

Cooperation between Chemical and Physical Networks in Crosslinked and Plasticized PVC

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SYNOPSIS

The effect of crosslinking of plasticized PVC on the mechanical properties has been investigated. Crosslinking was performed by using a dithioltriazine, and penetration as a function of temperature was used to follow the changes in mechanical properties. Changes in the melting behavior were detected by differential scanning calorimetry. Even rather low levels of gel content gave a substantial reduction in penetration in the interval 60–110°C, while a more complete reaction prevented major penetration up to at least 200°C. The penetration curve of heavily crosslinked materials showed several plateaus and the transitions could be related to melting of different crystallites formed by annealing at different temperatures. The physical network formed by the crystallites constitutes an important complement to the chemical network in plasticized PVC crosslinked by dithioltriazine. Both the amount and the melting temperature of the crystallites increased after annealing. The introduction of the chemical network further improved the heat resistance of the crystallites. The presence of the two networks will therefore show a synergistic effect with respect to the mechanical properties at increased temperatures.

INTRODUCTION

The mechanical properties of plasticized PVC are very favorable, although the material is used well above its T_g . The flow behavior is similar to that of a lightly cross-linked gel (i.e., a rubberlike behavior). This has been the subject of much debate, but the most reasonable explanation is the presence of a physical network consisting of small crystallites.^{1,2} At increased temperatures, however, plasticized PVC will flow under mechanical load.

An obvious way to increase the maximum application temperature of plasticized PVC is to introduce a permanent chemical network. This may, for example, be done by radiation crosslinking in the presence of "reactive plasticizers," a process used for the production of cable insulation.^{3–5} Alternatively, a difunctional nucleophile can be used to introduce crosslinks in PVC and in a series of papers Mori and Nakamura^{6–10} have discussed dithioltriazines in this respect.

In a recent paper¹¹ we presented results obtained with 2-dibutyl-4,6-dithiol-*s*-triazine (DB). The most important points were the effect of different catalysts on the crosslinking rate, and the changes in the molecular weight distribution during processing.

In the present work we mainly discuss the mechanical properties at increased temperatures of PVC crosslinked with dithioltriazine. We have used penetration measurements to evaluate the mechanical properties, and calorimetry to separately detect crystallinity. The major issue is the cooperation between the network formed in the chemical reaction and the physical network based on crystallites.

EXPERIMENTAL

Materials

The PVC used in this investigation was a suspension PVC from Kema Nord AB (now Norsk Hydro Plast AB), Sweden (S 706; $M_n = 50000$; $M_w = 127000$). 2-Dibutyl-4,6-dithioltriazine (Ziznet DB, Sankyo Kasei Corp.) was used without further purification

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as were magnesium oxide (extra pure, Merck), polyoxyethylene-laurylether (Brij 35, Kebo Grave AB), ditrimethylolpropane (DITMP, Perstorp AB), stearic acid (Naftozin N, Metall Gesellschaft AG) and di-2-ethyl-hexyl-phtalat (Beroxo AB). For thermal stabilization Naftovin T3 (tribasic lead sulfate, Metall Gesellschaft AG) was used.

Processing and Crosslinking

The following basic formulation was used; PVC 100 phr, DOP 40 phr, lead stabilizer 2.5 phr, and stearic acid 0.5 phr. For crosslinking, 3 phr DB and 3 phr MgO were added, as well as 2 phr Brij 35 or 0.5 phr DITMP (catalyst). After dry-mixing, plasticizer was added under agitation. The mixture was then processed on a two roll laboratory mill for 5 min at 145°C to sheets with a thickness of 1 mm. Crosslinking was, unless otherwise stated, performed at 90°C in a forced-air oven.

