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Plasticisation of Polymers

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The Review surveys published information on the development of theories of the plasticisation of amorphous and crystalline polymers by plasticising additives of low and high molecular weight, the phenomenon of antiplasticisation, the action of small additions of plasticisers, and the effect of the chemical structure, size, and shape of plasticiser molecules on the plasticisation of polymers.
The applicability of modern physical and physicochemical methods (thermomechanics, thermography, rheology, nuclear magnetic resonance, infrared spectroscopy, dielectric and mechanical losses) to the investigation of plasticised systems is reviewed.
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I. INTRODUCTION

The development of effective methods for the modification of macromolecular compounds[1] is of great value for future progress in this field, and plasticisation plays an important part among these methods[2]. Indeed, polymers rarely find practical use in the individual (pure) form, owing to their brittleness, difficulty of processing into goods, tendency to crack during storage and in use, etc. Plasticisation is able not only to eliminate these defects but also to confer a new combination of valuable technical properties on the modified polymer.

The problem of the plasticisation of polymers has attracted the attention of many investigators, whose results in this field have been partly summarised in earlier reviews[3-5] and a series of papers by Soviet and foreign authors[6-13]. The present Review is devoted mainly to the part played by the chemical structure of the plasticiser in the plasticisation of polymers, blended systems, and modern methods for investigating plasticised polymers.

For a long time the problem of the plasticisation of polymers was solved exclusively by empirical methods. With the development of the science of polymers, and the expansion of knowledge of their structure, views on the nature of plasticisation also changed. The development of ideas on plasticisation can be arbitrarily divided into several stages. The first stage is characterised by a particularly empirical approach to the selection of plasticisers, the role of which was reduced merely to a lubricating effect. Then, beginning with the work of Obrist[14] (during the 1920s and 1930s), colloid-chemical concepts predominated, polymer–plasticier systems being regarded as lyophilic colloids, in which the plasticisers formed solvate sheaths on the surface of unsymmetrical particles of the polymer as the disperse phase.

However, more fundamental investigations of the nature of macromolecular compounds had already begun in the 1930s. The work of Kargin, Papkov, and Rogovin[15] showed that colloid-chemical concepts were not applicable to plasticised systems. The main kinetic laws of the behaviour of polymers during dissolution and swelling were established[16], and the heats of dissolution of vitreous polymers were studied as a function of the density of packing of the structural units.

During this period plasticisation was first interpreted as a factor diminishing the brittleness of polymers, promoting the occurrence of relaxation processes, and preventing the formation and growth of cracks under the influence of specific deforming forces[17,18]. Subsequently a quantitative relation was found between the strength of polymers and the duration of the action of deforming forces on them[19-22].

Considerable successes in studying the structure of polymers and their orientation behaviour were achieved by X-ray and electron diffraction methods[23,24]. Some part was played also by determinations of differential heats of sorption[25]. Ideas developed on the nature of the fluidity and elasticity of polymers[26,27] have remained unchanged until the present time.

It was also established[28-30] that linear polymers can exist in three physical states—vitreous, viscoelastic, and viscofluid—depending on the temperature. Two additional (intermediate) physical states—constrained-elastic and constrained-plastic—have since been established[31]; nuclear magnetic resonance has revealed[32] the existence below the glass point T_{gl} of several transition temperatures, the dependence of which on the chemical structure of the polymers has been studied.

The next stage in the development of ideas on plasticisation covered the 1940s to the early 1960s. During this period a fundamentally new approach to investigation of the plasticisation of polar and non-polar polymers was apparent especially in papers by Zhurkov and his coworkers[33-35]. Their researches enables them to formulate the now widely known rule of plasticisation—"the rule of equal mole fractions"—according to which the plasticising effect of polar plasticisers on polar polymers is the same at equal mole fractions of the former and is independent of the size, chemical nature, or structure of the plasticiser molecules. Roughly similar conclusions were reached by Fuoss[36] from a study of the plasticisation of poly(vinyl chloride), but with copolymers of vinyl chloride the laws of plasticisation were more complicated.

In a comparative study of the effect of the volume and molar concentrations of various plasticisers on the glass point of polymers, Kargin and Malinskii found[37,38] that the fall in the glass point of non-polar and weakly polar polymers conforms fairly closely to the "rule of equal

volumes" which they had deduced, according to which equal volume fractions of plasticisers produce the same plasticising effect. Since this rule and the above "rule of equal mole fractions" are obviously consequences of two different mechanisms of plasticisation, they are each obeyed only by certain systems, in which one of the mechanisms predominates, while many actual systems may exhibit larger or smaller departures from either rule [39].

Kargin and Slonimskii [40] established that small plasticiser molecules, while located between and separating the macromolecular chains, do not necessarily diminish the interaction between them, since the plasticiser itself is able to interact with macromolecular chains. They attribute the change in viscosity resulting from introduction of the plasticiser, i.e. the plasticising effect, mainly to a change in the geometrical arrangement of the molecules [40].

