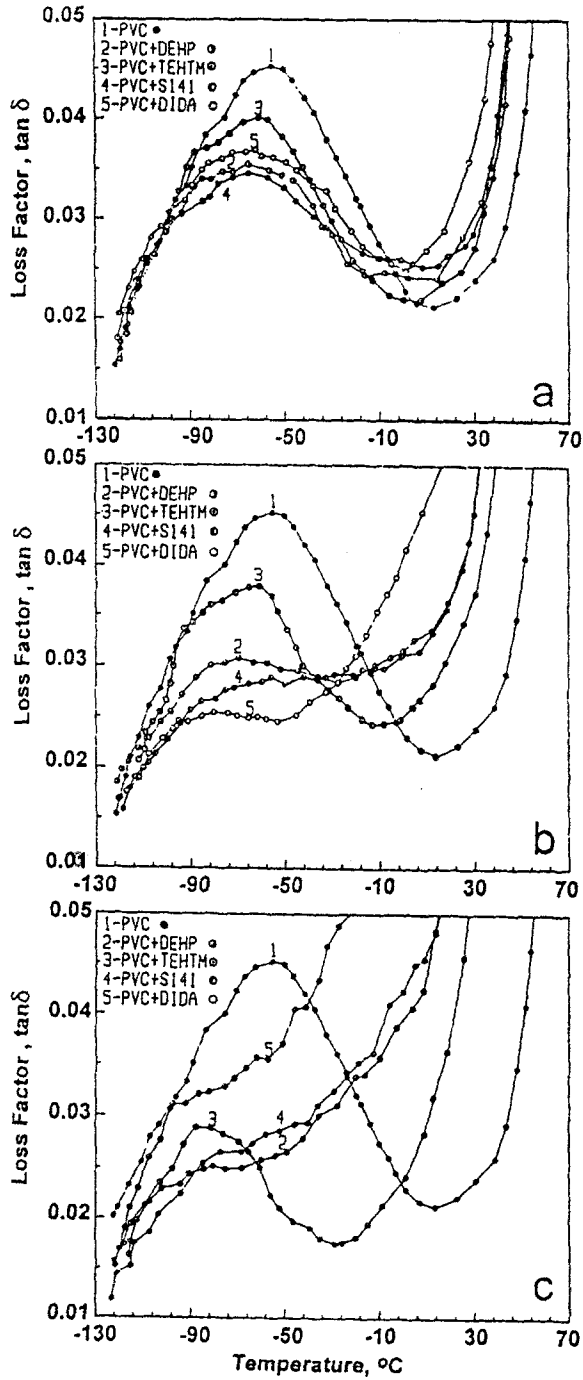


Fig. 3 Dynamic-mechanical spectra of PVC plasticized with S 141, DEHP, TEHTM and DIDA. Plasticizer content, w/w%: a-5, b-10 and c-13.5