Analysis

The gel content was determined by Soxhlet extraction with tetrahydrofuran as described earlier.¹¹ The mechanical properties were studied by recording the

penetration of a loaded probe using a Perkin-Elmer TMS-2. The tip of the probe was flat with a surface area of 0.89 mm² and the weight was 30 g (i.e., 320 mN/mm²). Calorimetric measurements were done with a Perkin-Elmer DSC 2. The heating rate was 10 K/min and the sample weight ca. 18 mg. Nitrogen was used as atmosphere and, unless otherwise stated, only one heating cycle was performed.

RESULTS AND DISCUSSION

The major reason to crosslink plasticized PVC is to increase the mechanical properties at increased temperatures. In most cases the effect of crosslinking on the mechanical properties have been followed by tensile strength or creep at increased temperature.^{6,9,10} In this work we have instead used penetration, which is an important technological property, for instance in cable insulation. As expected the penetration decreases with increasing degree of crosslinking. This is illustrated in Figure 1 where the penetration as a function of temperature is given for a series of samples containing the crosslinking system and heat-treated at 90°C. The rather low crosslinking temperature was chosen in order to

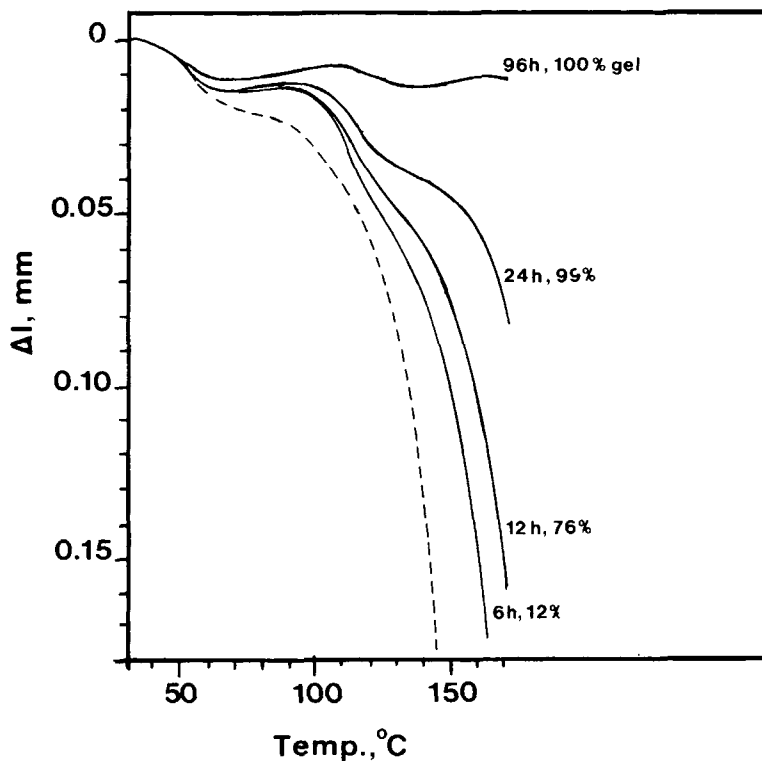


Figure 1 Penetration (Δl) as a function of temperature; (---), normal PVC; (—), crosslinked PVC (2 phr Brij 35).

more easily obtain materials with different amount of gel. At 180°C, for example, which could be a more realistic temperature for practical applications, 100% gel would be reached in 10 min.

As seen by the content of gel given in Figure 1, a relatively small amount of gel might be enough to give rather large improvements in the interval 60–110°C, which perhaps is the most important for practical applications. If penetration resistance is important at still higher temperatures (i.e., above 110°C), it is obvious that the conversion in the crosslinking reaction must be high. In order to have a completely crosslinked system there should, in theory, be at least one crosslinking point per macromolecule.¹² For the polymer used in this investigation that would imply one per 800 monomer units. The maximum number of crosslinks that could be obtained with the amount of DB used, 3 phr, is, on the other hand, one per 75 monomer units. Considering the rather large difference in time of heat treatment between the 99 and 100% gel samples, as well as the drastic effect on penetration, it is reasonable to assume that the crosslinking density is relatively high in the 100% gel sample.

