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Structural-relaxation Mechanism of Glassy-like Polymers Plasticization

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Abstract Structural and relaxation aspects of plasticization on the example of cellulose acetate plastics are studied. Three types of plasticization are examined: the plasticizer is miscible with the polymer at processing and operating temperatures; the plasticizer is miscible with the polymer at processing temperature and is immiscible at the operating temperature; the plasticizer is also immiscible at the operating temperature, but does not form the separate phase during molding. Plasticized material properties are determined not only by the manner of plasticizer effect on the material structure formation, but also by the extent of its influence on the relaxation rate at the test temperature.

Keywords Plasticization, Cellulose Acetate, Miscibility of Components, Structure, Glass Transition Temperature, Relaxation, Properties

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1. Introduction

Development of polymeric material processing technology is aimed at the increase of equipment performance. Hence, the article molding time becomes comparable or exceeds that of polymeric material relaxation. Sometimes, this is the necessary condition for adhering required property, for instance, when fibers or oriented films are manufactured. However, relaxation time of a polymeric material should commonly be shorter than the article molding time.

Plasticization is one of the methods reducing polymeric material equilibration time. Plasticizer must also perform this function in the finished product preserving its properties in temperature and mechanical stress ranges specified by operating conditions. It is noteworthy that complete separation of the plasticizer effect on pre-history of the sample and its behavior during experimental studies of plasticized polymer properties is hardly possible.

Physicochemical and process aspects of plasticization of polymers are optimally discussed in monographs[1-5]. The authors of these works have noted that many experimental facts are not adequately explained. The works[6-7] contain the data regarding compatibility and properties of diacetate of cellulose plasticizied with diehylphthlate. The general theoretical framework for quantifying changes in the “high-frequency” relaxation dynamics of mixtures based on classical transition state theory has been developed[8]. The antiplasticization-to-plasticization transition phenomena was observed in high-frequency dielectric measurements. The phenomena of antiplasticization was investigated was observed in the work[9]. Oligomeric polycaprolactone was used for the modification of cellulose acetate by reactive processing in the works[10, 11]. Plasticization of cellulose diacetate by graft copolymerization of ε-caprolactone and lactic acid was investigated in work[12]. The thermal and mechanical properties of blends of poly(ε-caprolactone) with cellulose acetate in different proportions were investigated by differential scanning calorimetry and tensile property measurements[13].

Structural and relaxation aspects of glassy polymer plasticization may be considered on the example of cellulose-acetate plastics. The subject of research is selected due to the following reasons:

- cellulose acetate can only be processed into articles in the plasticized state;
- cellulose-acetate plastics are operated under permanently varying stresses reasoned by the fact that articles from them are virtually exclusively used in combination with other materials (metal, glass, synthetic polymers), and when temperature changes, strains due to difference in thermal expansion coefficients occur.

In the recent decade, the investigations were aimed at creation of biodegradable plastics from cellulose acetate[10-13]. This ultimate objective defined the plasticizer selection. In this work, we attempted to clear out general approaches to analysis of the plasticizing action of various types of plasticizers.

2. Experimental

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The investigation was carried out on industrial production run of cellulose acetate which has hydroxyl group substitution degree 2.5 and average degree of polymerization 275. Plasticized compounds were produced by mixing components in a paddle mixer. Thermal plastication was carried out in a single-screw molding machine with screw diameter of 25 mm. Depending on the type and concentration of plasticizer the temperature in the course of extrusion varied to get melt viscosity of 10^3 - 10^4 Pa·sec. Test samples were produced with the molding machine providing 20 cm^3 as maximum injection capacity and clamping force of 10 t. Total manufacturing cycle of one cast molding was 60 sec. The time of molten state is provided during 10 min.

Films with thickness of 0.08 mm were prepared from 10% solution in acetone on the glass substrate.

Glass transition temperature was determined according to thermo-mechanical curves made at permanent tensile stress equal 0.4 MPa and rate of temperature increase is 2 deg/min. The phase separation point refers to the plasticizer concentration at which the glass transition temperature of cellulose acetate stopped decreasing in spite of plasticizer concentration increases.

