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Devolatilisation of Plastics

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Introduction

Anyone who has been working in the plastics industry for a few years will have come across the problem of devolatilisation in one form or another. It is a problem which crops up in polymer manufacture, where unreacted residual monomer, low molecular weight reaction products, solvents and other diluents have to be removed during and after the reaction, as well as during plastics processing, where residual amounts of the same substances, in addition to residues of processing aids, decomposition products and entrapped air or inert gases have to be removed.

Although mention has been made in the technical literature of the specific problems associated with devolatilisation, what is missing as far as the man in the moulding shop is concerned is a comprehensive resumé which would enable him to quickly familiarise himself with the problem and help him choose the right devolatilising equipment from the many types on the market today.

Devolatilisation has been carried out in the plastics industry ever since polymers have been produced on an industrial scale, although the reasons why this process is necessary differ in the different processing stages. Where large amounts of raw materials and solvents have to be removed during the reaction or immediately afterwards, the aim is quite clearly to produce a high quality polymer and to recover valuable substances for re-use.

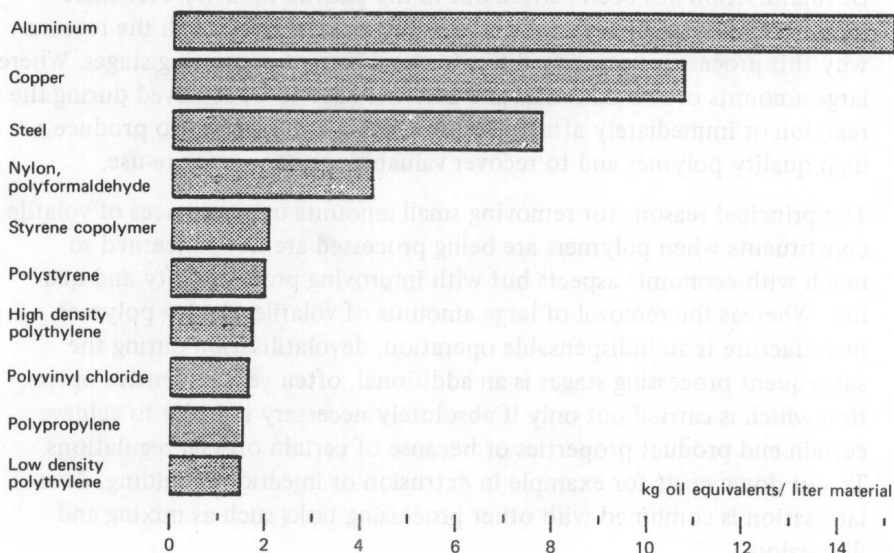
The principal reasons for removing small amounts or even traces of volatile constituents when polymers are being processed are not concerned so much with economic aspects but with improving processability and quality. Whereas the removal of large amounts of volatiles during polymer manufacture is an indispensable operation, devolatilisation during the subsequent processing stages is an additional, often very expensive operation which is carried out only if absolutely necessary in order to achieve certain end product properties or because of certain official regulations. To cut down costs for example in extrusion or injection moulding, devolatilisation is combined with other processing tasks such as mixing and dispersion.

In the early days of polymer chemistry, certain simplifications demonstrated that it was possible to adopt processes and equipment already established in the chemical industry for processes in the low to medium viscosity range (up to 100 Pas). Real pioneer work on the other hand had to be done on the devolatilisation of high viscosity melts and solutions (up to 50 000 Pas).

Since 1972, when oil not only became scarce but rocketed in price, there has been increasing awareness of energy problems and a conviction — which is slowly gaining ground — that it is more sensible to use oil as raw material than for producing energy. At the same time, plastics have been shown to possess considerable advantages over most other materials. Let us remember, too, that the entire petrochemical industry, including the plastics industry, uses up only about 5% of total oil consumption and plastics alone only 2.5 — 3%. The comparison of energy and raw material requirements for the production of plastics, compared with metals, is also very favourable, as shown in table 1.

Where it is necessary to replace components subjected to mechanical loads, chemical attack or high temperatures, or where surface finish is important or products have to be non-toxic to make them suitable for food packaging applications — in all such cases the advantages of plastics over the other

Energy and raw material requirements for making various materials



materials in current use will only be evident if the theoretically calculated properties are, in fact, realised in actual practice.