A decreased amount of DB would, of course, imply a decrease in the crosslinking density. For materials heated relatively long times and containing 2 and 3 phr DB, respectively, differences in penetration behavior could be observed only above 150°C (see Fig. 2). The results obtained at low contents of gel (Fig. 1) even indicate that it is not necessary to have a thorough-going chemical network in order to obtain substantial improvements in the interval 60–110°C.

It turned out that the penetration curve for the noncrosslinked reference sample was changed as

well after heating at 90°C (see Fig. 3). In the region where the crosslinked material has a plateau (60–110°C), the rate of penetration is moderated. This effect increased with the time of heating but the drastic effect observed for the crosslinked samples was not reached. Corresponding phenomena have been observed in studies of the effect of aging on dilute PVC–DOP gels using dynamic mechanical measurements.¹³ The behavior for a heat-treated sample with higher molecular weight ($M_w = 4 \times 10^5$) is included in Figure 3 as well. Although there is no gel at all in this sample, the penetration between 60 and 110°C is very similar to that of the crosslinked samples (cf. Fig. 1).

As mentioned in the Introduction, it is generally considered that the mechanical properties are due to the presence of a physical network. The crosslinks are believed to be composed of small crystallites with a size of about 10–15 nm.¹⁴ Although there is some uncertainty, the degree of crystallinity is usually stated as 5–10%.¹² The behavior of the reference sample in Figure 3 can thus reasonably be explained by annealing. This implies that the degree of crystallinity and, consequently, the crosslinking density would increase. Although a certain improvement is obtained by the enlarged physical network, this must be reinforced by a chemical network to avoid major penetration above 60°C. There is no need for a dense network, but a similar effect is obtained if a polymer with higher molecular weight is used.

At a temperature about 30°C above the annealing, or crosslinking, temperature (90°C), the crystallites formed by annealing have melted. This explains further penetration as observed in Figure 3 and for the less crosslinked samples in Figure 1. The pen-

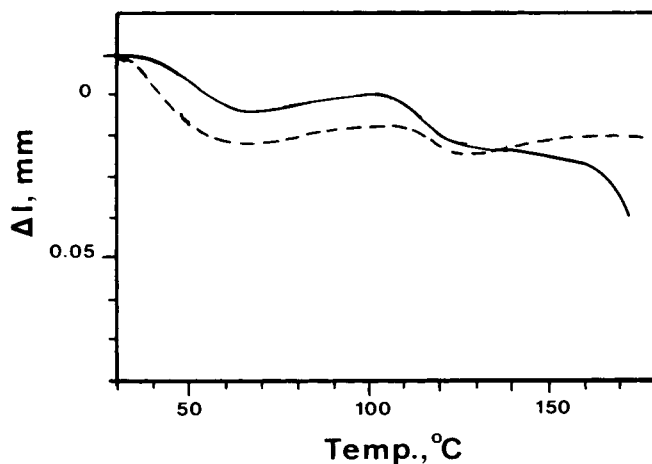


Figure 2 Penetration (Δl) as a function of temperature after crosslinking for 48 h at 90°C (1 phr Brij 35); (—), DB 2 phr; (---), DB 3 phr.

