Dynamic-Mechanical Properties and Structure of PVC-Filler Composites

JiřI Zelinger[a]; Viktor Heidingsfeld[a]

[a] Department of Polymers of the Institute of Chemical Technology, Prague 6, Suchbátarova

PLEASE SCROLL DOWN FOR ARTICLE

Dynamic-Mechanical Properties and Structure of PVC-Filler Composites

JIŘÍ ZELINGER and VIKTOR HEIDINGSFELD

*Department of Polymers of the Institute of Chemical Technology
Prague 6, Suchbátarova 1905*

The influence of fillers on the dynamic-mechanical properties of PVC composites with fillers has been studied.

It was found that polar silica fillers in a mixture with emulsion PVC are able to bring about the levelling of the minimum between α- and β-transition region in the dependence of tan δ vs T. On the contrary, however, the same fillers, and eventually carbon black, in a mixture with the suspension PVC do not show this effect.

This difference in the dynamic-mechanical behaviour, the shift of α-transition region towards higher temperatures were explained by the formation of negative (tensile) stresses in the polymer, connected with the increase of free volume of a part of the polymer matrix in the interfiller spaces.

A hypothesis was expressed that the mentioned changes were caused by the emulsifier present in the emulsion PVC which enables a good anchoring of the polymer matrix on the polar fillers' surface.

The hypothesis concerning the free volume increases in the polymer matrix was further supported by the determination of the impact strength.

INTRODUCTION

The quality of the interfacial boundary seems to be the substantial criterion for the level of physical properties of two-phase systems. It is known that the good mutual adhesion in a two-phase system glassy polymer-rubber enables the yielding of the glass polymer, thus, causing a pronounced increase of its impact strength.[1] On the other hand, a low adhesion of rubber particles to the glassy polymer results in decrease of impact strength due to the fact that in

this case the rubber particles act predominantly as stress concentrators and as structure defects respectively facilitating thus the fracture of the polymer.[2]

Also in the case of the system glassy polymer-filler, the quality of wetting of the filler surface by polymer is affecting the interfacial boundary and hence the physical properties of the system as well. It may be assumed that the filler particles, having a low adhesion to the polymer, are going to act predominantly as stress concentrators, whereas in the case of good interfacial adhesion, filler particles may cause a change in the structure of the polymer exerting a positive influence on the physical properties of the system.

It is the objective of this paper to show that in the case of good interfacial adhesion not only the mobility of the polymer chains in the adhesive layer but also the stress relations in the bulk polymer in the interfiller spaces is being changed.

EXPERIMENTAL PART

Materials

Two types of PVC served as the basic raw-material for the preparation of PVC composites with fillers. It was first of all Slovinyl–E, which is an emulsion polyvinylchloride (η in cyclohexanone $= 0.74$ dl/g), produced by CHZWP National Corporation, Nováky, Č.S.S.R. and later it was Slovinyl–S, which is a suspension polyvinylchloride ($\eta = 0.80$ dl/g), produced by CHZWP National Corporation, Nováky, Č.S.S.R.

Two types of fillers were used: silica fillers and carbon blacks.

Aerosil Standard, a colloidal SiO_2, prepared by a pyrogeneous method, was used from the range of silica filler types. The medium size of its particles amounts to 200 Å and its specific surface to 175 m²/g. It is produced by DEGUSSA AG, GFR. In addition Siloxid was used, a colloidal SiO_2, prepared by precipitation. The medium size of its particles amounts to 400 Å and its specific surface to 100 m²/g. It was produced by Spolek pro chemickou a hutní výrobu, Č.S.S.R. (Society for chemical and foundry products). There was also used a milled SiO_2, a sample prepared in the laboratory, the medium size of its particles was 50 μ and its specific surfaces less than 10 m²/g. Finally there was used Aerosil R 972 and pyrogeneous SiO_2, made hydrophobic by dimethyldichlorosilane. The medium size of its particles amounts to 160 Å and its specific surface is 120 m²/g. This was produced by DEGUSSA, GFR.