Diethyl phthalate vapor pressure over plasticized cellulose acetate was measured at 50ºC by Knudsen effusion method. The pressure in the system during the experiment was $(2\text{-}8)\cdot 10^{-4}$ Pa. Test samples were made in the form of films which were then triturated with the particles dimension of maximum 0.1 mm. The diethyl phthalate concentration at which minimum vapor pressure rate changes to pure plasticizer vapor pressure was referred to as the phase separation point.

Capillary viscosimeter with capillary length of 12.4 mm and diameter of 1.6 mm was used to carry out rheological analysis.

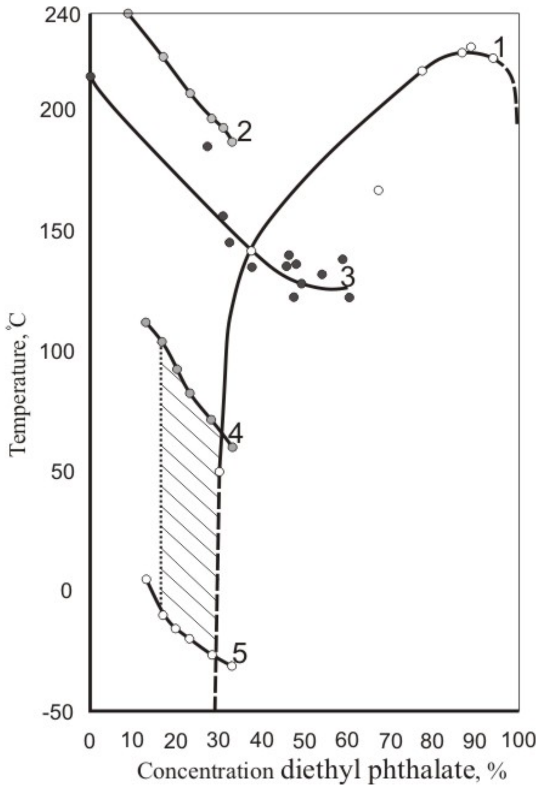
Vicat softening point was identified in liquid medium under the load of 10 N according to ISO 306. Friability temperature was assessed through analysis of srtrength-strain diagram (ISO R52) made at different temperatures in a tensile testing machine chamber. Friability temperature refers to the temperature at which brittle rupture was first observed with the test temperature decreases. Impact strength was assessed in unnotched samples according to the method of Sharpy (ISO 179). The flexural test measures the force required to bend a beam under three point loading conditions was determined according to ISO 178.

3. Results and Discussion

Strictly speaking, a possibility of using a particular compound as a plasticizer may be assessed by composing a diagram of the polymer-plasticizer system state and correlation of phase equilibrium curve location with the range of plasticizer concentrations and article operating temperatures used in practice.

Figure 1 shows experimental diagram of cellulose acetate – diethyl phthalate system state. The phase separation curve (1) is composed basing on results of differential scanning calorimetry method obtained at diethyl phthalate concentrations exceeding 60%[6]; by degeneration of cellulose acetate film glass transition temperature dependence on absorbed diethyl phthalate[7], and dependence on the composition of the polymer-plasticizer system with respect to diethyl phthalate vapor pressure at 50°C[14].

As observed in the Figure, the flow temperature determined as the temperature providing effective viscosity of $5\cdot10^3$ Pa·s[15] at the shear stress on the capillary viscosimeter wall equal $2.23\cdot10^4$ Pa lies intentionally above the separation curve, i.e. in the area of dynamic miscibility of cellulose acetate with diethylphthalate. For obtained articles, the field of formulations and operating temperatures is limited by "heat resistance" parameter from above and friability temperature from beneath. These parameters, together with the flow temperature, also limit the range of plasticizer concentrations actually used in industry.

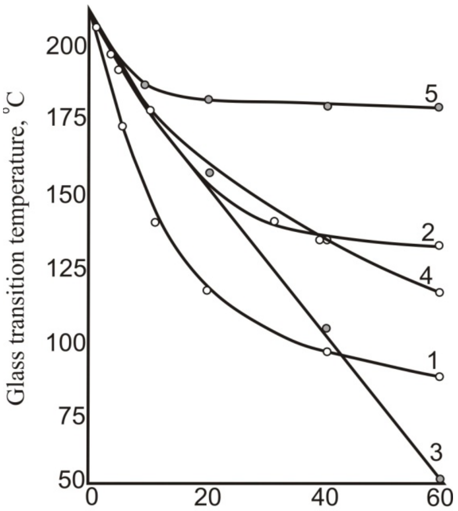


Curves: 1 – phase equilibrium; 2 – flow temperature; 3 – glass transition temperature; 4 – thermal stability; 5 – brittle point.
Dashed area represents the field of formulations and operating temperatures for cellulose acetate plastics.
In the same Figure, dashed lines indicate a field representing the range of industrial plasticizer concentrations with permissible operating temperatures.

