NEW TYPE OF PLASTICIZED POLY(VINYL CHLORIDE)

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Low-molecular-weight plasticizers are commonly used in the production of plasticized PVC. However, they readily migrate to the surface of the product, which results in the deterioration of physical properties and contamination of the environment. This drawback is eliminated by polymerizing vinyl chloride in water suspension in the presence of a polyester plasticizer and structure stabilizer such as triallyl isocyanurate or the ethylene/vinyl acetate copolymer. The data obtained from water and heptane extractions demonstrate a low extractability of the plasticizer used. Attention is focused on the explanation of the role of structure stabilizers in the polymerization process, and some properties of this new type of plasticized PVC and its possible application areas are discussed.

The problem of plasticized PVC continues to be the object of interest of specialists, because the materials used at present suffer from a number of drawbacks. The most frequently adopted way of production of plasticized PVC consists in mixing or calendering of plasticizer into a suitable type of PVC at enhanced temperature. The plasticizers used include in particular low volatile low-molecular-weight compounds such as esters of phthalic, adipic, sebacic, or phosphoric acids[1,2]. They are advantageous in possessing a high plasticizing efficiency and being relatively easily available and, especially, cheap. However, on the other hand, they exhibit a relatively high migration tendency resulting in separation of plasticizer or efflorescence of additives on the surface of products, in extraction with water or other liquids which come into contact with the products (such as aqueous solutions of inorganic compounds, organic solvents, as well as milk, fats, oils, blood etc.).

The migration of plasticizers has the consequence of worsening of mechanical properties of the products and contamination of the contents and/or environment with the separated plasticizer and/or other additives, such as various fillers or thermal and UV stabilizers. Thus the migration of plasticizers causes a number of problems in the applications of plasticized PVC in car production, agriculture, building industry, health service, or food-stuff industry. Therefore, a great effort has been directed toward the development of the plasticized PVC with reduced migration of plasticizers, particularly utilization of the effect of additives increasing the polarity of the PVC matrix, toward the development and application of special low-molecular (branched), oligomeric, and polymeric plasticizers, especially those based on esters and polyesters of phthalic, adipic, and sebacic acids, and toward production (by the action of plasma or polymerization of suitable, especially acrylate monomers[3-5]) of a surface layer on the products which would be impermeable for the plasticizers. Although a number of these procedures has brought positive results, their broad application is prevented by increased production costs of the products.

The application of the internal plasticizing effect represents a present way of development of plasticized PVC with nonmigrating plasticizer. The process consists in the copolymerization of vinyl chloride with suitable co-monomers whose structural units incorporated in polymeric chains show the ability of plastification of PVC. In this case the plasticizer is chemically bound in the PVC. The typical comonomers include vinyl phosphate[6] or alkyl acrylates[7] and maleates[8]. The copolymers of vinyl chloride with lower alkyl acrylates show improved rheological properties and lowered dirt pick-up of the surface, but they are not flexible enough for production of soft foils. Therefore, special acrylates have been developed containing two ester groups for increased plastification effect[8], and the materials obtained are particularly useful in semirigid applications. Another possibility of production of plasticized PVC is grafting of vinyl chloride on other polymers[9,10]. The internally plasticized PVC is an ideal material from the standpoint of migration, but its price referred to the plasticizer content is substantially higher than that of the PVC plasticized with usual plasticizers.

The present work represents an attempt at a compromise, i.e. a distinct reduction of migration of plasticizers without a too high increase in the production costs. The problem has been solved by the procedure consisting in the incorporation of plasticizer into the polymer during the suspension polymerization of vinyl chloride[11].

EXPERIMENTAL

Materials

Vinyl chloride (Spolana Neratovice, The Czech Republic), impurities content 90 ppm at most (water 71, methyl chloride 7, vinylacetylene 4.5, 1,3-butadiene 4, ethyl chloride 3.5, iron less than 0.5 ppm). Methylhydroxypropyl cellulose (Dow Chemical Co.) was used as a suspension stabilizer.

A mixture of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (Noury Initiators, The Netherlands; peroxide content 96%) and dilauroyl peroxide (Oxydo, Emmerich–Rhein, Germany; peroxide content 93.9%) were used as initiators.

Bis(2-ethylhexyl) phthalate (DOP; Urx Works, Valašské Meziříčí, The Czech Republic) and polyester of sebacic acid with propylene glycol (Reoplex-100, Ciba-Geigy, Manchester, G.B.; M.w. 5 000) were used as plasticizers. Triallyl isocyanurate (TAIC; Monomer–Polymer Dajac Laboratories, Trevose, PA, U.S.A.) and copolymer ethylene/vinyl acetate (EVA) (Levapren; Bayer, Germany), containing 47.5 wt.% of vinyl acetate, were used as structure stabilizers.