The following types of carbon black were used: P 1250–acetylene carbon black, the size of its particles amounted to 500 Å and its specific surface was 56 m²/g (producer: Stickstoffwerke, Piesteritz, GDR); Continex HAF–furnace oil carbon black, the medium size of its particles is 300 Å and its

specific surface 75 m²/g (producer: Witco Chemical Co., U.S.A.), and oxidized Continex HAF. The hydrophillic quality of the latter had been brought about by oxidation with the mixture $H_2SO_4-K_2Cr_2O_7$ in the laboratory.

PVC composites with fillers have been stabilized by Mellite 131, which is an organotin compound stabilizer, produced by Albright and Wilson, England.

Mersolat MK–30 of standard commercial quality, produced by Leuna-Werke, GDR, was used as an emulsifier.

Sample Preparation

The PVC composites with fillers studied in this paper was prepared by mixing on a roll mill at a temperature of 165±3°C. Mixing was carried out for 10 minutes. The plates were pressed at a temperature of 185°C at a specific pressure of 120 kp/cm². After cooling they were heat treated at a temperature of 90°C for 16 hours. The test specimens were prepared by cutting on a circular saw.

All composites were stabilized by 2 weight % of stabilizer (calculated on PVC).

In order to verify the influence of the emulsifier there was prepared a PVC–S composite with 8.5 vol % of Aerosil Standard to which had been added some 3 vol % of Mersolat MK–30.

With PVC–Aerosil composites the maximum attainable filler concentration amounted to 9.6 vol %. Composites containing a higher Aerosil content were not workable. In the case of PVC–S composites with a higher concentration of Siloxyd than 5.2 vol % processing resulted in a rapid destruction.

Measuring Methods

The measuring of the real part of the dynamic modulus in torsion G' and of mechanical damping tan δ in dependence on temperature was carried out on a torsion pendulum of current design with a recording device operating on an electric spark principle. The size of the test specimens was about $100 \times 20 \times 2$ mm. Measurements were being carried out in the temperature range from $-60°$ C to 100°C at a frequency of 0.6 to 1.5 Hz. As a criterion of the T_g shift has been regarded the shift of the left-hand side of the main maximum on the dependence tan δ vs T or the shift of the G' modulus in dependence G' vs T in the main transition region respectively.

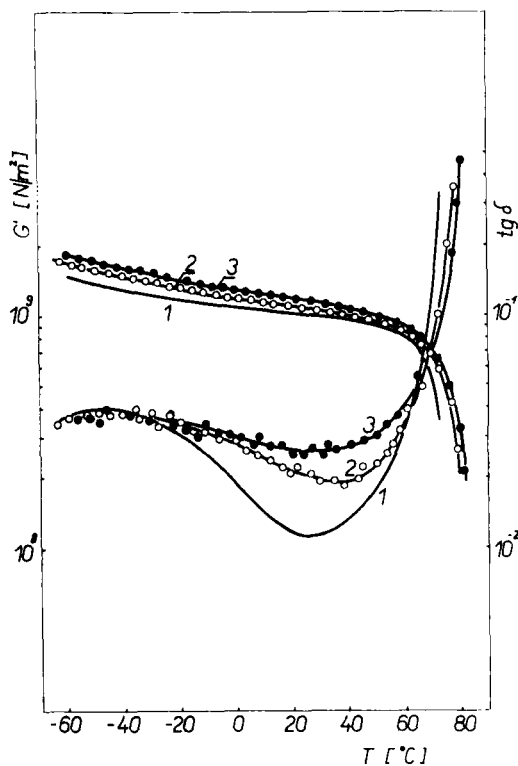The notched impact strength was measured by means of Charpy's method according to DIN 53–453.

FIGURE 1   Shear modulus G' and mechanical damping tan δ vs temperature for composites of emulsion PVC with Aerosil Standard.