To achieve this, it will usually be essential to devolatilise in order to remove all traces of monomers, oligomers, solvents, air, inert gases or to regulate the molecular weight of the polymer. Making the right choice of devolatilising equipment is the task of chemists and engineers concerned with the technological aspects of the process and responsible for reliable and economical production techniques.

This volume is intended as a guide which will, we hope, make it easier for processors to decide on what equipment to use for their particular problem. Its contents have been planned with this purpose in mind.

The first section is devoted to the theoretical basis of devolatilising polymer melts and solutions and looks at the different processes used and the selection criteria for equipment and machines on the market today for the different viscosity ranges. The second section goes into detail about processes, equipment and typical applications of the basic operations, namely flash vaporisation, thin-film vaporisation and screw devolatilisation. Finally, there is a section on devolatilisation in plastics compounding, extrusion and injection moulding.

It has not been possible to deal with all the fields of practical importance. The removal of vinyl chloride monomer during polymerisation to make PVC, or the convection or contact drying of polymer powders, for example, have not been described in detail. On the other hand, we thought it would be a good idea to include a paper on the problems of producing a vacuum, and the equipment that can be used for this purpose, since the success of any devolatilisation process greatly depends upon this equipment.

Baden-Baden, November 1980

Renato Gentili
Member of the
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of VDI-Gesellschaft
Kunststofftechnik

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Fundamental principles of polymer devolatilisation

Günter Padberg

The necessity of removing volatile substances such as unreacted monomer, low molecular weight reaction products, solvents and the like from polymers during or after their manufacture in order to obtain useful plastics materials, has had a decisive effect on manufacturing processes from the early days of plastics production some fifty years ago right through to the present time. The additional removal of volatiles and, possibly, processing aids during the conversion of plastics raw materials into finished and semi-finished products has been common practice for a long time now, but has, in the last ten years, experienced a considerable and widespread increase.

Polymer devolatilisation is the removal of dissolved, low-molecular weight constituents from polymers which may be in liquid or solid form. The low-molecular weight substances are converted into the gaseous state and are drawn off as vapours.

If one considers polymer devolatilisation together with other separation processes used in chemical process technology, the task would appear to be a very simple one. As long as the substances to be eliminated have boiling points at atmospheric pressure of less than 200 °C but vapour pressures greater than 1 mbar, the vapour pressure of typical high polymers will be extremely low and almost impossible to determine. Nevertheless, the removal of volatile substances from polymers is a complex and technically difficult problem and the various requirements have resulted in a whole range of processes, some of them involving the use of highly complicated equipment.

The explanation for this discrepancy is, of course, the fact that polymers consist of macromolecules. Typical thermoplastics consist of chain or filament-type molecules formed by the end-to-end arrangement of several thousand monomer units which determine the average molecular weight. The individual molecules can vary considerably in size from the mean figure in a given polymeric material, varying between molecules with ten monomer units to those with 10^6 monomer units. Apart from the size of these chain molecules, it is especially their tangled-up structure in solutions,

melts as well as in the glass-like, amorphous, solidified state which has the greatest influence on the devolatilisation process. The tangled-up structure is due to the fact that the long polymer chains, when in solution or in their pure form above the glass transition temperature, i. e. in their mobile state, assume the statistically most probable form which is the loose, random, tangled-up structure of a long thread. Since the individual chain molecule "balls" have a strong penetrating power in highly concentrated solutions and melts, with partial looping of the chain molecules, i. e. they form a net-like structure, the mobility of the molecules is greatly reduced, resulting in the high viscosities and slow diffusion processes in such systems. When polymer melts are cooled to below the solidification point, this tangled-up structure remains in the glass-like, amorphous solid whilst in the case of partially crystalline polymers this structure is confined to the always present amorphous zones in the solidified state.

Devolatilisation processes for various states of aggregation for polymers

Before we consider the physico-chemical principles of devolatilisation processes, let us briefly consider the many different such processes that are used in the plastics industry [1].

There can be no doubt that the most widespread method of polymer devolatilisation is the removal of volatile constituents from concentrated polymer solutions and melts. Also of major importance are the removal of dissolved volatile substances from polymers in their solid state, i. e. from powders and granules, as well as the devolatilisation of aqueous dispersions.