Figure 1. The state diagram for cellulose acetate (with substitution degree of 2.33) – diethylphthalate system

Designing of phase state diagrams for the polymer-plasticizer systems is highly labor-consuming process. This is the reason why, as a rule, for one or another plasticizer with a polymer, simplified miscibility evaluation methods are used, for instance, by minimal temperature of plasticizer-polymer mixture dissolution (transparent melt formation) at the same fixed concentration of the components. Miscibility is very often determined by degeneration of the glass transition temperature dependence on plasticizer concentration.

Figure 2 shows dependence of the glass transition temperature on plasticizers concentration for cellulose acetate plastics. In the studied range, dimethyl phthalate and triethylene glycol dipropionate reduce glass transition temperature of a polymer, as plasticizer concentration increases. Degeneration of the glass transition temperature dependence on bis(cyclohexenate)diethylene glycol concentration is observed already at 30% content of the plasticizer (curve 2), i.e. miscibility of this plasticizer with cellulose acetate is 30% of polymer mass or lower. This concentration is insufficient for obtaining plastics with the required selection of properties. Injection of higher bis(cyclohexenate)diethylene glycol concentrations causes partial separation of the plasticizer as a separate phase, as evidenced by occurrence of opalescence in samples obtained injection molding. As compared with plastics with equal portions of miscible plasticizers injected, such samples demonstrate increased heat stability and mechanical properties.



1 – dimethylphthalate; 2 – bis(cyclohexenate)diethylene glycol; 3, 4 – triethylene glycol dipropionate; 5 – samples (3) after annealing at 180°C. Samples 1-3 were obtained from melt, and sample 4 from solution.

Figure 2. Dependence of cellulose acetate glass transition temperature on plasticizer concentration and the injection method

This represents a version, in which excessive plasticizer (compared with its miscibility limit at the operating temperature) is separated in the form of the second phase directly during molding. However, as viscosity sharply increases during rapid melt cooling down, the phase separation may be avoided, and plasticizer concentration in the polymeric phase will exceed thermodynamic equilibrium level. This may be the long-term non-equilibrium state, in which the glass transition temperature is determined by the actual plasticizer concentration in the entire phase with the polymer. As the system is heated up above the glass transition temperature, however, conditions for the phase separation are formed and, as a consequence, the glass transition temperatures reaches the level of the equilibrium plasticizer concentration.

To confirm this fact, let us consider thermomechanical curves (Figure 3) of non-annealed (1, 2) and annealed (1’) cellulose acetate samples plasticized by triethylene glycol dipropionate and containing 40% (1, 1’) and 60% (2) of plasticizer from the polymer mass. Let emphasize once again that the plasticizer concentration increase leads to proportional glass temperature decrease for cellulose acetate in the whole range of concentrations (Figure 2, curve 3). On this basis, one might conclude that the components are miscible at the molecular level. However, thermomechanical curves have a feature - a knee and the second ascent indicating the presence of additional transition at 180°C (Figure 3, curves 1, 2). Temperature of this transition, observed at concentrations of 10% or higher, is independent of the plasticizer concentration[16].

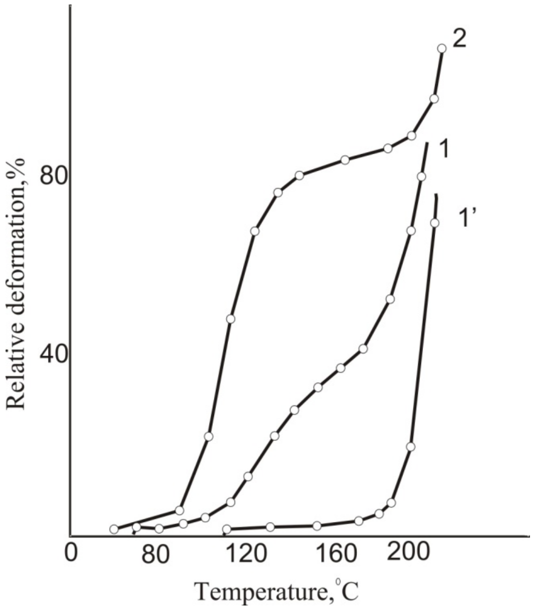


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Figure 3. Dependence of cellulose acetate glass transition temperature on plasticizer concentration and the injection method