    1   PVC–E.
    2   PVC–E + 5.1 vol % of Aerosil standard.
    3   PVC–E + 8.5 vol % of Aerosil standard.

RESULTS

In Figure 1 there are shown temperature dependences G' and tan δ of emulsion PVC (further on designated as PVC–E) with a carying content of pyrogeneous SiO_2 (Aerosil Standard). The filler not only increases the values of G' but also influences the shape of the temperature dependence of G'. The ratio of the modulus value of the PVC-filler composite and the modulus value of pure PVC in the glassy region increases with decreasing temperature. However, much more pronounced is the change in the character of the temperature dependence of tan δ. The addition of filler material results in levelling of the minima between the main and secondary dispersion regions.
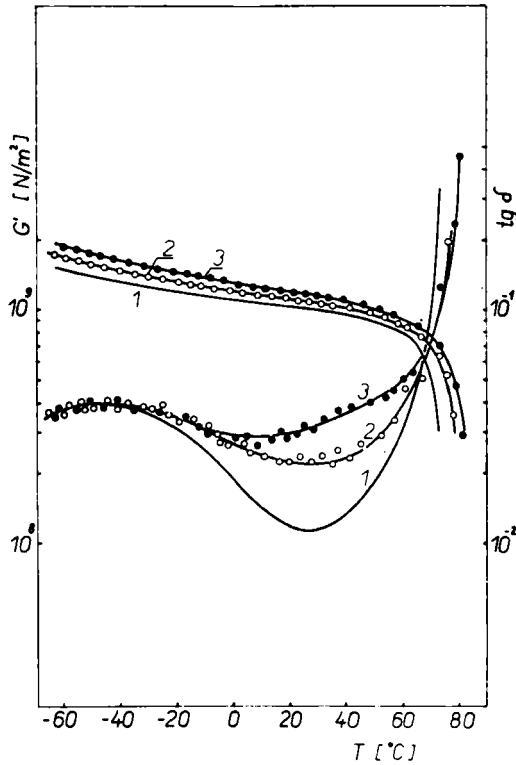
FIGURE 2 Shear modulus G' and mechanical damping tan δ vs temperature for composites of emulsion PVC with milled quarts.

    1   PVC–E.
    2   PVC–E + 4.8 vol % of milled quartz.
    3   PVC–E + 8.2 vol % of milled quartz.

    The dynamic properties of PVC–E composites were influenced by precipitated SiO_2 (Siloxyd) in the same way. The influence of milled SiO_2 on levelling the minimum is more pronounced than that in former cases (Figure 2).

    These relations differ with PVC-composites containing furnace and acetylene carbon blacks (Figure 3). Both types of carbon blacks with a growing concentration also increase the modulus value, but, in contrast to silica fillers, do not essentially change the shape of the temperature dependence G'. The course of the temperature dependence of tan δ remains also almost unaffected by furnace and acetylene carbon blacks.

    In Figure 4 are plotted the temperature dependences of the G' modulus and of tan δ PVC–S composites with pyrogeneous SiO_2. Similar dependences were determined on PVC–S composites with milled SiO_2, with furnace and
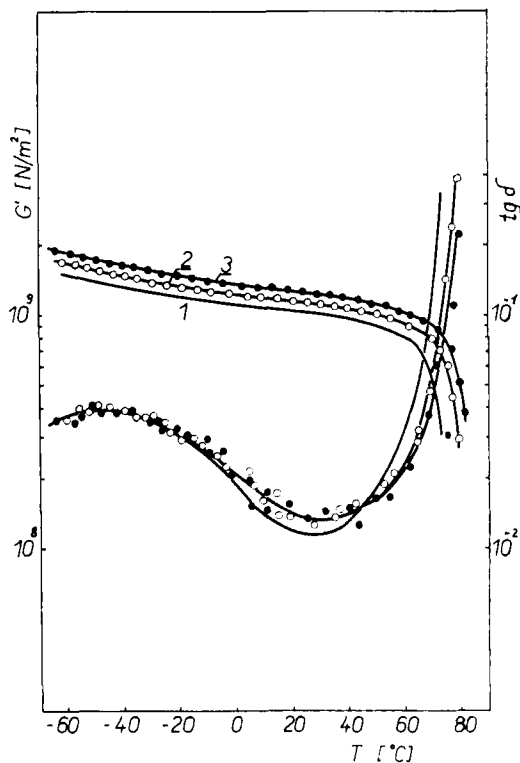
FIGURE 3 Shear modulus G' and mechanical damping tan δ vs temperature composites of emulsion PVC for furnace carbon black.