The removal of relatively small amounts of residual, dissolved volatiles from liquid polymers is usually done in vented extruders of different designs. Typical examples include the following:

- the removal of residual amounts of monomer and other hydrocarbons from styrene polymers, especially during the preparation of polystyrene beads from suspension polymerisation,
- the same process used in different manufacturing processes for polyolefins, especially HDPE and PP,
- the removal of polycondensation by-products such as water, methanol etc., as well as of oligomers from polyamides and polyesters.

The problems involved, and the various ways of solving them, are much the same as those encountered in plastics extrusion and injection moulding.

The removal of large amounts of monomers and solvents in the production of plastics is achieved with thin-film vaporisers and, especially, with flash evaporators, e. g.

- in the production of styrene polymers by different bulk polymerisation techniques, as well as from certain solution polymers,

- in the gradual separation of excess ethylene in the production of LDPE by high pressure methods.

Occasionally, flash vaporisation is also used to remove large amounts of volatiles in a vented extruder in combination with thin-film vaporisation through a devolatilising screw.

Solid polymers in the form of powders or coarse granules may be freed from dissolved, low molecular weight substances by means of stack, rotary, paddle or fluidised bed driers. Any moisture clinging to the outside or bound in the pores is removed at the same time. Typical plastics production examples include the following:

- in the removal of residual amounts of hydrocarbons in certain HDPE manufacturing processes,

- in the intermediate drying in the production of polyamides.

Unreacted monomer found in the manufacture of polymers by emulsion and suspension polymerisation can, in certain cases, be removed from the aqueous dispersion. The most important application of this process is in the manufacture of PVC. In the suspension polymerisation of vinyl chloride for example, discontinuous polymerisation is stopped at around 90% conversion. Most of the residual monomer which is present, in dissolved form, in the PVC is removed by bringing it to atmospheric pressure and, if necessary, by exhaustion at reduced pressure. This monomer is passed back into the production cycle. Until a few years ago, the roughly devolatilised PVC was then separated from the aqueous phase and dried, resulting in considerable amounts of vinyl chloride monomer being released into the atmosphere. After it was realised that vinyl chloride is a carcinogen, considerable efforts were made in the field of PVC devolatilisation.

Nowadays, equipment for the intensive devolatilisation of the aqueous dispersion is placed between the reactors and the drying equipment. This removes most of the dissolved monomer through the use of steam or inert gases as carriers or possibly by using vacuum. The preliminary devolatilisation stage may also be made more effective in the reactors by passing in steam [2]. In this way it has been found possible to drastically reduce

vinyl chloride emission as well as the residual vinyl chloride content in the PVC powder, i. e. by a power of ten or more.

The macromolecular chemistry of devolatilisation processes

Whereas the papers that follow are concerned primarily with technical ways of solving devolatilisation problems from the equipment point of view, this introductory paper deals with some important aspects from the point of view of macromolecular chemistry, namely:

- thermodynamic properties of polymer solutions,
- rheological properties of polymer solutions and melts,
- diffusion in liquid and solid polymer solutions,
- effect of devolatilising processes on molecular weight and other characteristic features.

In the section that follows, we shall briefly discuss some of the consequences of these properties for the technical principles of devolatilisation.

Vapour-liquid equilibrium of polymer solutions

A knowledge of the equilibrium relationship between the vapour pressure of a liquid component in a polymer solution, its concentration in the solution and the temperature, is of fundamental importance in considering a devolatilising process. It enables one to assess which residual content can be achieved at a given partial pressure of the volatile substance and at a given temperature. From this information it may already be possible to draw useful conclusions, e. g. whether a reduction of the partial pressure of the volatile substance by lowering the absolute pressure or using carriers is likely to result in a lower residual volatile content.

Because of the chain-like structure of the macromolecules and the resultant consequences for the statistical possibilities of arranging the chain segments, the thermodynamic properties of polymer solutions differ from those of low molecular weight mixtures.

The equation proposed by Flory and Huggins [3] is often used for the vapour pressure of a volatile substance dissolved in a high polymer:

$$\log \frac{P_1}{P_{01}} = \log (1 - V_2) + V_2 + \chi V_2^2 \quad (1)$$

where

P_1 = the true vapour pressure of the dissolved substance 1 above the polymer solution

P_{01} = the vapour pressure of the pure substance 1 at the temperature concerned

V_2 = volume of polymer in the binary mixture

χ = the so-called Flory-Huggins reciprocal effect parameter

Fig. 1 shows the vapour pressure curves for the system styrene/polystyrene, which were calculated with $\chi = 0.42$.