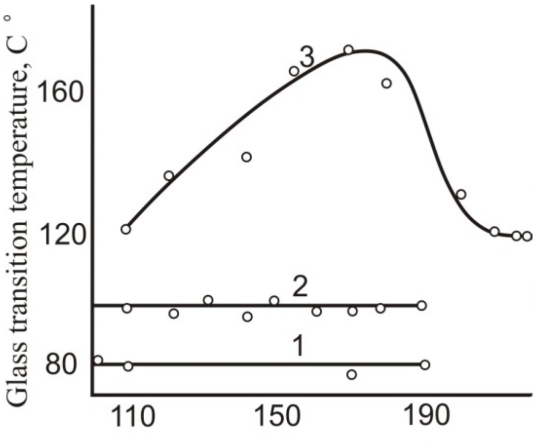
Samples preliminarily heat-treated has the glass transition which is, approximately, the second transition temperature on thermomechanical curves of primary samples, approaching the glass transition temperature of non-plasticized polymer (Figure 2, curve 5). This means that, similar to the case of heat treatment, during measuring data for thermomechanical curves of cellulose acetate - triethylene glycol dipropionate systems phases are separated.

Table 1. The effect of annealing on cellulose acetate plasticized by polyethylene butylenes glycol adipinate (MM-500)

Plasticizer concentration, %	Sample properties before and after annealing at 140°C during 1 hour									
	Tensile stress at break, MPa		Elongation at break, %		Specific blow viscosity, kJ/m^2		Heat resistance, °C		Friability temperature, °C	
	before mnealing	after annealing	before annealing	after annealing	before annealing	after annealing	before annealing	after annealing	before annealing	after annealing
33	34±1	36±1.5	25±2	16±1	82	35	64	85	- 5	- 5
29	38±4	39.5±1	16±4	14±2	82	58	78	93	- 5	- 5
23	51±1	53±3	12±2	14±3	23	56	91	103	5	- 5
17	75±1	80±9	10±1	10±1	25	48	110	120	15	20

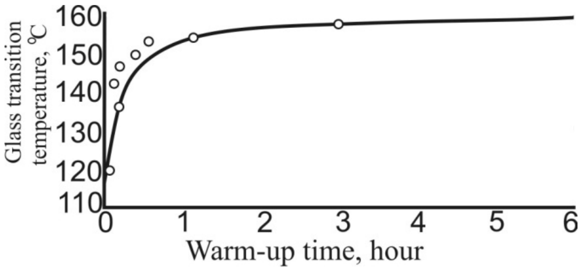
When composites with a plasticizer with good miscibility in melt and in oligoester plasticizer (limitedly, at operating temperatures) are processed, separation in the system has not enough time to happen due to increasing viscosity at melt cooling down, and the articles obtained are, to the first approximation, analogous to corresponding plastics based on diester plasticizers. Nevertheless, similar to the cellulose acetate - triethylene glycol dipropionate composite, the phase separation may not be obtained by annealing of samples. Hence, heat resistance of plastics is significantly increased without any change of their friability temperature (Table 1).

Absolute glass temperature change depends on temperature and duration of annealing (Figure 4 and Figure 5, respectively).



Plasticizer content is 40 mass % of the polymer: 1 – glycerol triacetate; 2 – dimethylphthalate; 3 – oligoester (MM 500). Annealing time is 1 hour.

Figure 4. Dependence of glass transition temperature on annealing temperature for cellulose acetate plastics



Oligoester (MM 500) content is 40 mass % of the polymer.

Figure 5. Dependence of glass transition temperature on annealing time at 140°C for cellulose acetate plastics

Glass transition temperature dependence on annealing temperature looks like a curve with a maximum, which is due to the fact that heating at temperatures close to the flow point may not cause the phase separation, because solubility of oligoester in cellulose acetate at these temperatures is sufficiently high. During further cooling of the samples in the air at a rate of 5 deg/min, plasticizer transition to the second phase cannot be completed.