Vinyl chloride suspension polymerizations were carried out in a 5-l stainless steel reactor of the duplicator type, equipped with a propeller stirrer, breaking partitions at the inner wall of reactor, and a pressure gauge, at 51 °C and with stirring at 500 r.p.m. The polymerizations were stopped at various time intervals to reach various sample compositions. The polymers were isolated by filtration, washed with water, and dried at 40 °C. The polymerization conditions are given in Table I.

Dried samples of plasticized PVC were used for the preparation of films. A mixture of PVC (195 g), stabilizers Mark WSPF (3 g) and Mark 517 (1 g), lubricants Wax E (0.6 g) and stearin (0.4 g) was first homogenized by stirring at 100 °C for 10 min. Then the mixture was processed in a two-roll mill Schwabenthan for 6 min, the roll temperature and rotation speed of rolls being 160 °C and 10 and 11 r.p.m., respectively. The films obtained were repressed to a thickness of 0.6 or 1 mm in a multistage press at 170 °C. The test tubings made of the polymer samples Nos 5 and 9 were prepared for the heptane extraction tests. A mixture of PVC (286 g), Mark WSPF (4.5 g), Mark 517 (1.5 g), Wax E (0.9 g), and stearin (0.6 g) was processed in the two-roll mill Schwabenthan at 160 °C for 5 min and then granulated and extruded in the shape of tubing with the external and inner diameters of 9.7 and 6.3 mm, respectively.

Methods

The migration tests were performed according to ISO R 177. The PVC disc (thickness 0.6 mm, diameter 50 mm) cut from the PVC film was placed between two polyethylene discs (thickness 1.8 mm, diameter 52 mm). The whole testing set was inserted between two glass plates, loaded with 5 kg, and kept at 70 °C 24 h and 10 days. Then the discs were separated, conditioned, and weighed. The results are given in Table II.

TABLE I
Suspension polymerization of vinyl chloride in the presence of the plasticizers and structure stabilizers[a]

Run/Sample	Polym. time, h	Conversion wt.%	Plasticizer wt.%	Structure stabilizer, wt.%
0	8.0	81.3	–	–
1	11.0	59.0	DOP/41.4	–
2	13.5	71.9	DOP/36.7	TAIC/0.1
3	13.0	68.9	DOP/37.7	EVA/1.7
4	7.5	31.8	Reoplex/56.7	–
5	14.0	76.4	Reoplex/35.3	TAIC/0.1
6	12.5	70.0	Reoplex/37.3	TAIC/0.17
7	9.75	43.0	Reoplex/49.2	TAIC/0.25
8	16.0	83.5	Reoplex/33.3	EVA/1.18
9	11.5	61.7	Reoplex/40.3	EVA/1.24
10	11.0	59.2	Reoplex/41.3	EVA/1.33

[a] Vinyl chloride (1 080 g), methylhydroxypropyl cellulose (72 ml of 3.8 wt.% aqueous solution), distilled water (2 100 ml), NaOH (60 ml of 1 wt.% aqueous solution), dilauroyl peroxide (2 g), bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (0.64 g), plasticizer (450 g).

The water extraction tests were carried out using a special apparatus; the concentrations of esters in the extracts were determined spectrophotometrically[12 - 14] (Table III).

The heptane extraction tests were performed in test tubes with ground glass joints at 23 °C. The sample was repeatedly extracted with 20 ml portions of fresh heptane, and the extractability of the plasticizer was determined as a time dependence of the weight of extracted plasticizer (Fig. 1). The

TABLE II
Weight loss (%) of plasticizer in various PVC samples due to migration into polyethylene

Time, days	1	3	4	6	9
1	2.9	2.1	0.6	0.2	0.1
10	10.3	9.9	0.9	0.4	0.2

TABLE III
Extraction of plasticizer from PVC with water

Sample	Plasticizer wt.%	Extraction time, h	Plasticizer in extract mol/l
A[a]	DOA[b]/39.5	360	30.3
B[a]	DOP/39.8	360	36.2
6	Reoplex/49.2	320	3.0
9	Reoplex/40.3	350	2.7

[a] Commercial PVC sample; [b] bis(2-ethylhexyl) adipate.