Here we have a system where both components are miscible in any proportion. Since the solution enthalpy in this system is very low, the reciprocal effect parameter, which is independent of temperature, enables one to estimate the vapour pressure in cases where its actual determination is very difficult.

Fig. 1 shows that the Flory-Huggins equation results in a linear relationship between vapour pressure and concentration in the liquid phase at concentrations of the volatile substance of less than 5% w/w. At low concentrations therefore, Henry's Law is fulfilled, as expected. This makes an appraisal easier in this concentration range that is of such special importance for devolatilisation, using but a few data.

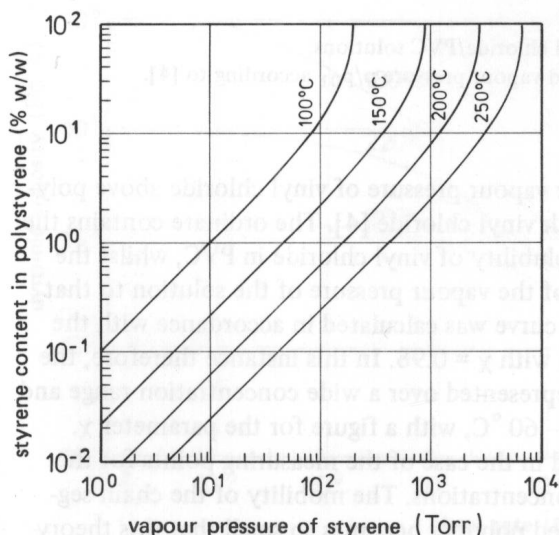


Fig. 1. Vapour pressure curves of styrene-polystyrene solutions.

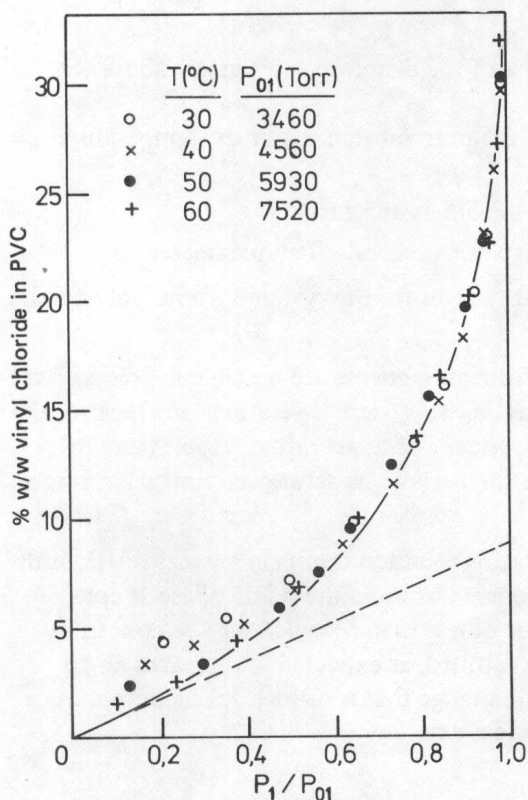


Fig. 2. Vapour pressure of vinyl chloride/PVC solutions. Saturation solubility vs. reduced vapour pressure p/p_{01} according to [4].

Fig. 2 shows figures for the vapour pressure of vinyl chloride above poly-vinyl chloride saturated with vinyl chloride [4]. The ordinate contains the figures for the saturation solubility of vinyl chloride in PVC, whilst the abscissa contains the ratio of the vapour pressure of the solution to that of pure vinyl chloride. The curve was calculated in accordance with the Flory-Huggins equation (1) with $\chi = 0.98$. In this instance therefore, the data can be satisfactorily represented over a wide concentration range and a temperature range of 30 – 60 °C, with a figure for the parameter χ . Complications are indicated in the case of the measuring points for the lowest temperatures and concentrations. The mobility of the chain segments in the glassy, solidified polymer becomes so small that this theory can no longer be applied.

In this example it is also interesting to note that the Flory-Huggins equation correctly describes the zone where no vinyl chloride monomer is dissolved in the PVC. At 30 – 60 °C a maximum of about 30% w/w vinyl chloride are soluble in PVC, whilst at higher vinyl chloride concentrations a separate liquid vinyl chloride phase is formed. In the vapour pressure curve according to Flory-Huggins, the ratio P_1/P_{01} reaches a value of 1 at a vinyl chloride concentration of 30 % w/w, i. e. the saturation vapour pressure of pure vinyl chloride.