Optimal annealing temperatures are by 30-50°C higher than the glass transition temperature of the primary composite. Hence, segmental mobility of the polymer is sufficiently high, but oligoester miscibility with cellulose acetate is comparatively low yet. Composites with plasticizers miscible with the polymer do not change their properties at annealing in the whole range of processing and operating temperatures (Figure 4, curves 1 and 2).

It is of interest that the glass transition temperature of not heat treated cellulose acetate samples, which were plasticized by triethylene glycol dipropionate, depends on the production method of test samples. When the samples are produced from solution, by gradual evaporation of the diluter, conditions for partial phase separation are formed (Figure 2, curve 4). However, when the samples are produced from the melt (by injection molding, curve 3), the phases have not enough time to separate and, consequently, at triethylene glycol dipropionate concentration of 40% or higher the glass transition temperature of samples obtained from the melt is much lower than that of samples obtained from the solution.

Therefore, we have three types of plasticization, when:

1) the plasticizer is completely miscible with the polymer at processing and operating temperatures (dimethyl phthalate, diethyl phthalate, glycerol triacetate);

2) the plasticizer is completely miscible with the polymer at processing temperatures, but is phase-separated during production of articles (bis(cyclohexenate)diethylene glycol);

3) the plasticizer is completely miscible with the polymer at processing temperatures and is not phase-separated during cooling of articles, despite the fact that thermodynamic miscibility limit at operating temperatures is lower than the actual plasticizer concentration in the polymer (triethylene glycol dipropionate, oligoester plasticizers).

In all considered cases, we deal with the systems characterized by the Upper Critical Mixing Temperature (UCMT). However, it is seen that, despite thermodynamic immiscibility of components at operating temperatures, thermodynamic miscibility between the plasticizer and the polymer at the flow point may be sufficient sign for successful operation of articles. In this case, we deal with kinetic miscibility of the plasticizer with the polymer. Lubricants or structural plasticizers (does not matter how we call them) work according to the kinetic miscibility mechanism.

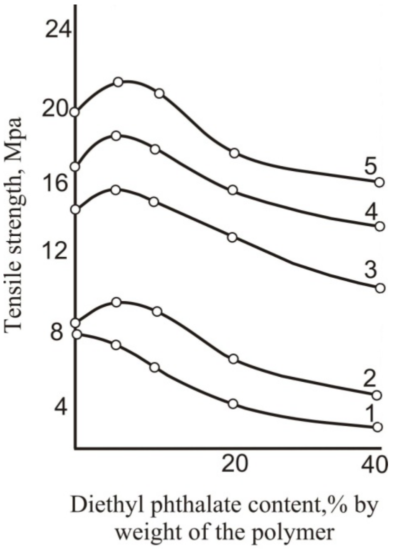
Certainly, before such systems can be recommended for use in practice, we have to prove that the phase-separated plasticizer does not migrate to the surface of articles or this migration does not hinder their operation in any way.

The above-considered examples again require attention to be paid to the role of prehistory of the studied sample. The structural sample, i.e. the answer to the question how the structure of real samples differs from the ideal, thermodynamically equilibrium one, is of importance for articles molding from solution and even for production of films from plasticized cellulose acetate solutions.

We believe that in case of the so-called “anti-plasticization” we also deal with common plasticization, however, prehistory of the studied samples, technique and temperature of tests are so that their results are interpreted mistakenly as “anti-plasticization”.

It is commonly known that mechanical properties of films molded, even from diluted solutions, depend greatly on the solution concentration[4]. Plasticizer injection is identical to the change of polymer concentration in the solvent the more so that, as a rule, the solvent is selected so that it dissolves both the polymer and the plasticizer. It is found on the example of various industrial cellulose acetate samples (Figure 6) that when diethyl phthalate is injected in the amount of 3-10% of the polymer mass elongation at break is not decreased, but, in contrast, increases and then begins to decrease, as greater concentrations of the plasticizer are injected[17]. In this case, elongation at break increases with the plasticizer concentration in the whole range of 0 to 40%.