1 PVC–E.
2 PVC–E + 5.9 vol % of furnace carbon black.
3 PVC–E + 9.8 vol % of furnace carbon black.

acetylene carbon blacks. In this case an increase of the modulus by all filler material is brought about in contrast to composites with emulsion PVC, however, the character of the temperature dependence of the G' modulus as well as of the tan δ, unlike to original PVC, is remaining almost unchanged. Primarily, there does not occur any levelling of the minima between the main and secondary dispersion regions not even in presence of silica fillers.

It is evident from the results mentioned that the course of the temperature dependence of the tan δ remains in any case unaffected while silica fillers are exerting an influence only in composites on the basis of emulsion PVC. All filler materials, however, shift the main transition region to higher temperatures.

By comparing Figures 1, 2 and 4 we may conclude that in the change of the temperature dependence of tan δ, besides the filler also the emulsifier is taking
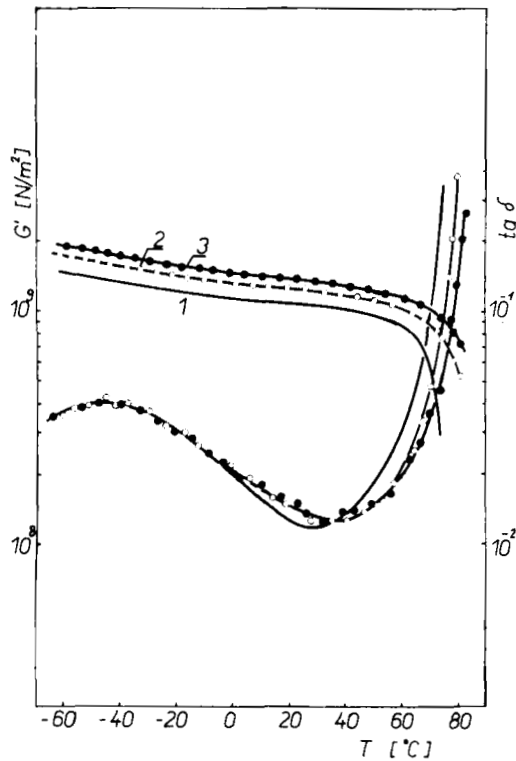
FIGURE 4 Shear modulus G' and mechanical damping tan δ vs temperature for composites of suspension PVC with Aerosil standard.

1 PVC–S.
2 PVC–S + 5.1 vol % of Aerosil Standard.
3 PVC–S + 8.5 vol % of Aerosil Standard.

part. We may assume that the emulsifier, as a surface active substance has a substantial influence on wetting of the filler particles' surface by polymer. To verify this assumption, a PVC–S composite with Aerosil and an emulsifier (see also Experimental Part) was prepared. As an emulsifier was used Mersolat MK–30, that means essentially the same emulsifier which was used in the production of emulsion PVC. The results obtained are shown in Figure 5 proving thus that the addition of an emulsifier results in the change of temperature dependence of tan δ in the system PVC–S + SiO_2 filler.