The Flory-Huggins equation has become established and proved successful for such technical appraisals, there being a clear relationship between the reciprocal effect parameter and temperature in certain systems. In many instances one also observes a relation between concentration and χ , which cannot be ignored and which means that the theoretical conditions have not been fulfilled. Improved equations for the thermodynamic properties of polymer solutions have been developed [5, 6, 7], but little practical use has evidently been found for these so far.

Rheological properties of polymer solutions and polymer melts

One of the characteristic features of polymer solutions and melts is their high viscosity. As we have already indicated in the introduction, the viscosity of such fluids is affected by the tangled-up structure of the long-

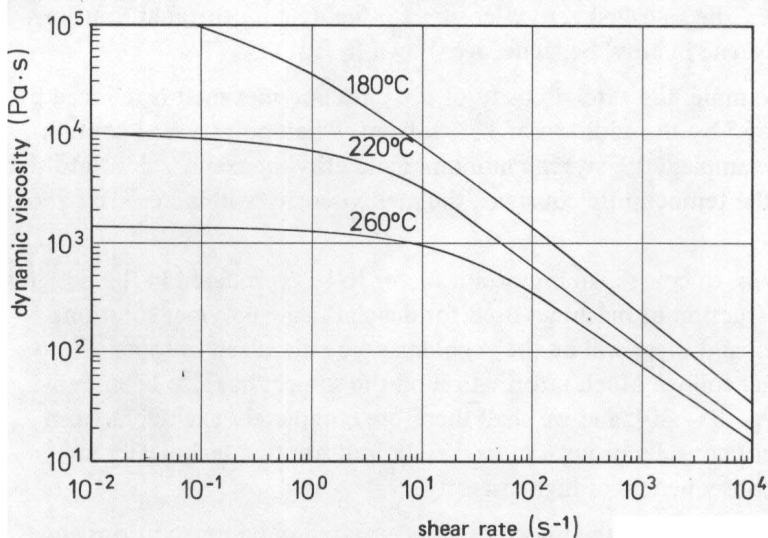


Fig. 3. Flow curve for a pure polystyrene (MFI = 2.5).

chain molecules and their mutual penetration. Fig. 3 shows a typical example for the flow characteristics of polymer melts in the form of flow curves for a standard polystyrene over a wide range of temperatures and shear rates.

The viscosities vary between 10^1 and 10^4 Pa · s ($10^4 - 10^7$ cP) at temperatures of $180 - 260^\circ\text{C}$ in the shear rate range indicated. This melt exhibits a viscosity that is independent of shear rate only at shear rates of less than 0.1 sec^{-1} , i. e. Newtonian flow, whereas the viscosity increases with increasing shear rates under conditions of greater shear stress. The non-Newtonian flow is due to the fact that, as shear rate increases, the polymer "balls" become increasingly stretched in the direction of flow, so that the mutual penetration of these tangled-up masses and thus the momentum transport in a direction at right angles to it decreases.

The fundamental course of such flow curves is maintained if the polymer contains small to moderate amounts of a soluble, low molecular weight compound such as a monomer or solvent. On the other hand, the level of the curve is lowered considerably already by small amounts of solvent since the mobility of the chain segments of the polymer molecules is greatly increased through solvation, thereby reducing the effect of penetration by the tangled-up masses.

Data taken from the literature [8] for the critical viscosity at very low shear rates, the so-called zero viscosity, for highly concentrated solutions of polystyrene in ethyl benzene, are shown in fig. 4.

In this example, the zero viscosity of the pure polymer melt is reduced by a factor of 5 by the addition of 10% solvent. When polystyrene containing, for example, 20% styrene monomer and ethyl benzene is devolatilised, keeping the temperature constant, the melt viscosity will increase by about 25 times.

Viscosity is, of course, an important factor to be considered in the design and construction of machines used for devolatilising polymer solutions and melts, and these will be the problems to be discussed in some of the papers that follow. Much information on the subject has also been published, e. g. [9 - 20], and we shall therefore completely exclude it from our present considerations. Let us merely indicate two technically important consequences of high viscosity.