Energetic interaction of plasticiser molecules with certain functional groups in polymer macromolecules and the formation of a kind of molecular sorption compound have been noted qualitatively also in several other papers [41-43]. The action of plasticisers on polymers has been attributed [44] to the presence in polymer and plasticiser of groups capable of interaction, the most advantageous mutual arrangement, the shape of the plasticiser molecules, and purely geometrical factors.

A typical plasticiser is not distributed randomly in a polar polymer, since it interacts predominantly with the polar groups in the latter, blocking their force field [11]. It was established that agglomerating plasticisers significantly depress the glass point of polymers [40].

Kargin and his coworkers [45-47] showed that the rules of "equal mole fractions" and "equal volumes" applied to crystalline polymers, graft copolymers, and block copolymers.

New ideas on the structure of linear polymers, put forward by Kargin, Kitaigorodskii, and Slonimskii [48-50], provided a more accurate explanation of the nature and mechanism of plasticisation. This work opened up a new stage in the development of the theory of plasticisation.

Kargin et al. [51] studied the plasticisation of a rigid-chain polymer (cellulose) showing poor compatibility with plasticisers, and discovered two different mechanisms of plasticisation. They examined the action of plasticisers on cellulose in terms of the bundle theory of the structure of linear polymers. Plasticisation takes place within a bundle if the interaction energy of plasticiser molecules with active groups of the polymer chains is stronger than the intermolecular interaction in the polymer itself. The action of plasticisers which are completely miscible with the polymer leads to breakdown of any secondary structures. If the interaction of plasticiser molecules with the reactive groups in the polymer chains is significantly weaker than the intermolecular forces in the polymer itself, the plasticiser is able to interact only with molecules on the surface of the secondary structures: plasticisation is then accomplished only between bundles (interstructural plasticisation), without any significant change in the elastic properties of the system. Polymer materials obtained by interbundle plasticisation are characterised by great durability, high specific impact strength, and frost resistance [52,53].

Kozlov et al. [54] showed that plasticisation was possible both within and between bundles in the case of polycarbonates, which are characterised by relatively slow relaxation and crystallisation processes, and tend to form clearly developed secondary structures.

Kargin et al. [55] found that plasticisation of crystalline polystyrene produces a significant change in the conditions for formation of secondary structures characteristic of the unplasticised polymer. They note that with crystalline polymers equal fractions by volume of different plasticisers lead to the formation of spherulites of different sizes: the "rule of equal volumes" is not observed.

The new ideas on the mechanism of plasticisation are applicable, of course, also to amorphous linear polymers such as poly(vinyl chloride). [56,57] Thus the introduction of small quantities of a plasticiser into this polymer increases its degree of order [58-62]. In this case the plasticisers do not soften the polymer, but make it more rigid and brittle. The reflections on the X-ray diffraction photographs become sharpest at a plasticiser content of ~ 10 wt.%. [58,61]

With several vulcanised rubbers it has also been noted [63] that their mechanisal properties vary non-monotonically with small additions of plasticisers. This phenomenon has been explained by differences in the mobility of structural units, the stress peak at the apex of a microdefect being smoothed out.

It is possible [57] to explain the hardening of poly(vinyl chloride) by small portions of plasticisers in terms of interstructural and intrastructural plasticisation. Small additions of polar plasticisers cause interstructural plasticisation, the rigidity and strength of the polymer increasing, while the dielectric loss angle diminishes [64]; large portions of the same plasticisers, however, lead to intrastructural plasticicsation, accompanied by the opposite changes in the properties of the given polymer system. It is obvious that systems containing small proportions of plasticisers exhibit two opposite tendencies—to denser packing of chains and bundles, and to disorder under the influence of thermal motion—with the former ultimately predominating [65,66].

The variation in glass point produced by the introduction of small additions of plasticisers into crystalline polymers is oscillatory in character, as a consequence of structural changes in the polymer [67]. In several cases small additions of a plasticiser may cause the structural plasticisation of multicomponent systems, as has been demonstrated [68] for the Viniflex lacquer–tritolyl phosphate system.

Lipatov [69-71] investigated the vitrification of polystyrene and poly(methyl methacrylate), filled with glass powder and containing various quantities of a plasticiser (dimethyl phthalate), and established that the plasticisation of filled polymers is an interstructural effect, depending on the destruction of polymer–filler surface and polymer–polymer bonds.

2. PLASTICISATION AND CHEMICAL STRUCTURE OF PLASTICISERS

The above rules of plasticisation suggested by Soviet scientists played an important part in the development of ideas on the nature and mechanism of the phenomenon. The question naturally arises as to the extent to which the chemical structure of a plasticiser, or at least its homologous series, influences the plasticising effect. (The plasticising effect can be defined as the relative depression of the glass point, as the relative durability and increase in elasticity, or as the relative change in other physical properties of the polymer, under the influence of equimolecular portions of different added plasticisers.)