On the basis of the same consideration has been followed the opposite procedure when emulsion PVC was mixed with SiO_2 made hydrophobic (Aerosil 972), that is to say with a silica filler material, the polarity of which had been intentionally suppressed due to an adjustment carried out successively.[3]
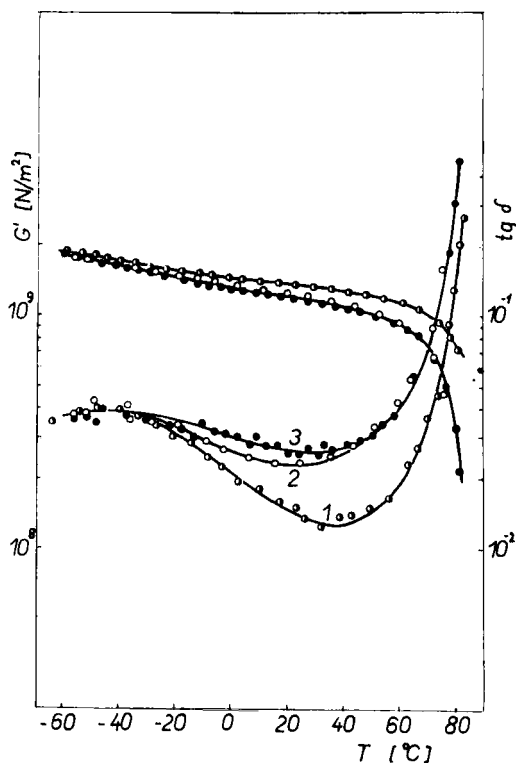
FIGURE 5   Shear modulus G' of mechanical damping tan δ vs temperature for composites of PVC with Aerosil Standard.
1   PVC–S + 8.5 vol % of Aerosil Standard.
2   PVC–S + 8.5 vol % of Aerosil Standard and 3 vol % of emulsifier (Mersolat).
3   PVC–E + 8.5 vol % of Aerosil Standard.

It was found that by this type of Aerosil as well as by carbon black, the temperature dependence of the G' modulus and of tan δ of the composite remains unaffected (Figure 6). In addition to this an analogous PVC–E composite was prepared with oxidized carbon black. The result obtained (Figure 7) shows that oxidized carbon black in composite with emulsion P has the same effect as silica fillers, even though, it is apparent that the surface modification by oxidation cannot entirely suppress its originally non-polar character.

DISCUSSION

It is obvious from the above-mentioned results that PVC, despite being a polar polymer, is incapable of immediate interaction with polar fillers. It is due to this emulsifier that this interaction is being brought about.
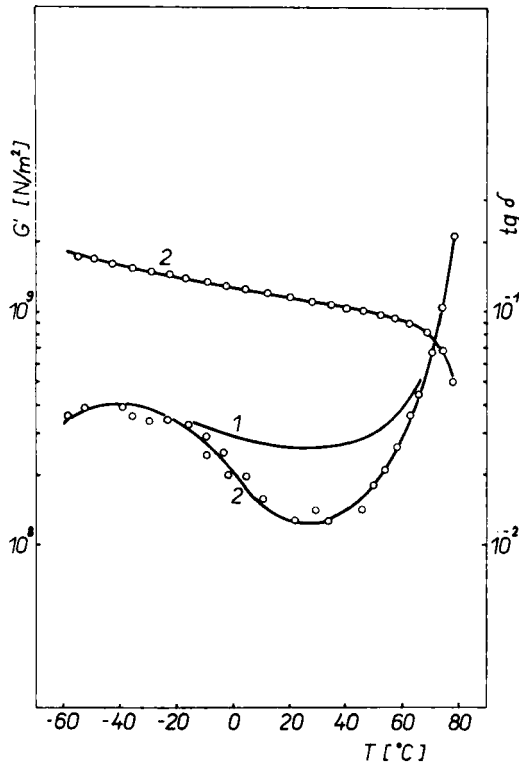
FIGURE 6 Shear modulus G' and mechanical damping tan δ vs temperature for composites of emulsion PVC with different types of Aerosil.

    1 PVC–E + 8.5 vol % of Aerosil Standard.
    2 PVC–E + 8.5 vol % of Aerosil R 972.

The levelling of the minima between α- and β-transition regions on the curve of the temperature dependence of tan δ noted in the case of PVC–E composites with silica fillers or oxidized carbon black can be accounted for due to internal stress in the polymer-fillers systems.