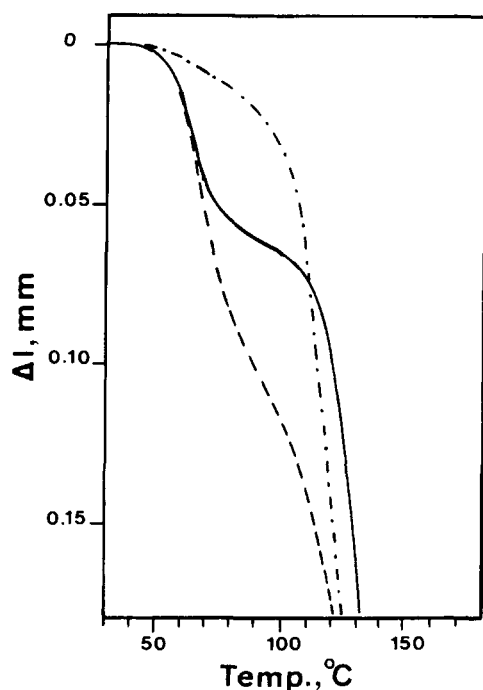


Figure 3 Penetration (Δl) as a function of temperature for materials without crosslinker; (---), normal PVC, no annealing; (—), normal PVC, annealed for 144 h at 90°C; (-·-·-·-), high molecular weight PVC ($M_w = 4 \times 10^5$), annealed for 24 h at 90°C.

etration curve for more strongly crosslinked materials shows, on the other hand, a profile with several plateaus separated by distinct transitions at 40–60, 120–135, and 180–200°C, respectively (see Fig. 4). It is reasonable to assume that these transitions are related to the disintegration of different kinds of crosslinking points. It should be noted, however, that no penetration occurs above 200°C (the maximum deflection in the TMA curve in Fig. 4 corresponds to 3–4% penetration). This indicates the presence of a relatively dense and strong temperature-independent network connected via covalent bonds.

In Figure 4, the result of a parallel DSC experiment is given as well. It is obvious that the transitions in the penetration curve are associated with endotherms in the DSC trace. Admittedly, the DSC peak related to the transition at 40–60°C is somewhat indistinct. However, the starting temperature in the DSC run was 23°C, and the measuring system had not equilibrated before the first peak. If a lower starting temperature is used, this peak will be more clearly defined, see below. In the following discussion the peaks will be referred to as peak 1, 2, and 3, respectively, according to Figure 4.

The general behavior of the DSC trace with three endotherms could be the result of annealing at three

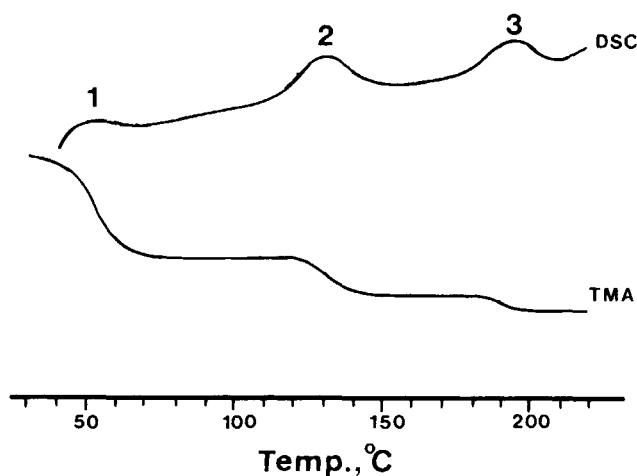


Figure 4 Thermogram (DSC) and penetration curve (TMA) for PVC crosslinked for 144 h at 90°C (0.5 phr DITMP).

successively lower temperatures; roll-milling at 145°C, crosslinking at 90°C, and storing at room temperature, for peaks 3, 2, and 1, respectively. If the crosslinking temperature is increased, peak 2 is displaced correspondingly to higher temperatures. In Figure 5 the DSC curves for two samples crosslinked at 90 and 120°C are given. The maximum of peak 2 is situated at 110 and 140°C, respectively (i.e., about 20°C above the annealing temperature). Similar results have been reported earlier for non-crosslinked plasticized PVC.¹⁵

As a somewhat lower initial temperature was chosen for the DSC runs given in Figure 5, peak 1 is much more well defined in these cases. The relation between peak 1 and storing (or annealing) at room temperature is illustrated in Figure 6. The upper curve was obtained after crosslinking for 96 h at 90°C. After rapid cooling the second trace was

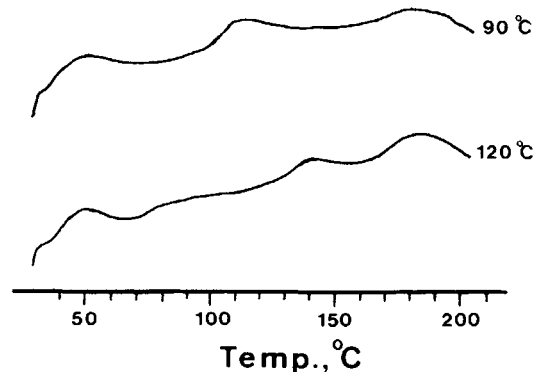


Figure 5 Thermogram for PVC crosslinked for 24 h at 90°C and 4 h at 120°C, respectively (0.5 phr DITMP).