In the early papers of several foreign and Soviet workers [72-76] no great importance was attached to the chemical structure of plasticisers. Only the compatibility of the components, not the plasticising effect, was actively influenced by the chemical structure of polymer and plasticiser. The relative effect of plasticisers on linear polymers was regarded as depending mainly on their concentration: plasticisers having molecules of about the same size and shape exerted similar plasticising effects.

Baker [77] studied the X-ray photographs of plasticised crystalline polymers, and suggested that the original crystalline structure changes in the presence of an agglomerating plasticiser. With lubricating plasticisers an amorphous halo is merely superimposed on the phase pattern of the polymer. However, in a study of vinyl polymer–tritolyl phosphate systems, Alfrey [78] did not detect any changes in the original crystalline structure of the polymers under the influence of the plasticiser. Nevertheless, the specificity of the action of plasticisers, and the need to take chemical structure into account when selecting them, have been noted in many cases [79].

The influence of the chemical nature, size, and shape of the plasticiser molecules on the plasticisation of linear polymers by equimolecular proportions of trioctyl phosphate, tritolyl phosphate, etc. has been determined [80-82]. Plasticisers differing in the length of the hydrocarbon radicals and in molecular weight also behaved differently in compositions [83]. The effect of the chain length of the non-polar part of the plasticiser molecule on the glass point has been studied with polyvinylbutyral [84] and with other systems [85].

Experiments on synthetic rubbers showed [86,87] that with a divinylstyrene rubber the maximum plasticising effect is given by non-polar plasticisers, low contents of which satisfied the "equal volume rule" quite well. Significant deviations from this rule were observed with higher plasticiser contents, the glass point of the rubber then being lower in the presence of non-polar plasticisers than with polar plasticisers; the effect of the chemical structure of the plasticiser becomes appreciable in this case.

Many foreign scientists found that the plasticising effect depended on structural features of the plasticisers [88-90]. In particular, the mechanical properties of linear polymers were found [91] to vary with the chemical structure of the plasticiser (influence of the length of the hydrocarbon chain and of the relative content of polar groups in methacrylic esters on the plasticising effect). Here difference in chemical structure had a substantial effect on the modulus of elasticity and the strength of specimens having the same content of different plasticisers.

Polar plasticisers are usually more effective than feebly polar plasticisers towards poly(vinyl chloride). [92] The solvent power, compatibility, and effectiveness for poly(vinyl chloride) have been shown [93,99] to diminish appreciably with decrease in the relative content of polar groups in ester plasticisers.

The minimum pour point of plasticised polymers exhibited [94] a specific dependence on the structural characteristics of plasticisers having the same molecular weight: the elasticity of the polymers increased to a certain point with increase in the chain length of lateral hydrocarbon radicals in the plasticisers used—phthalic esters.

The bonds in the polymer–plasticiser system are complicated in nature [95,96], depending on their structural characteristics. It is emphasised that small quantities of different plasticisers are retained to different extents by the polymer. A point is reached at which increase in the plasticiser content does not lead to further bonding to the polymer chains. It is this portion of the plasticiser which is liable to migrate in the first instance.

Study of dielectric losses [97] and vitrification [98] in some linear polymers established that the plasticiser molecules associate with a definite number of active groups in the macromolecules depending on their chemical nature.

The role of plasticisers has been reduced [100] mainly to diminishing the steric hindrance to rotation of functional groups in macromolecular chains. The efficiency of the plasticisers is determined in considerable measure by their structure.

An electron-microscopic study [101] of the cellulose nitrate–dibutyl phthalate and cellulose nitrate–softener systems revealed that the texture of the resulting films varies substantially and depends on the solvent power of the plasticisers, i.e. on features of their structure.

The effect of chemical structure is apparent [102] both in differences in the compatibility of polymers with plasticisers, which depends on interaction energy between polymer and plasticiser molecules and on the entropy of mixing, and in differences in the plasticising effect, which depend on the shape and size of the plasticiser molecules. Poly(vinyl chloride) has been used to study the plasticising effect as a function of the structure, polarity, size, and shape of the plasticiser molecule [103,104]. With 1- and 2-naphthols the position of the functional group OH in the naphthalene molecule has been shown [105] to be important in determining the magnitude of the effect: thus 1-naphthol is a more effective plasticiser and is more compatible with this polymer than is 2-naphthol, although the polarity of the latter is the higher (the dipole moments of 1- and 2-naphthols are respectively 1.0 and 1.3 D).

The structure (degree of branching) of lateral hydrocarbon radicals in the plasticiser molecules has an appreciable influence on the plasticising effect [106]. Thus oxides of tetrahydrophthalates having branched side-chains are less effective towards poly(vinyl chloride) than are plasticisers of the same type containing linear chains. A similar effect has been observed in other systems [99].