This internal stress enabling the increase of the free volume causes the deformation of the main transition region, the expansion of which to lower temperatures is manifesting itself as levelling the minima between α- and β-transition regions. It is possible to find here an analogy with phenomena noted in the case of quenched PVC when the expansion of the free volume was accounted for by the unbalanced adjustment of strained PVC chains. Even in this case the levelling of the minima between both transition regions was noted.[4,5]

There exist in the polymer-filler system, compressive hydrostatic stresses caused by differing coefficients of the temperature expansion of the filler and
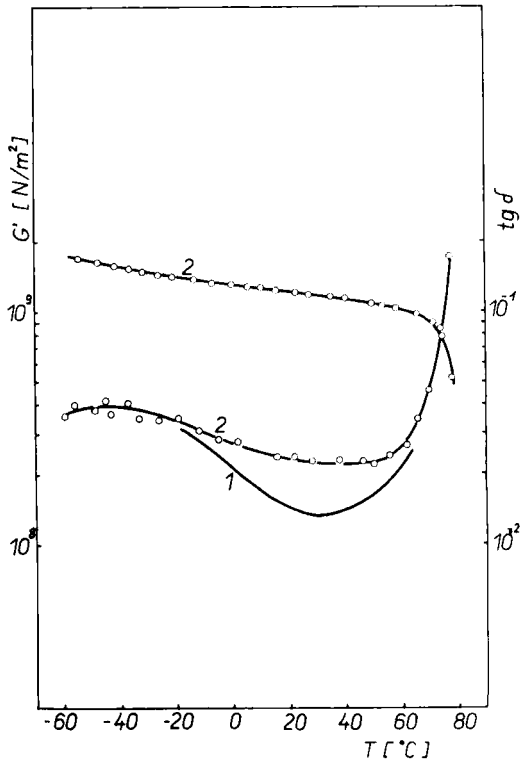
FIGURE 7 Shear modulus G' and mechanical damping tan δ vs temperature for composites of emulsion PVC with carbon black.
    1   PVC–E + 9.8 vol % of furnace carbon black.
    2   PVC–E + 9.8 vol % of oxidized furnace carbon black.

of the polymeric phase. These stresses, no doubt, increase the polymer adhesion to the filler surface, but are, however, incapable of increasing the free volume.[6,7]

It may be admitted, however, that under certain conditions the filler material is able to cause tensile stresses in the polymeric phase.

This is valid in the case, when it is assumed that filler particles or more probably their chains or aggregates, are forming a space structure by mutual contact. This structure can be irregular, with local differences,[8] but sufficiently stiff to restrict the contraction of bulk polymer in the interfiller spaces during the cooling process. The total filler volume in the system is most likely enlarged by the adsorbed layer of the polymer.[9] Thus, it is possible to explain the fact that changes in the dynamic properties become effective at lower filler concentrations when the volume fraction of the filler $\phi_m = 0.64$ has not been reached and when the random close packing for spheres is being taken into consideration.[10]

If we assume a good anchoring of the bulk polymer by means of the adsorbed layer to the filler surface—the case of PVC–E with silica fillers—the tensile stresses are likely to be able to bring about an increase of the free volume and hence the broadening of relaxation time distribution to shorter times. In the case of composites of PVC–S and eventually in the case of the PVC–E/carbon black system there does not set in a sufficient adsorption of the polymer surface layer to the filler surface. In the course of cooling the polymer is torn off from the filler surface and the stresses in the bulk polymer relax. The assumed compression pressures are probably not sufficiently strong to bring about the anchoring of the polymer to the filler surface in this case.

The physical state of the polymer in the interfiller spaces can be accounted for by various influences. In the adsorbed polymer layer itself we have to take into account the lower mobility of polymer segments in respect to their adsorption to the filler layer. The free volume increase due to tensile stresses may be taken into consideration not sooner than the boundary of this layer had been reached, i.e. in a distance of 30–200 Å from the filler surface.[9] It is also likely that the state of the polymer in the interfiller spaces will be influenced by the particle size. One might imagine that at the same filler concentration with large-sized particles larger interfiller spaces are being formed—in comparison with filler material consisting of small-sized particles. This, provided that there is an approximately similar strong adhesion layer, which enables the formation of larger regions with an increased free volume.[11,12] This corresponds with the case of the system PVC–E with milled silica (Figure 2), where the largest changes in the shape of the tan δ dependence on the temperature in the minimum region have been measured.