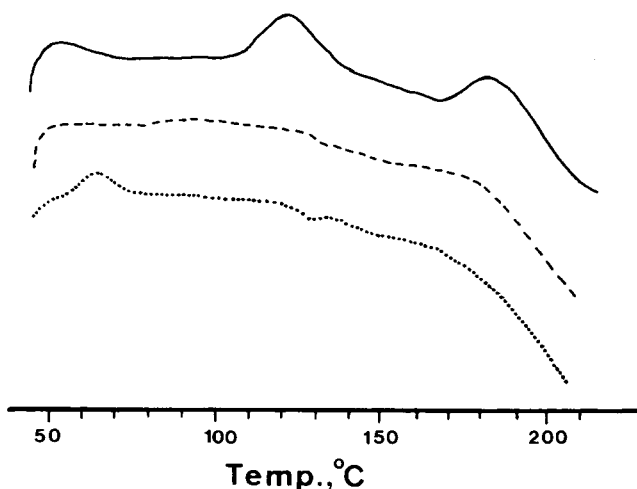


Figure 6 Thermograms for PVC crosslinked for 96 h at 90°C (0.5 phr DITMP); (—), first run; (---), second heat cycle after rapid cooling; (···), third heat cycle after annealing for 24 h at 37°C.

recorded immediately. Except for a broad and less well defined endotherm at higher temperatures no distinct peaks similar to those in the first run can be observed. After repeated cooling and annealing at 37°C for 25 h a third run was performed, and a new endotherm, corresponding to peak 1, could be observed at about 60°C. A similar behavior has been reported earlier for dilute PVC-DOP gels.¹⁶

Figure 7 shows the effect of increased time of heat treatment at 90°C on the thermogram for samples with and without the crosslinking system. In accordance with earlier reports¹⁵ the peak temperature for the endotherm at about 110°C increases somewhat with the time of treatment. If the peak temperatures in the noncrosslinked and the crosslinked samples are compared, it is obvious that peak 2 is displaced towards higher temperatures to a greater extent in the latter case. This is illustrated in Figure 8 using the DSC traces obtained for the samples heated for 144 h. It should also be noted that there is a very distinct difference between the two samples with regard to the behavior of peak 3. For the noncrosslinked sample, peak 3 is not influenced by the annealing time (see Fig. 7). This is what could be expected as this endotherm extends from 155 to 208°C with a flat maximum at about 160°C [i.e., well above the annealing temperature (90°C)]. For the crosslinked material, on the other hand, this endotherm becomes sharper and the peak is displaced towards higher temperatures.

The peak temperatures are summarized in Table I. The shift of the maximum of peak 2 towards higher temperatures is up to 15°C larger in the crosslinked