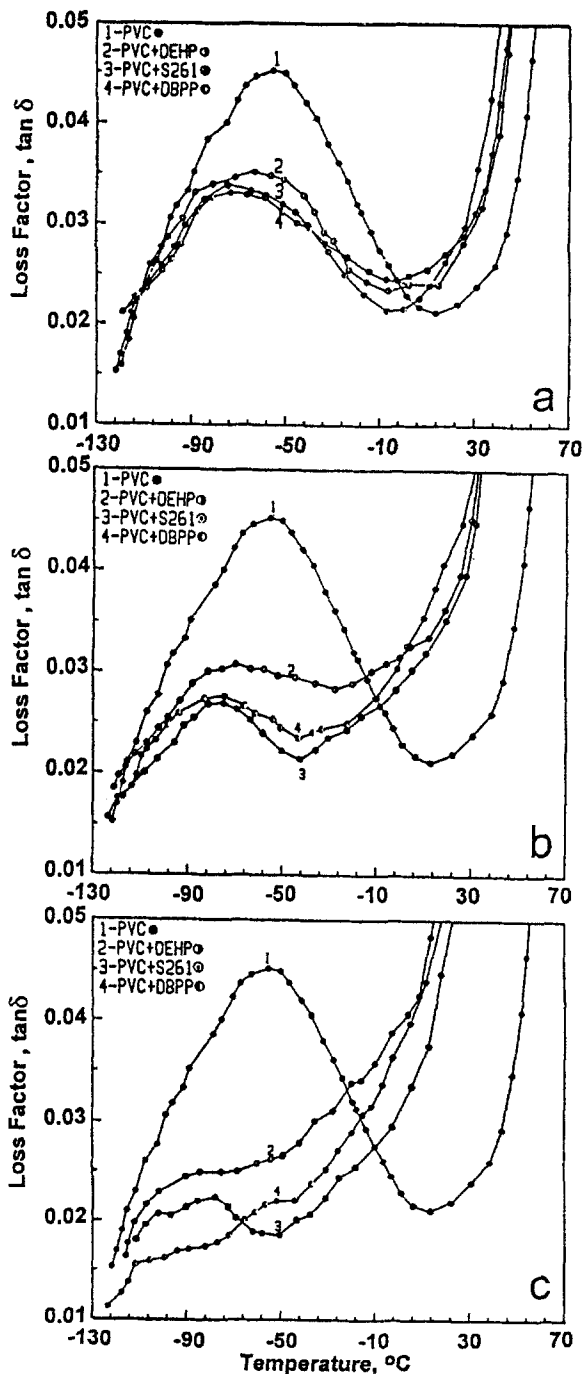


Fig. 4 Dynamic-mechanical spectra of PVC plasticized with S 261, DEHP and DBPP. Plasticizer content, w/w%: a-5, b-10 and c-13.5



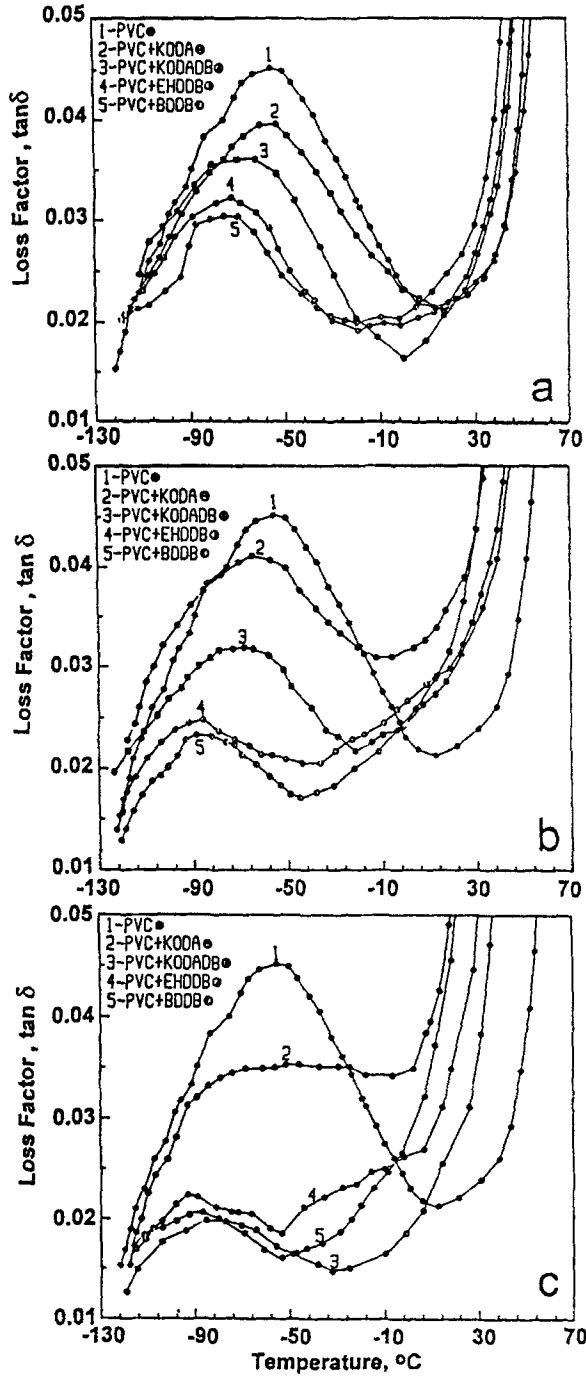


Fig. 5 Dynamic-mechanical spectra of PVC plasticized with KODA, KODADB, EHDDB and BDDB. Plasticizer content, w/w%: a-5, b-10 and c-13.5