According to some authors, the increase of the polymer adhesion to the filler surface, as a result of the decrease in mobility of the polymer segments in the adsorbed layer, brings about the increase in value of the G' modulus and a shift of T_g to higher temperatures of the whole system.[6,9]

Our results contradict these conclusions:

With composites where one might assume a good mutual adhesion of both phases there was noticed, on the contrary, a smaller increase of the G' modulus and a smaller shift of the T_g to higher temperatures in contrast to composites where a low adhesion might have been anticipated (Figure 5). It is possible to explain this fact by the aforementioned broadening and shift of the main transition region to lower temperatures due to a negative (tensile) stress in the interfiller spaces. For this the conclusion can be drawn that in the case of the composites PVC-filler neither the value of the G' modulus nor the value of T_g are being increased by the adhesion of both phases. Their values are given by the mechanical reinforcement dependent predominantly on the filler concentration.[6,13,14,15] By the addition of filler material with good adhesion the
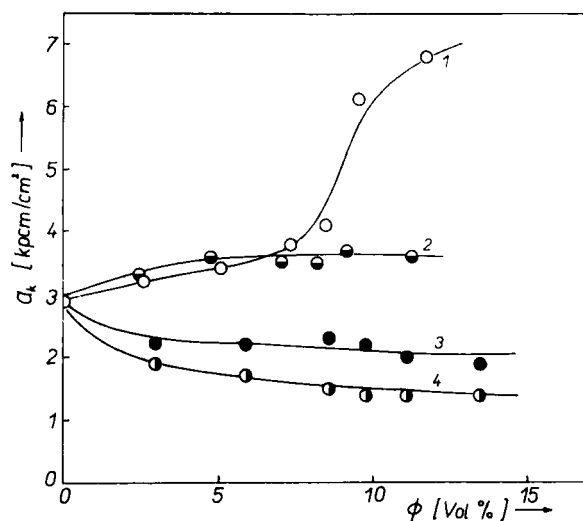
D

FIGURE 8　Notched impact strength vs volume fraction of filler in emulsion PVC.
1　Aerosil Standard.
2　milled SiO_2.
3　furnace carbon black.
4　acetylene carbon black.

effect of simple mechanical reinforcement is restricted due to the increase of the free volume of the polymer in the interfiller spaces.

The conceptions about the influence of the filler on the behaviour of the matrix are supported also by some results obtained by the determination of the notched impact strength of the polymer.

It follows from Figure 8 in the case of PVC–E with silica fillers that the impact strength increases whereby this increase is particularly marked at composites with Aerosil. In the case of analogical composites PVC–S, however, the value of the notched impact strength was affected only slightly (Figure 9). Both types of carbon blacks decrease the value of notched impact strength in the composite with PVC–E as well as with the composite with PVC–S.

It is well known that filler particles generally become effective in glassy polymers as structure defects and as stress concentrators initiating polymer fracture and decreasing the energy required for its destruction.[16,17] These generally negative effects may be restricted and suppressed respectively by changes which the filler material is able to cause in the mobility of the matrix segments in the interfiller spaces.

It may be assumed that the negative stress in the case of composite PVC–E with silica fillers has a restricting influence which causes both the increase of
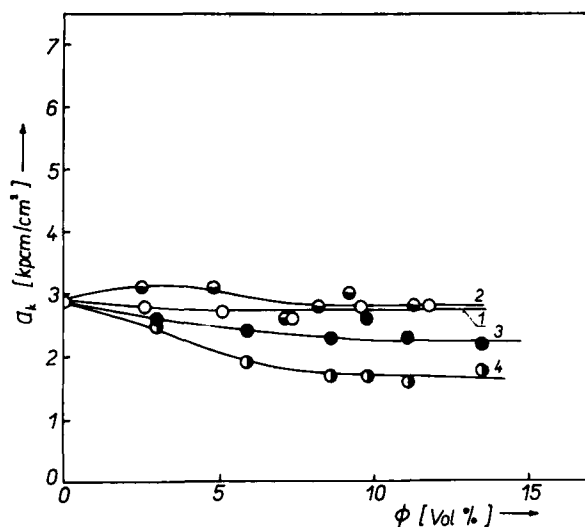
FIGURE 9 Notched impact strength vs volume fraction of filler in suspension PVC.

