Plasticizers - Glass transition temperature - Plasticizing efficiency - Solubility - Viscosity

Hydrocarbons (C₂ to C₁₀) with specific chemical nature and constitution are used to investigate their plasticizer efficiency with regard to low-temperature flexibility and processing behavior. Irrespective of the nature of the rubber used the highest plasticizer efficiency is observed in the order of the molecule structure: linear branched > cyclic. The efficiency region of the hydrocarbons is limited by the critical solubility concentration which is increases inversely from cyclic to linear hydrocarbon structures. It is demonstrated that the plasticizer efficiency is increasing when the radius of gyration of the molecule increases. Similarly graded influences from the free volume or the thermal expansion coefficient of the hydrocarbons are established.

Structure-Property Relationships for Non-Polar Plasticizers in Polydienes I¹

Influence of molecular structure on plasticizing efficiency of hydrocarbons

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Plasticizers (softeners) are widely used in rubber technology in order to facilitate the processing of filled rubber mixes and/or to improve the low-temperature flexibility of a polymeric compound [1–3]. Among other effects, their presence also leads to changes in the dynamic properties, like storage modulus or damping behavior. In addition they can impair the efficiency of crosslinking systems (sulfur or peroxide).

The most widely used plasticizers are undoubtedly high-boiling fractions of mineral oils. It is not only difficult to classify the oils by their chemical composition [4]. But the drawback of compounding effects and technical benefits to the theories that could explain the main effects of plasticizers [7]. The one most easy to visualize is the lubricity theory which considers more effective sliding and cooperative motion of the macromolecules in the presence of molecular species able to reduce intermolecular friction. The gel theory [9] considers the masking of intermolecular interacting groups (i.e. polar ones) by plasticizer molecules. Finally, the most advanced approach holds that the purpose of the plasticizer is to increase the “free volume” in the system [10]. The cooperative motion of the polymer chains is improved and therefore both the glass transition temperature and the viscosity of the system are decreased as a function of the plasticizer concentration.

Empirical observations show that the effects depend on
(i) the concentration of the plasticizer [11],
(ii) the freezing temperature and
(iii) the viscosity of the plasticizer [12].

A prediction of the glass transition temperature of the softened polymer mixture based on a mixing rule can be made only if the softener is soluble in the rubber.

\[
T_g(\text{mix}) = C_1 \frac{T_{g1}}{C_2} + C_2 \frac{T_{g2}}{C_1}
\]

(1)

As far as single-phase systems are concerned, the efficiency E of a given plasticizer can be defined as the change in a specific property caused by a plasticizer concentration unit:

\[
E = \frac{\Delta P}{\Delta C}
\]

(2)

where P – the property under consideration (i.e. glass transition temperature, viscosity, plateau modulus etc.) and C – the concentration (preferably in mol %)

For a better comparison of the plasticizing efficiency it is recommended the concentration is expressed in mol %.

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Using substances with the same or a very similar molecular weight, vol.% or weight % may alternatively be used.

Due to the wide variety and the large constitutional distribution of materials claimed to be plasticizers, a deeper knowledge about the specific effects of representative molecular model species on rheological, viscoelastic and thermal properties of rubber mixes could be technically obtained. Therefore the aim of the present contribution is to investigate the influence of the molecular structure of well defined hydrocarbons as model plasticizers on the low-temperature properties and the viscosity of non-polar types of rubber (NR, BR, SBR, EPDM). In addition to these general goals, other influencing factors like the polymer solvent-interaction-parameter $\chi$ (reduced free energy of mixing) and the solubility of the model plasticizers are investigated. For selected unsaturated species, the incorporation into the elastomer network during vulcanization as well as the reduction of the crosslinking efficiency is briefly examined.

**Experimental**

**Materials**

Non-polar EPDM, NR, BR and SBR types of rubber were used in the as-delivered state. The characteristics are given in Table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Commercial Name</th>
<th>Tg (°C)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,4-polybutadiene</td>
<td>cis-BR</td>
<td>-104</td>
<td>-6</td>
</tr>
<tr>
<td>cis-1,4-polysoprene</td>
<td>NR</td>
<td>-63</td>
<td>+38</td>
</tr>
<tr>
<td>Poly(ethylene-co-propylene)</td>
<td>EPDM</td>
<td>-51</td>
<td>-</td>
</tr>
<tr>
<td>Poly(butadiene-co-styrene)</td>
<td>SBR</td>
<td>-49.5</td>
<td>-</td>
</tr>
<tr>
<td>1,2-polybutadiene</td>
<td>1,2-BR</td>
<td>-40</td>
<td>-</td>
</tr>
</tbody>
</table>

**Sample preparation**

Unfilled mixes with a plasticizer content of 40 % vol. were prepared in a laboratory mixer (Haake Rheocord) at a filling factor of 73 % and a rotor speed of 20 rpm. The mixing time was extended until a constant torque was reached. Higher concentrations of plasticizers were obtained by supplementary swelling.