Tager and his coworkers [107,108] used a thermomechanical method to investigate the effect of plasticisers of a new type—diphenic and naphthalic diesters and diphenic monoesters—on the glass point of polystyrene and poly(methyl methacrylate) with the same plasticiser content in the polymers. It was found that the lower the critical temperature of mixing the lower was the glass point of the plasticised polymers. As the alkyl radical in the plasticiser molecule became more bulky, the glass point first fell appreciably, and then rose. This diminution in the efficiency of the plasticisers is attributed to an unfavourable geometrical arrangement in the polymer phase of plasticiser molecules having long aliphatic radicals.

Among these compounds diphenic diesters show an outstanding plasticising effect, which is explained by the less rigid character and large set of conformations of their molecules, as a consequence of which they can be distributed among the polymer macromolecules in a large number of ways. This creates favourable conditions for better compatibility of the components and a stronger plasticising action. With naphthalic esters, which contain a rigid, planar fused-ring system, the number of possible conformations is considerably smaller, compatibility with the polymer is less, and the plasticising effect is weaker.

In the papers cited above it is concluded that the equal mole fraction and equal volume rules have limited

applicability, and that peculiarities of chemical structure must be taken into account both in selecting plasticisers and in interpreting individual facts relating to the phenomenon of plasticisation.

Considerable interest attaches to work [109] on the antiplasticisation of polymers, which is analogous to interstructural plasticisation [2]. Certain classes of organic compounds have been shown to antiplasticise polycarbonates based on bisphenols. Additions of up to 30% increase the modulus of elasticity and the strength and decrease the elongation per unit length. The depression of the glass point of the polymers is appreciably smaller than when the usual plasticisers are used.

Antiplasticiser molecules, while being polar compounds, are relatively rigid owing to the presence of cyclic structures [110]. Aromatic compounds usually exert a greater antiplasticising action than do saturated alicyclic compounds, and polycyclic compounds are more effective. Antiplasticiser molecules should also have a definite minimum size (the thickness or cross-section of such molecules should be not less than 5–5.5 Å).

An antiplasticising effect is observed [111] on the introduction into a polycarbonate of up to 15 wt.% of certain aromatic compounds containing sulphur and nitrogen, but ordinary plasticisation is observed with greater additions. Substances having a high glass point exert an appreciable antiplasticising action, but substances of lower glass point are able to plasticise the same polymers [112].

Under otherwise similar conditions the compatibility of polymers with antiplasticisers diminishes with rise in the glass point of the latter. In general antiplasticisation occurs only when polymer and antiplasticiser molecules are rigid and polar. Antiplasticisation usually improves the resistance of polymers to cracking under stress.

Antiplasticisation cannot be explained solely by crystallisation of the polymer. New bonds, detected by differential thermal analysis and by infrared spectroscopy, are formed between polar groups of the polymer and of the plasticiser. Antiplasticisation increases the density (decreases the free volume) of the polymer.

o-Tolidine as a modifying additive to poly(vinyl chloride) possesses the properties of an antiplasticiser, since it improves substantially the breaking stress under tension and diminishes the elongation per unit length [113].

Plasticisers have varied effects on the thermal stability and on the thermo-oxidative degradation of poly(vinyl chloride). [114] Oxides of hexahydrophthalates, while effectively plasticising this polymer, also stabilise it to light and to heat [115].

Maloshuk and Voyutskii [116] have shown that, in the plasticisation of the acrylonitrile copolymer SKN-40, the equal mole fraction rule is adhered to closely only by plasticisers which are of completely the same type chemically. Straight-chain and branched-chain plasticisers, as well as plasticisers of different classes, give different cohesion values.

An interesting phenomenon was discovered by Kozlov and his coworkers [117] when studying the action of mixtures of plasticisers on polystyrene. A mixture of a plasticiser of low molecular weight (phenyltributoxysilane) and an oligomeric plasticiser (polydiphenylsiloxane) gives a substantial synergic effect, and the observed displacement of glass and melting points considerably exceeds the additive values. In the plasticisation of poly(vinyl chloride) with mixtures of dibutyl phthalate (intrastructural plasticiser) and a chloroalkane (interstructural plasticiser) a transition was observed from one type of plasticisation to the other [118].

The work of various investigators, who have attempted to use the principles of the theory of interstructural and intrastructural plasticisation to make a quantitative estimate of the contribution made by the structural characteristics of plasticisers and to determine their role in the various stages of structure formation, opens up new opportunities for greater knowledge of the nature of polymers.

3. PLASTICISATION OF POLYMERS BY COMPOUNDS OF HIGH MOLECULAR WEIGHT

During recent years communications have appeared on the possibility of obtaining technically valuable polymeric compositions, which have been termed blended systems. Thus a non-volatile plasticiser—a butadiene—nitrile rubber—was suggested [119–121] for modifying thermoplastic rigid-chain polymers. A study has been made rather earlier [122] of products of the blending of SKB [a synthetic butadiene rubber] with natural rubber. Slonimskii and Komskaya [123] investigated products of the blending with one another of such rubbers as SKB, SKS-30 [a butadiene–styrene synthetic rubber], SKN-18 [a butadiene–acrylonitrile synthetic rubber], natural rubber, etc.