The results of the dynamic-mechanical spectra reveal essentially two different mechanisms concerning the suppression of the  $\beta$  peak of PVC effected by the plasticizer. In the first case, the suppression occurs as a consequence of the PVC-plasticizer interaction, the  $\alpha$  transition occurring still well separated at higher temperatures, thus not influencing at all the  $\beta$  transition. This is valid mainly for the dibenzoates studied (see for instance in Fig. 5 the respective loss factor curves for 13.5% w/w content of KODADB, EHDDDB and BDDDB, respectively) which exhibit a high compatibility with PVC due to the phenyl rings of the ester group, but also are characterized by the higher  $T_g$ 's. In the second case the  $\beta$  suppression occurs as a result of the overwhelming shift of the  $\alpha$  transition to low temperatures, resulting finally in a total overlapping onto the  $\beta$  transition (see for instance the loss factor curve in Fig. 2 for DIDA, which has a very low  $T_g$ , but also the smallest compatibility). Except of KODA for all other studied plasticizers the reduction or the suppression of the  $\beta$  transition is probably due to an interplay of the two effects, i.e. the plasticizers being characterized by a relatively low  $T_g$  and a medium compatibility.

At 5% w/w plasticizer content the two transitions of PVC do not overlap yet and the intrinsic antiplasticizing ability of the plasticizer can be related directly to the respective flattening of the  $\beta$  transition. In the three groups established, this ability decreases in the order:

- I. S 141 > DEHP > DIDA > TEHTM
- II. S 261 = DBPP > DEHP
- III. BDDDB > EHDDDB > KODADB > > KODA

Thus the  $\beta$  suppression ability of the plasticizers decreases as the compatibility increases (expressed by low values of the compatibility criteria  $B$  and  $CTS$ , respectively), respective as the efficiency (related to low  $T_g$ ) increases. For the same efficiency (i.e. the same  $T_g$ ) decisive for the  $\beta$  suppression is the higher compatibility – compare for instance in Fig. 3 the flattening of the  $\beta$  peaks for DEHP and S 141.

The attribution of the  $\beta$  suppression ability of the plasticizers is, however, more complex. Thus for instance in the blends of PVC with the benzoate plasticizers, BDDDB, EHDDDB and KODADB the  $\beta$  suppression is governed by the compatibility, but the efficiency (even if the smallest) varies in the same order (Fig. 2 for compatibility and efficiency criteria and Fig. 5 for  $\beta$  suppression ability). On the other hand, although more effective and even more compatible (even if the compatibilities are very small) than DIDA, the  $\beta$  suppression of KODA is less effective (compare the respective curves 2, Fig. 5a and 5, Fig. 3a).

The only one exception of the above formulated rules is TEHTM. Even if much less efficient but more compatible than DIDA its influence upon the  $\beta$  transition is the poorer.

These rules maintain their validity even at a 10% *w/w* plasticizer content, although the shapes of the  $\beta$  peaks are changed because of the influence of the  $\alpha$  transitions shifted to the lower temperature range (Figs 3b–5b). Remarkable is, however, the strong flattening of the  $\beta$  transition peak in the blend with DIDA, exceeding those of the more compatible DEHP and S 141 (Fig. 3b). The effect is obviously determined by the influence of the shifted  $\alpha$  transition and not by the superior solution capacity of DIDA, as postulated by Huang [20]. According to data published by Kwak [21] aliphatic esters exhibit really higher solution capacities than phthalates do. Again TEHTM and KODA show the smallest  $\beta$  suppression, the  $\beta$  transition peaks being still marked.