**Crosslinking**

The systems were crosslinked by sulfur (TMTD/S) or peroxide (DCP) at the corresponding rheometer optimum ($t_{95}$). The crosslink density was determined from stress-strain curves by using the Mooney-Rivlin equation [13].

**Differential Scanning Calorimetry (DSC)**

The glass transition temperatures (first derivative of the heat flow vs. temperature) and low temperature solubility limits were determined with a Du Pont differential scanning calorimeter 910 at a heating rate of 100 °C/min.

**Viscosity**

The viscosity of the softened mixes was recorded with a capillary viscosimeter (Goetfert) as a function of shear rate and temperature.

**Result and discussion**

**Effects on glass transition temperature**

The hydrocarbons used in this study are solvents for the particular rubbers in a specific concentration range. As long as the polymer-hydrocarbon systems form real solutions (single-phase systems) a linear decrease in the glass tran-
sition temperature of the rubber as a function of the hydrocarbon concentration is observed. The efficiency of the hydrocarbons as plasticizer (see Eq. 2) is exhibited only in the single-phase region (below the critical solubility limit). For this reason the solubility ratios as a function of the molecular structure of hydrocarbons and then their effectiveness as plasticizers are considered first.

Tg-Concentration-Phase Diagrams

Tracing the DSC-thermograms as a function of the hydrocarbon concentration results in two groups of Tg-concentration-phase diagrams:

(i) entirely miscible systems demonstrate only one Tg at any concentration and no other thermal transition typical for the hydrocarbon or the rubber respectively

(ii) partially miscible systems show a linear Tg-decrease up to the critical solubility limit (at high or moderate polymer concentrations). If the solubility limit is reached the Tg is no longer concentration-dependent. Above this limit there is no further reduction of Tg. The plasticizing efficiency (see Eq. 2) tends to zero.

Representative examples for the two groups of phase behavior are shown in Fig. 1. Cis/trans-decaline is miscible with EPDM and leads to a continuous decrease of the Tg if the concentration increases. In contrast to this, dodecane (NDA) decreases the Tg of EPDM only until the critical solution concentration is reached and the specific signal for the melting process becomes obvious [15]. Above of this critical concentration the Tg of the rubbery phase remains almost constant.

Irrespective of the chemical nature and the microstructure of the rubber, systems of the first group contain C6 to C12 hydrocarbons with very low melting temperatures. The solubility of pure species is driven by a large contribution of the mixing entropy [16]. By increasing the molecular weight of hydrocarbons the solubility is impaired because a reduced gain in mixing entropy and a high tendency of phase separation due to the crystallization enthalpy [19].

The more interesting species are non-crystallizing C10 or C12 hydrocarbons, which contain of mixtures of isomers, like cis/trans-decaline, TNB and TIB. Because these species exhibit considerably lower freezing points than many of the technically used mineral oils, they are able to attain solubility over the technically interesting concentration range.

As for cis/trans-decaline / EPDM (Fig. 1a) the isomer mixtures TNB, IDA and TIB are nearly miscible with NR (Fig. 2) and can exhibit their plasticizing efficiency over a broad concentration range. By adding 30 % vol. of TNB to NR the Tg is decreased to −93°C. Effects of a similar magnitude are observed for IDA and TIB.

Changing the thermodynamic characteristics of the rubber/plasticizer-system the Tg-concentration-phase diagrams are changed correspondingly. The use of SBR 1500 encourages phase separation of the non-polar hydrocarbons TNB, IDA and TIB respectively (Fig. 3). This can be attributed to the solubility parameter difference between NR and SBR (18). However, in a technical interesting concentration range up to 50 %vol. the plasticizing effect is clearly demonstrated by the non-crystallizing isomer mixtures.