Study of the physicochemical nature of the phenomenon began during the same period, blending being interpreted [124–127] mainly as the plasticisation of one polymer by the other. Reznikova et al. [128] accomplished the plasticisation of poly(vinyl chloride) by butadiene–acrylonitrile synthetic rubber, studied the effect of the composition of the copolymer on compatibility and plasticising effect, and showed that the nitrile groups ensure compatibility between the copolymer and the poly(vinyl chloride), while the butadiene part exerts the actual plasticising action. Investigation of the mechanism of plasticisation established that the "mole fraction rule" was not applicable to the plasticisation of poly(vinyl chloride) by macromolecular plasticisers such as the above synthetic rubber. The limited mutual compatibility of the polymer components was also noted.

Voyutskii [102] showed that the mutual solubility of polymers is determined mainly by the change in the heat content of the system: in most cases polymers dissolve one in another only if the heat of mixing is positive. Compatibility depends also on the shape and structure of the macromolecules of the blended polymers.

Poly(vinyl chloride) can be blended in all proportions with chlorinated polyethylene [129], to give compositions of great strength, frost resistance, and good dielectric properties. Polyesters of phosphoric and cycloalkylphosphinic acids and their derivatives have also been proposed [130] as plasticisers of high molecular weight. The use of polymeric plasticisers is correctly assessed [131] as one of the most important methods for modifying polymers.

Alekseenko, Mishustin, Voyutskii, and their coworkers [132–135] undertook broad investigations of the blending of polymers. They noted the decisive role played by the polarity of the interacting components: the greater the polarity of the polymers, the greater their compatibility. In an investigation of ternary mixtures of polymers Alekseenko and Mishustin showed [136] that the plasticising action on poly(vinyl chloride) and poly(vinyl acetate) of a series of other polymers depends on the polarity of the latter. Blending requires that the polymers should be of similar polarity, and that denser packing of the macromolecular chains should be possible. However, these

workers note that the polarity of individual macromolecules may not completely balance out on blending, and the resulting system may interact with other polar polymers with the formation of ternary systems. Polar and non-polar rubbers are able to blend together [132,137] only if polar components predominate in the compositions, when the molecules of the non-polar rubber become polarised, and the polarities of the components are equalised. The possibility of blending a butadiene–vinylidene chloride rubber with rigid polymers—poly(vinyl chloride) and poly(vinyl acetate)—was also investigated [138]. The compatibility of these polymers with the rubber was assessed from the tensile strength and the elongation at rupture of films obtained by rolling followed by extrusion. A butadiene–vinylidene chloride rubber was shown to have a plasticising effect on poly(vinyl chloride); the nature of the polar groups was found to have little significance, only the polarity of the interacting substances being important.

Addition to polyethylene of the synthetic rubbers—SKB, SKS-30, DVKhB-70, SKS-30-1, SKN-18, SKN-26, SKN-40—and also polyisobutylene has been recommended to facilitate processing into articles and modification of the properties [139]. Addition of up to 25% of polyisobutylene and of the rubbers DVKhB-70 and SKS-30-1 (a ternary copolymer of butadiene, styrene, and methacrylic acid) improves the physicochemical constants of polyethylene specimens, but addition of the rubbers SKB and SKS-30 impairs its physicomechanical properties. Polyethylene blends with the above rubbers in all proportions, but does not blend with highly polar rubbers of the SKN type.

In a study of the compatibility of cellulose nitrate and poly(vinyl chloride) with several synthetic rubbers (e.g. DVKhB-70, SKN-140, SKS-30, and SKS-30-1) Alekseenko [140] observed the differing behaviour of a mixture of solutions of the polymers in a common solvent. The inadequate stability of certain mixtures with time is explained by incompatibility of the components. Mixtures of the polymer solutions may separate into layers because the energy of interaction between macromolecules of the polymers exceeds that between solvent and polymer molecules. The experiments showed that separation into layers might result also from the formation of aggregates containing the initial components in various proportions.

Polymers can be blended as latices and as aqueous dispersions; blended systems are obtained also by mixing and then extruding the finely powdered polymers; and latices or dispersions can be mixed with solutions of the polymers, and then dried and extruded [141]. Investigation of a system comprising poly(vinyl alcohol) and a carboxylated rubber showed that the latex composition considerably surpasses in mechanical properties a blended system of similar composition obtained by rolling, which is explained by a more uniform distribution of poly(vinyl alcohol) chains between the rubber globules.

In a study of the possibility of blending certain polymers Slonimskii and Struminskii [142,143] found that binary mixtures of equally concentrated solutions of polybutadiene and a butadiene–styrene copolymer, natural rubber and polystyrene, separate into two phases, although the heat of mixing of the polymers is positive. This anomaly was explained by change in the packing density of molecules of the initial polymers on mixing.