The results of the DMA study confirm the assumption of an existing correlation between the  $\beta$  suppression ability and the PVC-plasticizer interaction. At low concentrations of plasticizer, the stronger PVC-plasticizer interaction is responsible for the stronger bonding of the plasticizer to the amorphous PVC matrices [22], filling the holes along the macromolecular coiled chains. The aromatic rings of the plasticizer are disposed parallel to the polymer backbone, participating in the interaction, but hindering at the same time the (cooperative or not) mobility of short segments of the polymer chain [23]. The influence of the aromatic rings of the plasticizers is crucial, as molecular simulation by using the Cerius [1, 6] program has confirmed. Comparing the simulated molecular structures of DEHP and of the corresponding aliphatic di-2-ethylhexyl-adipate, DEHA, (not used in this study as plasticizer) revealed for both esters quite similar configurations and quasi-equal distances among the carbonyl groups (3.025 Å for the phthalate, respective 3.216 Å for the adipate) as well as similar arrangements of the aliphatic 2-ethylhexyl sequences. The only significant difference is induced by the aromatic rings of the phthalate, which in the same time are responsible for the increased interaction and for the antiplasticizing activity. The aliphatic esters – less compatible with PVC – are especially located in the holes situated in the neighbourhood of the chain ends, thus not hindering the mobility of the chain segments [24]. Additionally the aliphatic esters may dissolve the weak entanglements of the chain, contributing thus to an increase of the chain mobility. This could be an explanation of the dramatic shift of the  $\alpha$  transition towards lower temperatures and the observed strong overlapping onto the  $\beta$  transition.

Taking into account the combined influences of both mechanisms upon the  $\beta$  suppression, the order of the  $\beta$  suppression predicted by compatibility criterion only may be misleading. Thus, for instance, the aliphatic ester DIDA, although less compatible, but much more efficient (lower  $T_g$ ) than the more compatible S 261 is definitely more effective in the  $\beta$  suppression. The same is valid if DIDA is compared with the even much more compatible dibenzoate plasticizers. That means that a very good compatibility does not necessarily account for

the better  $\beta$  suppression. Good efficiency is needed too (generally  $T_g > 190$  K). That means, the very efficient plasticizer DIDA suppresses the  $\beta$  transition, even if the compatibility with PVC is very poor.

The unfavourable combination of both poor efficiency ( $T_g > 190$  K) and compatibility ( $B > 1.0$ , resp.  $CST > 130$ ) is shown by TEHTM. The observed  $\beta$  suppression ability might be supported at most by the compatibility, even if very small, but not by a greater polarity [25].

## Conclusions

The suppression of the  $\beta$  transition of PVC by the action of incorporated plasticizers may be the result of both the PVC-plasticizer interaction and the overlapping by the  $\alpha$  transition, due to an exceptional shift to lower temperatures of the  $T_g$  of the blend. The overall  $\beta$  suppression ability of a plasticizer is thus related to both his efficiency (characterized by a low  $T_g$ ) and his compatibility. The  $\beta$  suppression effect is the largest of the (very) compatible and efficient plasticizers (i.e. alkyl-aryl phosphates and phthalates), medium for very efficient but incompatible aliphatic diesters and the lowest for the very compatible but inefficient plasticizers (S 261 and dibenzoates). The smallest  $\beta$  suppression effect is shown by the both poor compatible and poor efficient TEHTM.

The real intrinsic  $\beta$  suppression, on the other hand, depends on the PVC-plasticizer interaction only. It is observed exclusively at very low concentration of the plasticizer ( $< 5\%$  w/w) and it is directly proportional to the PVC-plasticizer compatibility. From this point of view, it seems the  $CST$  criterion has larger validity than the  $B$  criterion (Fig. 2). Finally the compatibility criterion illustrates the intrinsic  $\beta$  suppression ability of a plasticizer, however, more accurately than the efficiency criterion of Kinjo and Nakagawa [13], widely accepted in the present.

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