More common is the phase separation at moderate concentrations when pure hydrocarbons are employed. As a matter of fact the particular melting temperature of the hydrocarbon is of secondary importance for the phase separation. It was observed that pure hydrocarbons with high melting temperatures (Tm), above the Tg of the pure rubber, can be active in decreasing the Tg of the entire system. This results in typical eutec-
Prominent examples were found in the group of C\textsubscript{12} hydrocarbons:

(i) NDA(T\textsubscript{m} = -6 °C) is able to decrease the T\textsubscript{g} of EPDM up to 40 °C below the own T\textsubscript{m} of -6 °C (Fig. 1b)

(ii) CDA acts in NR or SBR as a plasticizer at more than 120 °C below the T\textsubscript{m} of 62 °C (Fig. 4)

Even taking account of the current lack in thermodynamic data about the systems under consideration, one can attribute the observed phenomenon to the free energy of solvation of rubber chain segments, which has to be higher than the free energy of crystallization of the hydrocarbons. The critical solubility limits at low temperatures for the investigated systems are indicated in Tab. 3. Disregarding the special impacts at the liquid-liquid phase separation at low temperatures, i.e. the easier enthalpy-driven crystallization of larger hydrocarbon molecules, the following points can be drawn from the data in Tab. 3.

(i) The critical solubility limit of hydrocarbons decreases with the number of carbon atoms

(ii) Specific interaction between polymer and the hydrocarbons extend the single-phase concentration range.

(iii) Regardless of the polymer matrix, pure cyclic hydrocarbons show a better solubility as linear or branched hydrocarbons.

(iv) Compared with n-alcanes or i-alcanes, olefins have higher concentration limits in polydienes.

(v) The critical solubility limit increases for unsaturated hydrocarbons in polydienes in the sequence: NR < BR < SBR

(vi) In EPDM the critical solubility limit of the decreases in the sequence: saturated hydrocarbons > olefins > aromates

**Plasticizer Efficiency: T\textsubscript{g}-Decrease**

The slope of any T\textsubscript{g}-concentration relationship at high polymer concentrations represents the plasticizer efficiency with regard to low-temperature flexibility of the polymer. By comparing T\textsubscript{g}-concentration-phase diagrams of C\textsubscript{12}-hydrocarbons in polydienes it becomes obvious that the most powerful influence is exerted by the shape of the molecules (Fig. 5). The nominal results for all systems investigated are shown in Table 4 and 5.

Concentrating on C\textsubscript{12}-hydrocarbons in polydienes first, the effects of the molecular structure can be easily observed. The largest plasticizer efficiency in terms of T\textsubscript{g}-decrease is provoked by linear hydrocarbons NDE and NDA followed by the slightly branched TNB and than by the more compact molecule species TIB and IDA. The smallest effect is obtained from cyclic molecules CDE > CDA > CDT. From these results it can be stated that the plasticizing efficiency with regard to low-temperature flexibility of rubber generally decreases in the sequence of the molecular shape:

linear > branched > cyclic

The contribution to the T\textsubscript{g} lowering controlled by the molecular shape is
only slightly influenced by existing double bonds in NDE, TNB, TIB, CDE and CDT. The increased polarisability of these materials that favor the dipol-dipol interactions and hence the solubility, is of minor significance for the Tg-decrease. The same type of influence of the double bond becomes evident in linear and cyclic mono-olefines. NDE in all investigated polydienes has a more efficient impact than does the saturated NDA. The relative effect appear for the cyclic C12 hydrocarbons CDE and CDA. Shape effects due to the presence of one or more double bonds in the molecule have to be also considered.

One possibility of obtaining a better understanding of the structure-property relationship of molecular structures: (linear > branched > cyclic), arises when the internal flexibility of the molecule as well as the space needed for the respective structures for rotation and translation movements on a molecular scale. With regard to linear and branched molecules an increasing degree of branching the backbone of the molecule increases the stiffness (inflexibility) of the molecules. By reducing the length of the backbone the radius of gyration and the moment of inertia is also reduced. In the same direction the physically not quite uniquely defined “free volume” decreases. Therefore in single phase systems the plasticizing effect is controlled by factors which contributes to the “free volume”, like the molecular moment of inertia and consequently the thermal expansion coefficient.

This structure-property effect is particularly apparent from the comparison NDE > NDE > TNB >> IDA as well as NDA > CDA and CDE > CDT > CDA for all examined polydienes (Tab. 4).