Lel'chuk and Sedlis [144] studied the compatibility of macromolecular substances with the aim of determining the possibility of plasticising poly(vinyl chloride) with polymeric plasticisers. Plasticising power was measured by the depression of the glass point of the composition compared with that of the unplasticised polymer. butadiene–nitrile rubber containing 35–40% of acrylonitrile showed the best compatibility and efficiency.

Berlin, Kargin, and their coworkers [145,146] examined the blended systems formed by poly(vinyl chloride) with methylvinylpyridine rubber (SK MVP) and with nitrile rubber SKN, and showed that a certain schedule of treating the mixtures on rolls yields graft copolymers by chemical interaction between functional groups of the poly(vinyl chloride) and those of the rubbers. With SK MVP rubber as modifier cross-links of the pyridinium type are formed, and with SKN *N*-substituted nitrilium salts may be formed. Addition of small quantities (5–10%) of the above modifiers produces a sharp improvement in the stability of poly(vinyl chloride) to impact loads.

Slonimskii et al. [147] investigated the mechanical properties of polymer mixtures, and showed in particular that the X-ray photographs of mixtures of crystalline and amorphous polypropylene and polyisobutylene confirmed the incompatibility of the components: the mixtures are two-phase colloidal systems. Addition of an amorphous component diminishes the strength of polypropylene and prevents development of the high stresses necessary for the production of constrained viscoelastic deformations, so that the elongation of the specimens on rupture is decreased. It was shown also that mixtures of crystalline polymers, e.g. polypropylene and polyethylene, exhibit microheterogeneity. A similar situation can be observed with a mixture of polypropylene and polyisobutylene.

Polytetrafluoroethylene possesses superior physicomechanical and dielectric properties and great chemical stability. However, it cannot be fabricated into articles by injection moulding, extrusion, hot pressing, etc., but requires special, laborious procedures. Numerous attempts to improve the workability of polytetrafluoroethylene by adding small quantities of greases, fillers, polyisobutylene, etc. have not yielded practical results.

The possibility of modifying polytetrafluoroethylene with high-density and low-density polyethylene has been studied [148,149]. After careful grinding and mixing, the polymers were blended in the solid phase by pressing or on rolls at 150–155°C. With increase in the polyethylene content the breaking stress on stretching increased substantially, the optimum content being 30 to 50%. It is interesting that, whatever the proportions of the components, blended systems of this type give X-ray photographs characteristic of the original crystalline polymers. Differential thermal analysis has established [150] that the melting ranges in the blended systems coincide with those of pure polyethylene and pure polytetrafluoroethylene. This indicates that this blended system is formed not by chemical interaction, with the formation of some new chemical compound like a block copolymer, but by secondary intermolecular bonds between the chains of the initial polymers, without change in their original crystalline structure. The above compositions constitute an example of polymer systems in which the introduction of a macromolecular modifier (polyethylene in the present case) results not in a weakening but in a strengthening of intermolecular interaction.

Experiments by several workers [144] on the blending of poly(vinyl chloride) with various brands of nitrile rubbers also confirmed that up to 150–160°C the latter act as plasticising additives in the compositions. Blended systems have been obtained from polyethylene, polystyrene, DVKhB rubber, and other polymers [151].

Dogadkin et al. [152,153] showed that polymer mixtures of optimum composition improve the resistance of vulcanised rubbers to fatigue on repeated deformation, in comparison

with those based on the individual rubbers. In mixed systems the disintegration of specimens subjected to repeated deformations also begins with the growth of microcracks formed at the site of some structural defect. However, a microcrack arising in a medium of lower modulus of elasticity slows down or ceases its further growth on meeting a rubber particle of higher modulus, owing to the possibility of stress relaxation at the apex of the crack. If, on the other hand, the microcrack arises in a medium of higher modulus of elasticity, the overstresses at the apex of the growing crack readily relax on encountering particles of a disperse phase having greater pliability.

In most cases blended systems do not form true solutions [154]: i.e. they are not thermodynamically compatible. Hence they are microheterogeneous (heterophase).

Most blended systems can be regarded as a kind of plasticised system [155] primarily because, as with ordinary plasticisation, the polymeric component of the mixture having the more rigid chains shows some depression of its glass point, increase in deformability, and decrease in the strength of the material, although all these effects are less strongly developed than with agglomerating plasticisers of low molecular weight.

Zelenev and Bartenev [156] studied the relaxation properties of mixtures of polar and non-polar rubberlike polymers over a wide temperature range. They showed that, with non-compatible rubbers (SKS-30 and SKN-26) below the glass point, no significant changes occur in the properties relative to those of the pure rubbers, whereas in the case of a mixture of compatible rubbers (SKS-30 and natural rubber) the low-temperature maximum of mechanical losses diminishes and moves to higher temperatures. Mechanical losses and X-ray diffraction have been used [157] to investigate the relaxation properties of some heterogeneous polymer compositions based on a crystallising isoprene rubber SKI-3 blended with a partly crystalline polymer (isotactic polypropylene), and to establish that polypropylene causes the formation of ordered structures: i.e. it is a structure-forming agent.