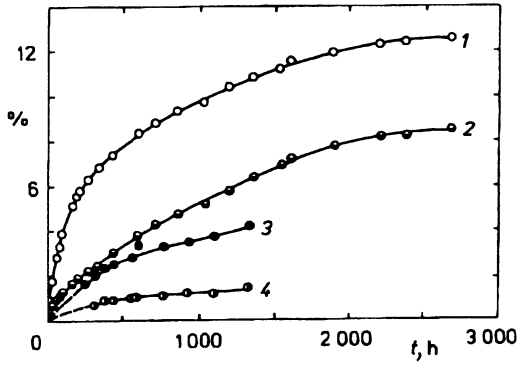

FIG. 1
Time dependence of the percentage of plasticizer extracted from PVC tubing samples (see Table IV): *1* 5A, *2* 5B, *3* 9A, *4* 9B

samples Nos 5 and 9 were tested as tubings (5A and 9A) and as O-rings prepared from the tubings by cutting into 70 pieces on a lathe (5B and 9B). The surface specification of the samples is given in Table IV. The mechanical properties were determined by standard procedures[15] by measuring films of 1 mm thickness prepared from the samples Nos 5 – 10 (Table V).

RESULTS AND DISCUSSION

Synthesis of Plasticized PVC with Reduced Migration of Plasticizer

The hot calendering of the mixture of PVC and plasticizer rapidly produces the plasticized PVC and this process results from the operation of the dipole–dipole interactions between the ester groups of plasticizer and C–Cl bonds of PVC. The consequence of these interactions is an easy solvation and separation of individual polymeric chains of the PVC matrix by the plasticizer molecules, which is facilitated, too, by the amorphousness of polymer and porosity of the polymeric grains processed.

TABLE IV
Surface specification of PVC samples for heptane extraction

Sample	Weight g	Total surface cm^2	Inner surface cm^2
5A	3.7543	35.36	13.52
5B	3.8375	96.22	–
9A	4.2991	35.18	14.38
9B	4.5047	105.56	–

TABLE V
Some properties of films prepared from various samples of plasticized PVC with reduced plasticizer migration

Property	5	6	7	9	10
Tensile strength, MPa	19.9	14.2	19.6	12.8	19.5
Breaking elongation, %	322	274	312	455	427
Modulus, MPa	15.2	8.9	10.6	8.7	11.3
Tear resistance, N/mm	14.7	23.4	37.2	–	18.5
Hardness Shore A, °Sh	82.5	76	78	82.2	88
Shore B, °Sh	35	24	26	32	35
Frost resistance, °C	–23	–8	–	–10	–12

Hence the stability of the polymeric system thus plasticized is only determined by the physical bonds created between the plastification component and polymeric phase, and as a consequence the plasticizer molecules easily migrate. A simple solution of this problem, directed to a reduction of migration of plasticizer, can be found in partially chemically binding the plastification component to PVC, which has another favourable consequence in increased polarity of the plasticized system, i.e. in formation of stronger physical bonds. This procedure can be tested by carrying out the polymerization of vinyl chloride in the presence of plasticizers and investigating their transfer activity.

A series of suspension polymerizations of vinyl chloride were carried out in the presence of a low-molecular plasticizer DOP and a polymeric plasticizer Reoplex-100, a polyester of sebacic acid and propylene glycol. The products obtained were repeatedly reprecipitated in a THF–methanol system, and the plasticizer content was determined by elemental analysis. The transfer activity of the plasticizer used was found to be very low because the products only contained ca 0.1 mole % of chemically bound DOP and 1 – 3 mole % chemically bound Reoplex-100, respectively (the grafted copolymer PVC/Reoplex-100). Hence it is obvious that the polymerizations of vinyl chloride in the presence of plasticizers produce practically the same type of plasticized PVC as that obtained from the calendering process.

However, the utilization of the polymerization procedure opens still another possibility of reduction of plasticizer migration. If the polymerization of vinyl chloride is carried out in the presence of both a plasticizer and a small amount of cross-linking agent, it can be presumed that the sparse polymeric network formed will slow down the migration of plasticizer, especially so with the application of polymeric plasticizers where the polymerization can be expected to form complex entanglements of polymeric PVC chains and polymeric plasticizer. A typical cross-linking agent is triallyl isocyanurate (TAIC). A similar effect can also be reached by making use of the branching process, e.g. on the basis of the transfer activity of the ethylene–vinyl acetate copolymer (EVA). In such cases, both the cross-linking and branching agents can stabilize the plasticized system against the migration of plasticizer and therefore we denote them as structure stabilizers. On the basis of this idea, suspension polymerizations of vinyl chloride were carried out in the presence of DOP and Reoplex-100, TAIC or EVA being present in small amount as the cross-linking or branching agents, respectively (Table I). The products obtained were shaped into films and the migration of plasticizer into polyethylene was monitored by the standard procedure. The results of this procedure are shown in Table II: the values shown indicate a great difference between the migrations of DOP and Reoplex-100 polyester. The application of structure stabilizers lowers the migration of both plasticizers. However, the migration values of DOP go on to be very high (sample No. 3). As compared with the PVC samples plasticized with DOP, the effect of cross-linking/branching agents is stronger in the samples plasticized with Reoplex-100, the most effective suppression of plasticizer migration being observed with the EVA copolymer. Hence, the results obtained confirmed the above-mentioned hypothesis concerning the potential suppression of plasticizer migration by the formation of a sparse polymeric network and/or complex entanglements of polymeric chains in the plasticized PVC. As the plasticized PVC described represents a new type, the attention was focused on the evaluation of some of utility properties of this material.