As a result of the branching, the backbone is reduced from 12 C atoms to 9 for TNB or to 7 C atoms for IDA. In addition the molecular stiffness of IDA is increased because of 2 quaternary and 1 tertiary C-atom in the molecule. A larger stiffening and radius of inertia reducing effect is achieved for CDT by the introduction of 3 double bonds in the C12-ring. As evidence supporting this interpretation, the correlation between the plasticizing efficiency and thermal expansion coefficient of selected C12 hydrocarbons is given in Fig. 6. By increasing the thermal expansion coefficient of the plasticizer more “free volume” is introduced in the system irrespective of the rubber matrix. The magnitude of the effect observed is controlled by the nature of the rubber matrix, which also is influencing the “free volume”.

| Table 3. Critical low temperature solubility concentrations of hydrocarbons in rubbers |
|---------------------------------|--------|--------|--------|
| Hydrocarbons | BR | NR | EPDM | SBR | 1,2-BR |
| Octane | n.d. | n.d. | 28 | n.d. | n.d. |
| Decane | 2 | n.d. | 18 | n.d. | n.d. |
| Dodecane (NDA) | 3 | 7.5 | 14 | 7.5 | > 20* |
| Dodecene (NDE) | 8 | 15.5 | n.d. | 20 | > 20* |
| Tri-n-butene (TNB) | 60 | - | n.d. | 75 | > 20* |
| Isododecane (IDA) | 10 | 90 | n.d. | 55 | > 20* |
| Tri-i-butene (TIB) | n.d. | 80 | n.d. | 60 | > 20* |
| Cycloododecane | 20 | 15.0 | n.d. | 12.5 | > 20* |
| Cycloodocene (CDE) | 32 | 55.0 | n.d. | 60.0 | > 20* |
| Cycloodecatriene (CDT) | 80 | 58.0 | n.d. | 65 | > 20* |

| Table 4. Plasticizer Efficiency ΔTg/ΔC (% vol.) \( \text{of C}_{12} \) Hydrocarbons in all purpose rubber |
|---------------------------------|--------|--------|--------|
| Hydrocarbon | BR | NR | SBR | 1,2-BR |
| NDA | 0.55 | 1.02 | 1.45 | 1.49 |
| NDE | 0.57 | 1.11 | 1.62 | 1.64 |
| TNB | 0.27 | 0.98 | 1.30 | 1.31 |
| IDA | 0.22 | 0.56 | 0.55 | 0.75 |
| TIB | 0.56 | 0.66 | - | - |
| CDA | 0.05 | 0.21 | 0.44 | 0.51 |
| CDE | 0.19 | 0.49 | 0.62 | 0.68 |
| CDT | 0.08 | 0.31 | 0.44 | 0.75 |

![Fig. 6. Correlation between the thermal expansion coefficient of \( \text{C}_{12} \) hydrocarbons and the plasticizer efficiency](image)
Equivalent structure-property relationships are also observed for EPDM (Tab. 5). Here it is reconfirmed that for a constant carbon number, the plasticizing effect of cyclic hydrocarbons (cyclooctane, decaline and CDE) is significantly smaller than for the linear model plasticizers (octane, decane and NDA). Unsaturated linear hydrocarbons, such as NDE, are perceptibly more effective in non-polar EPDM than the corresponding saturated substances (NDA). The investigated alkyl-benzenes likewise show a high effect. The results show that effects from the molecule size and shape are overlapped by effects of the polymer-hydrocarbon interaction.

Apart from the plasticizing efficiency, account must also be taken of the available solubility range when considering the technically useful effect. By doing the comparison it becomes obvious that the most effective plasticizers also have the lowest low-temperature solubility. This limiting structure-property relationship highlights the advantage of isomer mixtures like TNB with a high plasticizing efficiency over a large concentration range.

**Polymer-Solvent Interaction**

The $\chi$ parameters determined by the equilibrium swelling measurements represent a measure for the thermodynamic solvent quality of the hydrocarbons in the respective types of rubber (Fig. 7). There is a concentration dependency of the $\chi$-parameter in all systems investigated. Therefore comparisons are made at constant volume fraction of the polymer in the swollen network. In all investigated polydienes the results show an improvement of solvent quality, marked by a decrease in the $\chi$-parameter, in the sequence IDA < NDA < NDE < TNB < CDE < CDT.

Firstly, the influence of the double bonds and secondly that of the molecular structure is evident. In the reverse direction, the plasticizing efficiency of the C12 hydrocarbons is decreased.

With substantially more detailed information for EPDM, the same quantitative relationship occurs (Fig. 8). The careful evaluation of the equilibrium swelling behavior shows that the interaction with hydrocarbons is influenced as follows:

(i) With the number of the C-atoms in the molecule, the interaction is favored
(ii) Double bonds worsen the interaction incrementally in proportion to their number.