It has been shown [158] that butadiene–nitrile rubber (SKN-40) has a considerable plasticising effect on cellulose acetate–butyrate, which conforms to the equal-volume rule and is molecular in character.

The chemical structure of the plasticising components obviously plays a considerable part in the plasticisation of polymers by macromolecular substances. Furthermore, the re-formation of supermolecular secondary structures on contact of a polymer with another, plasticising polymer probably occurs differently from in the presence of a plasticiser of low molecular weight.

It must be remarked that, on the whole, blended systems have not yet been studied at all adequately, and many interesting theoretical and practical papers may be expected to appear in this field in the near future. Thus ternary systems, consisting of two polymers and an antiplasticiser, which increase significantly the strength of blended systems while maintaining all other performance figures, may be of great interest [151].

4. MODERN METHODS OF INVESTIGATING PLASTICISED SYSTEMS

The thermomechanical method proposed by Kargin and Sogolova [159], and subsequently modernised by Teitel'baum [160], has been of great value in studying the mechanism of the plasticisation of polymers at all stages. Thermomechanical curves can be obtained in principle by use not only of compressive forces [161] but also of stretching [162], bending, twisting, etc. forces. The thermomechanical method is interpreted [163] as recording creep (the gradual accumulation of deformation) with a constant load and a gradual rise in temperature at a constant rate. Such regularities in plasticisation as the equal mole fraction and equal volume rules, and to a considerable extent the laws of interstructural and intrastructural plasticisation, were discovered by the successful application of the principles of the thermomechanical method of investigation [164].

The thermomechanical method has been used [165] to study the plasticisation of polymers undergoing crystallisation (cellulose triacetates). Plasticisers (butyl stearate and tritolyl phosphate) depress the glass point, but, because of the crystallisation of the polymer, the plateau of rubberlike elasticity on the thermomechanical curves is located below that for the pure polymer: i.e. the deformability is not increased but is diminished.

Infrared spectroscopy has been widely used to investigate the structure and properties of individual macromolecular compounds [166,167]. It enables us to assess the nature of the forces of intermolecular interaction between certain groups in the polymer chains and the plasticiser, as was first demonstrated by Zhurkov and Levin [168].

An investigation was made by infrared spectroscopy [169] of the interaction between poly(vinyl chloride) and an antiplasticising additive (*o*-tolidine). The appearance in the absorption spectrum of the composition of a band at 3200 cm^{-1} indicates the formation of a hydrogen bond between the amino-group and the polar CHCl group of the polymer. Hydrogen bonding in this case may explain the significant hardening of the polymer on being blended with *o*-tolidine. However, the number of papers on the application of infrared spectroscopy to investigate the plasticisation of polymers is extremely small.

The thermographic method is of great value for investigating plasticised systems, and is quite widely used at the present time to study [170] individual macromolecular compounds. Mikhailov et al. [127] studied the polyethylene–polypropylene system by this method, and showed that blending is observed at quite definite proportions of the components, one of which (polyethylene in the present case) is a plasticiser for the other.

Under the influence of polar agglomerating plasticisers the positions on the differential thermal analysis curves of the effects due to vitrification and breakdown of the crystalline phase are displaced to lower temperatures in the intrastructural plasticisation of poly(vinyl chloride) [171]. At certain temperatures modifying additives (*o*-tolidine, 4,4′-dinitrobiphenyl, etc.) containing active functional groups NH_2 and NO_2 were found to interact chemically with the CHCl groups of the polymer. Thermography also reveals the change in the endothermicity of pyrolysis of the polymer produced by plasticisers, which permits monitoring of the effect of water of crystallisation and other forms of moisture on the course of plasticisation [172].

Thermographic investigation [173,174] of the plasticisation of poly(vinyl chloride) with anthracene, anthraquinone, and *p*-terphenyl showed that anthraquinone displaced the endothermic effects on the differential thermal analysis curves to higher temperatures, whereas the other two compounds produced a shift to lower temperatures. Thus this method of investigation enables us to assess the effectiveness of plasticisers with a given polymer. At the same time cases can be observed of depression of the crystallisation point of plasticisers under the influence

of a polar polymer, and the presence of a small amount of crystalline phase can be recorded in such a polymer as suspended poly(vinyl chloride).

A thermographic study has been made [175] of the effect of plasticisers on transition temperatures in poly(vinyl chloride). This method can also be used [176] to study transformations in blended systems, e.g. a poly(vinyl chloride)—butadiene–acrylonitrile elastomer.

Nuclear magnetic resonance, which enables the mobility of molecules as a whole, of groups, and of atoms to be studied directly, has also acquired great value for investigating individual polymers [177] and plasticised systems [178]. When applied to plasticised polymers this method may yield information on the molecular motion of the plasticiser in the polymer phase, which has been studied [179] for plasticised polystyrene.