Evaluation of Properties of Plasticized PVC

For the presumed applications of the material in building industry and agriculture, e.g. as roofing, soil humidity isolation, foils for gardening and greenhouses, one of the decisive properties is the extractability of plasticizer by water. For comparing the extraction efficiency we also tested the commercial samples of PVC plasticized with bis(2-ethylhexyl) adipate (DOA) and DOP (Table III). From the values given it can be seen that the extractability by water is low for the samples Nos 6 and 9, the latter sample (which uses the ethylene/vinyl acetate copolymer as the structure stabilizer) again giving the best result.

Another interesting application area for the developed type of plasticized PVC is handling aliphatic hydrocarbons (e.g. various membranes, tubing for petrol in cars etc.). Therefore, we were interested in the problem of comparison of suitability, for these purposes, of the materials synthesized with the use of EVA copolymer and materials prepared in the presence of TAIC. Testing tubings were produced from the polymerization products Nos 5 and 9 (samples 5A and 9A) and extracted with heptane. For comparison extraction experiments the tubings were cut to obtain O-rings of 1 mm thickness (samples 5B and 9B). The surface area of the individual samples is given in Table IV. The extraction course is represented in Fig. 1.

Out of the whole amount of plasticizer contained in the sample 5A 8.48% was extracted with heptane in 2 692 h; the average extraction rate in the whole time interval was $1.2 \cdot 10^{-8}$ g s^{-1} and the average extraction rate referred to the surface area unit was $3.3 \cdot 10^{-10}$ g cm^{-2} s^{-1}. In the time interval from 2 210 to 2 692 h the average rate decreased to the value of $2.3 \cdot 10^{-9}$ g s^{-1} which was independent of the magnitude of surface area (Fig. 1, curves *1* and *2*). At this rate of extraction, the lifetime (defined as the period after which the plasticizer content decreases to 50% of the initial value) would be 24.6 years.

From the sample 9A, 1.49% of the plasticizer was extracted after 1 344 h. The average extraction rate and that referred to surface area unit were $5.5 \cdot 10^{-9}$ g s^{-1} and $1.6 \cdot 10^{-10}$ g cm^{-2} s^{-1}, respectively. In the interval of steady extraction rate, from 560 to 1 344 h, the mean extraction rate decreased to $2.6 \cdot 10^{-9}$ g s^{-1} and the mean extraction rate per surface area unit to $7.4 \cdot 10^{-11}$ g cm^{-2} s^{-1}. From the stabilized values of steady rate (Fig. 1, curves *3* and *4*) calculated lifetime is 26.8 years for the extraction of plasticizer from the inner surface of sample 9A.

If the courses of extraction curves *1* – *4* in Fig. 1 are compared, then it is obvious that the plasticized PVC with the structure stabilizer EVA (samples 9A and 9B, curves *3* and *4*) shows a different behaviour during the extraction with heptane:

– The sample 9B with larger surface area is extracted faster than the parent sample 9A during the whole extraction process, the ratio of rates being from 1 : 2.6 to 1 : 3.2, which corresponds well to the ratio 1 : 3 of the surface areas of the two samples (Table IV).

– After the initial faster extraction of plasticizer from the surface layer the extraction rates gradually decrease down to the limit values. The ratio 1 : 3.3 of the limit rates is adequate to the ratio of surface areas of samples. In contrast to samples 5A and 5B, however, the samples 9A and 9B did not show the gradual approaching of the extraction rates: after 500 h steady but different extraction rates were reached.

The given data of extraction with heptane show that both the types of plasticized PVC resist very well the action of heptane, and these materials can be used in the above-mentioned applications.

It can be stated that the usual procedure of suspension polymerization of vinyl chloride carried out in the presence of polymeric plasticizers and small amounts of cross-linking/branching agents gives a new type of plasticized PVC characterized by a lowered migration of the plasticizers. From the above discussion it follows that the migration of plasticizers is suppressed the more effectively the higher is the concentration of structure stabilizers in the polymerization of vinyl chloride. On the other hand, however, a. higher structure stabilization of plasticized material affects negatively its workability and also some properties of final products, such as transparency (especially with increased amounts of EVA copolymer). Thus the given procedure of preparation of plasticized PVC makes it possible to prepare a number of materials differing in the migration of plasticizers, and the choice of a particular material for a given application will represent a compromise between the optimization of workability and the extent of reduction of migration of plasticizers. The basic characteristics of the foils made of the investigated films 5 – 7, 9, 10 are given in Table V for illustration.

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