**Table 5. Plasticizer Efficiency (C/mol)**

<table>
<thead>
<tr>
<th>Group</th>
<th>$\Delta T_g$/$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane C8</td>
<td>95</td>
</tr>
<tr>
<td>Iso-octane C8</td>
<td>93</td>
</tr>
<tr>
<td>Cyclo-octane C10</td>
<td>33</td>
</tr>
<tr>
<td>Decane C10</td>
<td>128</td>
</tr>
<tr>
<td>cis/trans-decaline C12</td>
<td>69</td>
</tr>
<tr>
<td>Butylbenzene C12</td>
<td>156</td>
</tr>
<tr>
<td>Dodecane C12</td>
<td>138</td>
</tr>
<tr>
<td>1-Dodecene 218</td>
<td></td>
</tr>
<tr>
<td>Tri-n-butene 252</td>
<td></td>
</tr>
<tr>
<td>Iso-dodecane 140</td>
<td></td>
</tr>
<tr>
<td>Cyclo-hydrocarbons 67</td>
<td></td>
</tr>
<tr>
<td>Cyclo-dodecatriene 80</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 8. Influence of the molecular structure on the polymer-solvent interaction for hydrocarbons in EPDM**

**Fig. 7. Concentration dependence of the $\chi$-parameter of the C12 hydrocarbons in a) NR and b) SBR**

**Fig. 9. Relationship between the polymer-solvent interaction parameter $\chi$ and the plasticizer efficiency a) $\Delta T_g$/$\Delta c$ and b) $\Delta T_g$/$\Delta c \times m^2$**

quantity (and position in linear molecules)
(iii) Branches worsen the interaction in proportion to their quantity in the molecule
(iv) Cycloalkanes show the best interaction
If the plasticizer efficiency $\Delta T_g/\Delta C$ ($^\circ$C/molecule$^{-1}$) is correlated with the thermodynamic solvent quality, expressed by the $\chi$-parameter, linear relationships $\chi$ vs $\Delta T_g/\Delta C$ are obtained for groups of hydrocarbons with the same carbon number (Fig. 9a). Taking into account the contribution of the moment of inertia of the hydrocarbons (m$^2$), for all groups a single master-relationship is obtained (Fig. 9b). This relationship underlines the importance of the molecular shape for the plasticizer efficiency.

So there is a causal relationship between the molecular structure and the plasticizing efficiency and the plasticizer efficiency and the thermodynamic solution quality of the molecular species. A moderate to a poor solution quality (middle to high $\chi$-parameters) leads to a similar graded increase of the plasticizer efficiency as the moment of inertia does. Therefore it holds:

$$\Delta T_g/\Delta C \propto \chi m^2 \quad (3)$$

The optimal effect is obtained if the plasticizer molecules demonstrate a larger anisometry and molecular mass and interact to a lesser extend with the rubber chains.

### Influence of the Rubber

If the plasticizing efficiency of a hydrocarbon is followed in various types of rubber, it is established that with decreasing $T_g$ of the rubber, the efficiency decreases roughly in a linear way (Fig. 10). Hence the plasticizing effect decreases in the sequence:

1.2-BR > SBR > NR > BR.

As expected for the more effective hydrocarbons (NDA, NDE, TNB) the slope of the linear dependencies are higher than for the cycloalkanes (CDE, CDA, and CDT).

Starting from the assumption that the free volume of rubber is approximately equal for its respective glass transition temperature, this result can be understood by virtue of the temperature-dependent decrease of the inner mobility of the molecules and their “free volume”.

### Effects on melt viscosity

To evaluate the effect of interaction between plasticizer and rubber on rheological behavior of on unfilled mixes, two systems were selected that have different effects: EPDM decaline (good interaction) and EPDM dodecanes (bad interaction). The comparison of the melt viscosity at temperatures of 80 °C to 120 °C in the single-phase concentration range (up to 30 Vol.%) shows a considerably greater decrease in viscosity for EPDM dodecane than for the system EPDM-Decaline with the good interacting.

The higher viscosity lowering caused by dodecanes can be explained both by the “free-volume” theory [10] and by the “lubricant” theory [8]. Moreover, the better solvent decaline causes a stronger coil expansion of the EPDM chains, whereby internally generated retraction forces oppose the transport process.

As the two representative examples show, the plasticizing effect is also higher in relation to melt viscosity when the solvent is poor or moderate.

### Conclusions

The efficiency of non-polar plasticizers is strongly related to the constitution of the molecules. High moments of inertia of the molecules and larger thermal expansion coefficients guarantee an efficient decrease of the $T_g$ of the rubber under consideration. In addition a poor interaction between the plasticizer and the rubber is required for a better efficiency in both the $T_g$-decrease and the rubber melt viscosity.

### References


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