1 Aerosil Standard.
2 milled SiO_2.
3 furnace carbon black.
4 acetylene carbon black.

the free volume and the increase in segment mobility, hence the increase of impact strength. Again an analogy may be found with quenched PVC where together with the increase of the free volume, an increase of impact strength may also be noticed. The small effect on impact strength of milled SiO_2 is most likely due to the particle size of this filler material where large-sized particles are exerting the same intensive efficiency as structure defects by overcoming the anticipated increase of the free volume.

Fillers with an unsatisfactory adhesion to the matrix have an influence only as structure defects, generally decreasing the impact strength of the polymer. The more marked influence of the acetylene black can be accounted for by its tendency to form chains.

The significance of the quality of the interfacial boundary with regards to impact strength is illustrated in Table I. From this table it follows that the increase in adhesion of the filler particles to PVC, in the case of furnace black by oxidation as well as in the case of the PVC–S composite with Aerosil by addition of an emulsifier, results in increasing impact strength. Both adjustments are able to suppress the negative function of the filler as a stress concentrator due to changes in the free matrix volume.

TABLE I

The influence of carbon-black oxidation and of an emulsifier on impact strength a_k

PVC–E	$a_k = 2.9$ kpcm/cm^2
PVC–E + 9.8 vol % furnace carbon black	$a_k = 2.2$ kpcm/cm^2
PVC–E + 9.8 vol % oxidized furnace carbon black	$a_k = 3.8$ kpcm/cm^2
PVC–S	$a_k = 2.7$ kpcm/cm^2
PVC–S + 8.5 vol % Aerosil Standard	$a_k = 2.8$ kpcm/cm^2
PVC–S + 8.5 vol % Aerosil Standard + 3.0 vol % emulsifier (Mersolat)	$a_k = 6.5$ kpcm/cm^2

References

1. S. Newman and S. Strella, *J. Appl. Polymer Sci.* **9**, 2297 (1965).
2. P. Zítek, S. Myšík, and J. Zelinger, *Angew. Makromol. Chemie* **6**, 116 (1969).
3. R. Bode, H. Ferch, and H. Fratzscher, *Kaut. Gummi Kunststoffe* **20**, 578 (1967).
4. G. Pezzin, G. Ajroldi, and C. Garbuglio, *J. Appl. Polymer Sci.* **11**, 2553 (1967).
5. J. Maláč, *J. Appl. Polymer Sci.* **13**, 1767 (1969).
6. D. H. Droste and A. T. Dibenedetto, *J. Appl. Polymer Sci.* **13**, 2149 (1969).
7. W. H. Haslett and F. J. McGarry, *Modern Plastics* **40**, No. 4, 135 (1962).
8. A. V. Galanti and L. H. Sperling, *J. Appl. Polymer Sci.* **14**, 2785 (1970).
9. P. P. A. Smit, *Rheol. Acta* **5**, 277 (1966).
10. T. B. Lewis and L. E. Nielsen, *J. Appl. Polymer Sci.* **14**, 1449 (1970).
11. S. Newman and W. P. Cox, *J. Polymer Sci.* **46**, 29 (1960).
12. E. Šimůnková, J. Zelinger, V. Kubánek, and J. Králíček, *J. Appl. Polymer Sci.* (in press).
13. E. Guth, R. Simha, and O. Gold, *Kolloid-Z.* **74**, 266 (1936).
14. E. Guth, *J. Appl. Phys.* **16**, 20 (1945).
15. J. J. Brenna and T. E. Jermyn, *J. Appl. Polymer Sci.* **9**, 2749 (1965).
16. E. H. Andrews, "Fractures in polymers", Ch. 4, 5, Oliver and Boyd (1968).
17. "Encyclopedia of polymer science and technology", P. I. Vincent, Short-term phenomena, **7**, 315, John Wiley (1968).