The efficiency of plasticisers can be determined by measurement of the spin–spin and spin–lattice relaxation times T_2 and T_1. [180] The influence of the chemical structure of plasticisers on their efficiency can also be followed in these nuclear magnetic resonance experiments. The method enables the type of plasticisation (intrastructural, interstructural, or mixed) to be established [181] for a given polymer, e.g. poly(vinyl chloride), by determining the concentration dependence of the dimensionless quantity T_2/T_1^0, which may serve to characterise the interaction between polymer macromolecules and the plasticiser.

The dielectric loss method [182,183] provides an efficient means for revealing the relation between the properties of polymer systems and their molecular structure. It has been used to study molecular relaxation over wide ranges of temperature and frequency in the rubberlike elastic state of pure and plasticised polymers [184,185], and to calculate relaxation times, the form of their distribution, and correlation factors in the expression for the effective dipole moment [186,187]. These parameters are sensitive to the molecular structure both of the polymers themselves and of plasticising additives present in them. The dielectric loss method can also be used to study [188-191] the influence of the chemical nature and structure of plasticisers on the plasticising effect as shown by the dielectric characteristics of the polymers.

The dielectric loss method has been used to establish [192,193] the dependence of the plasticising effect with poly(vinyl chloride) on the size and shape of the plasticiser molecules, the type, number, and position of functional groups and of benzene rings, and also the displacement of the temperature of maximum tan δ relative to the pure polymer.

Rheological investigations of polymer–plasticiser systems are acquiring great value, providing a basis for processing schedules, and establishing the structure of the melt and certain physical properties of plasticised systems [194-200].

Viscometry has been used [201] to investigate the interaction of poly(vinyl chloride) with plasticisers as a function of the nature of the latter. Viscosity and the points at which swelling, gel formation, and dissolution of the polymer start show an extremal dependence on the type of plasticiser.

The resonance method [202] (determination of the dynamic mechanical characteristics) is of great interest for the investigation of plasticised systems. Zelenev and Bartenev [203] studied the effect of plasticisation (with dibutyl phosphate, dioctyl sebacate, and dibutyl sebacate) on the relaxation properties (mechanical losses) of polar and non-polar rubberlike polymers over a wide temperature range. At high temperatures plasticisers are more effective with non-polar rubbers, and at low temperatures with polar rubbers. The action of plasticisers has different mechanisms in the regions of the main, low-temperature, and high-temperature mechanical-loss maxima. In each case there are differences with polar and with non-polar rubbers. Study of vulcanised filled mixtures of polar and non-polar rubbers has shown [204] that the combination of dynamic mechanical with physicomechanical measurements gives a fairly complete idea of the character and properties of compositions based on mixtures of rubbers, in particular on their degree of microheterogeneity.

The resonance method enables us to trace [205] the dependence of the velocity of sound on the composition of the mixture and the glass and pour points. Its use reveals the ordering and denser packing of poly(vinyl chloride) macromolecules at low concentrations of a plasticiser of high molecular weight, and also the increase in the velocity of sound and in the strength of poly(vinyl chloride) with increase in the SKN-40 content [206].

In several cases plasticisation itself can be used as a method for studying the structure and other properties of polymers [207]. By varying the plasticiser content in poly(vinyl chloride) in suspension and in a latex, for example, a transition in structure can be observed. At plasticiser concentrations below 50% the supermolecular secondary structures of the polymer form a fibrillar network immersed in a continuous liquid phase. At higher concentrations the structure consists of fibrils which have coalesced to enclose droplike inclusions. This leads to an anomalous variation not only in strength but also in electrical conductivity, permeability to gases, and several other properties.

Plasticisation has been used [208] to study the variation in the strength of poly(vinyl chloride) with time. Interstructural (interbundle) plasticisation with small amounts of plasticisers is found to increase the durability of poly(vinyl chloride)–plasticiser systems.

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Despite definite advances in the plasticisation of polymers and methods of investigation, several important and complicated problems, in our view, face this branch of science and technology, including

(*a*) development of a unified theory of plasticisation, which will enable the type of plasticiser having a definite plasticising effect to be selected for each type of polymer from the chemical structure of the interacting component;

(*b*) study of the part played by different types of plasticisers at separate stages in the formation of supermolecular secondary structures during polymerisation and processing, which will predetermine a combination of physical properties of the polymers [209];

(*c*) research into the possibility of obtaining synergic effects in the action of mixtures of plasticisers for a wide range of polymers;

(*d*) separation and application of general-purpose plasticisers combining several functions—like e.g. oxides of tetrahydrophthalates [106], which are not only efficient plasticisers but also good stabilisers for poly(vinyl chloride); and

(*e*) further study of the plasticisation of network polymers, the plasticisation of polymers by macromolecular compounds [210,211], and the formation of blended systems by mixing latices and aqueous dispersions of polymers [212,213].

Successful solution of this far from complete list of problems will permit a substantial broadening of our views on the phenomenon of plasticisation and improvement in the technical standard of the production and application of plasticised polymeric materials.

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