Increasing ultimate tensile stress and yield stress at elongation in the range of low plasticizer concentrations (the co-called anti-plasticization) is observed only in tests carried out at temperatures intentionally far from the glass transition temperature of the polymeric materials, because relaxation processes are decelerated at low temperatures and, as a consequence, the plasticizer effect on mechanical properties is mostly provided by its influence on the sample prehistory. In the extreme case (at the friability temperature), the relaxation time is extremely long and properties are defined by the structural factor exclusively, i.e. by the extent of plasticizer participation in formation of more or less structurally homogeneous sample.



Test temperature, °C: 1 – 100; 2 – 50; 3 – 0; 4 – (-20); 5 – (-40)

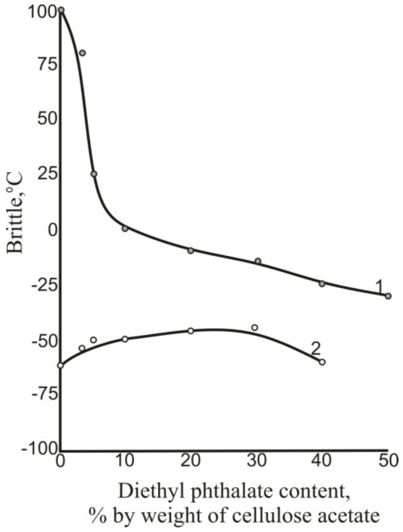
Figure 6. Dependence of tensile stress at break on diethylphthalate concentration for cellulose acetate films

As the test temperature approaches the glass transition point, increasing mobility of structures caused by plasticizer begins dominating. The plasticizer concentration increase reduces the glass transition temperature and, consequently, is identical to the test temperature increase that significantly obsoletes plasticizer contribution into the sample prehistory.

The plasticizer effect of the sample prehistory is specially demonstrated by comparison of concentration dependences of friability temperature for samples obtained from melt or solution (Figure 7).

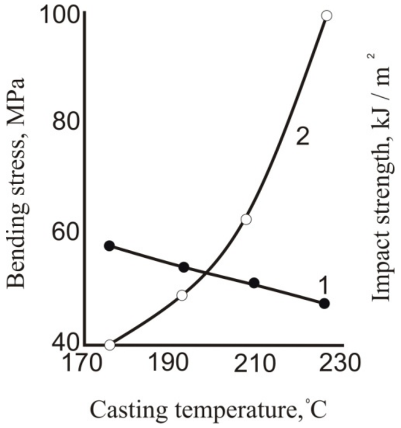
If the sample was molded from solution, melt flow increase with plasticizer concentration promoted formation of more homogeneous structure approaching the equilibrium. The friability temperature smoothly decreases simultaneously with increasing plasticizer concentration (Figure 7, curve 2). When samples are obtained from solution (curve 1), plasticizer influence on the structure formation is less expressed and is overlapped by decrease of plasticizer molecule mobility at the test temperature, if it is significantly lower than the plasticizer freezing point. In this case, plasticizer is able to prevent development of rubber-like deformation playing the role of the inert filler.

Interpretation of the test results, especially for samples molded from solution, requires consideration, anyhow, of structural homogeneity of tested samples. For instance, the bending stress value at deformation rate of 5 mm/min is virtually independent of molding temperature for test samples (Figure 8, curve 1), whereas blow viscosity is determined by the molding temperature, because with the melt temperature increase structurally more homogeneous samples are formed.



Method of preparation: 1 – from melt; 2 – from solution

Figure 7. Brittle temperature dependence on diethylphthalate concentration



Plasticizer – diethylphthalate, 40 mass % of the polymer

Figure 8. Dependence of bending stress (1) and blow viscosity (2) on molding temperature for cellulose acetate plastic

4. Conclusions

It should be concluded that the three types of plasticization are existed: the plasticizer is miscible with the polymer at processing and operating temperatures; the plasticizer is miscible with the polymer at processing temperature and is immiscible at the operating temperature; the plasticizer is also immiscible at the operating temperature, but does not form the separate phase during injection molding.

The reducing of the relaxation time for macromolecules, plasticization allows production of structurally homogeneous materials and, at the same time, promotes relaxation of stresses, which occur during operation of the article, i.e. provides deformation of polymeric material, in the given operation range without integrity break (without degradation). We believe that these are premises for stating definitions of "plasticizer" and "plasticization".

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