Because of their high viscosities, concentrated polymer solutions and polymer melts exhibit exclusively laminar flow. The heat exchange with

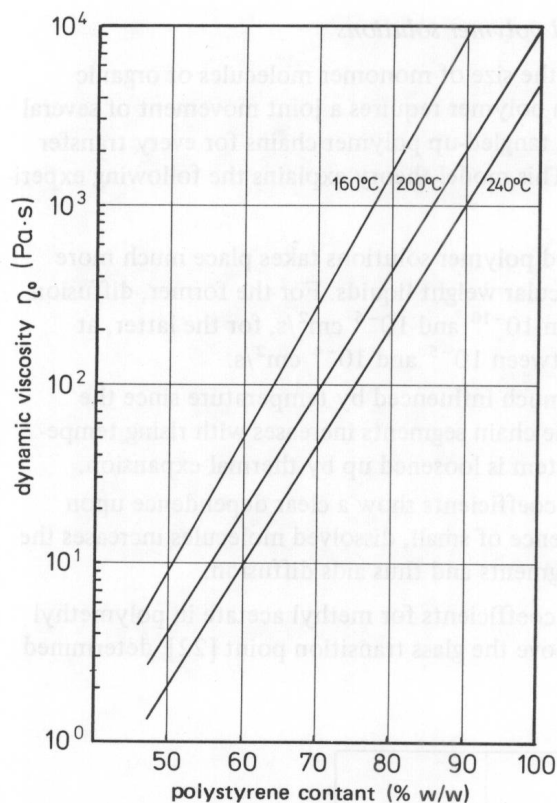


Fig. 4. Zero viscosity of concentrated polystyrene solutions in ethyl benzene, according to [8].

the heating or cooling surfaces is very poor compared with that of low viscosity liquids, since the pure conduction of heat through high viscosity liquids or, at least, through thick boundary layers with laminar flow, determines heat transport. On the other hand, mechanical treatment in the machines employed leads to the production of often considerable amounts of heat due to the dissipation of mechanical energy, because of the high viscosity. We shall not discuss these considerations further, although they are of great importance for the design of devolatilising machines.

It is not possible to achieve an effective, convective material transport through turbulent mixing in the liquid phase. This is why the slow molecular diffusion determines the speed of material exchange processes such as devolatilisation.

Diffusion in liquid and solid polymer solutions

The diffusion of molecules the size of monomer molecules or organic solvent molecules through a polymer requires a joint movement of several chain segments of adjacent, tangled-up polymer chains for every transfer of the dissolved molecule. This model theory explains the following experimental findings [21].

Diffusion in concentrated polymer solutions takes place much more slowly than in low molecular weight liquids. For the former, diffusion coefficients vary between 10^{-10} and 10^{-6} cm^2/s , for the latter, at similar temperatures, between 10^{-5} and 10^{-4} cm^2/s .

The rate of diffusion is much influenced by temperature since the thermal movement of the chain segments increases with rising temperature and the entire system is loosened up by thermal expansion.

The measured diffusion coefficients show a clear dependence upon concentration. The presence of small, dissolved molecules increases the mobility of the chain segments and thus aids diffusion.

Fig. 5 shows the diffusion coefficients for methyl acetate in polymethyl acrylate at temperatures above the glass transition point [22], determined

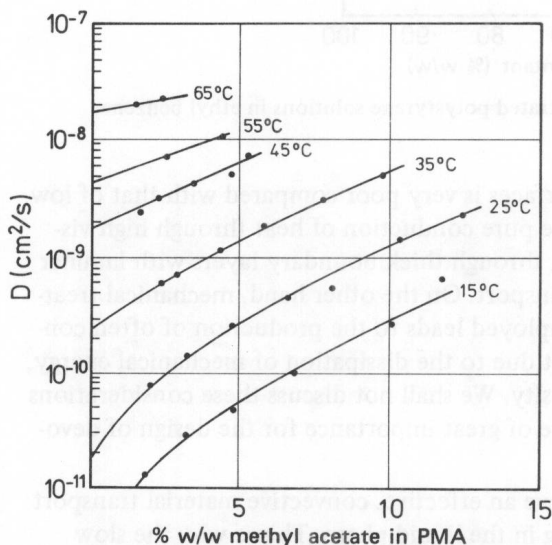


Fig. 5. Effect of concentration and temperature on the diffusion coefficient of methyl acetate in polymethyl acrylate, from desorption measurements, according to [22].