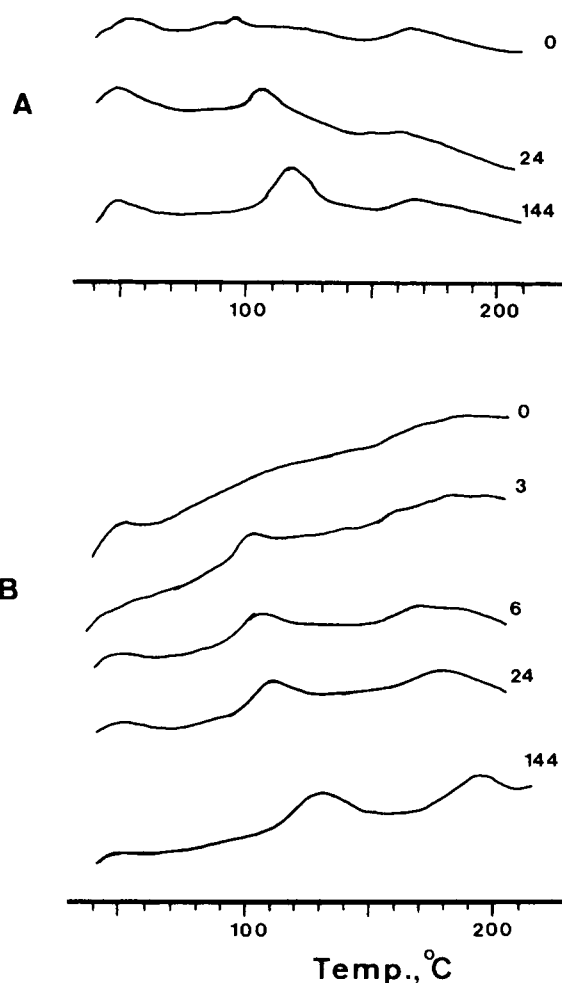


Figure 7 Thermograms for normal (A) and crosslinked (B) PVC heat-treated different times (h) at 90°C.

material after 144 h heat treatment at 90°C. The effect on peak 3 is still more obvious. In the noncrosslinked sample the maximum temperature is

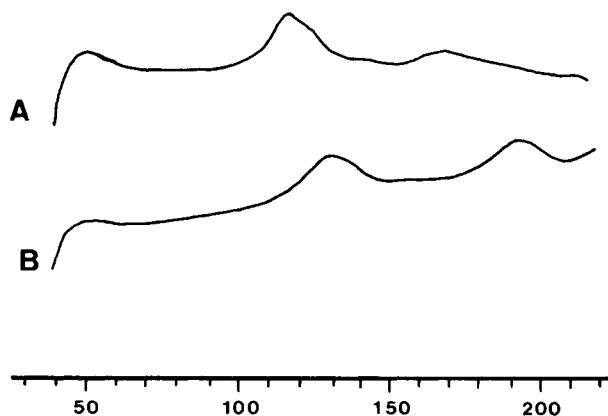


Figure 8 Thermograms for normal (A) and crosslinked (B) PVC, heat-treated for 144 h at 90°C.

Table I Effect of Annealing at 90° on DSC Peak Temperatures (°C)

Annealing Time, h	Sample			
	Normal		Crosslinked	
	Peak 2	Peak 3	Peak 2	Peak 3
0	—	161	—	161
3	—	—	101	—
6	—	—	105	171
24	105	161	112	178
48	—	—	114	—
144	116	162	130	193

approximately constant, whereas it increases as much as 30° if the system undergoes simultaneous crosslinking. The increase in peak temperature for the noncrosslinked sample should reasonably be explained by increasing crystal size or increased ordering within the crystallites. The additional increase observed for the crosslinked sample, in particular for peak 3, is much more difficult to explain as an annealing effect only.

In the crosslinking material studied in this investigation, crosslinks are formed during the annealing. One would not expect that the amount of crystals melting at high temperature (peak 3), or their homogeneity, would increase when crosslinks are introduced. There should be no negative effect on the high temperature crystals either, as they have been formed before the crosslinking reaction was started. The introduction of crosslinks implies, however, that the chain mobility in the amorphous phase decreases, in particular in the neighborhood of crosslinking points. As the crystallites are relatively small in PVC, about 10–15 nm,¹⁴ the structure of the amorphous phase in the vicinity of the crystallites should be important. A decreased mobility could cause an increase in the temperature necessary to melt the crystallites. This effect should thus increase with increased crosslinking density.

The maximum melting temperature of pure PVC, T_M^0 , is stated to be ca. 220°C.⁵ In a plasticized material the corresponding temperature, T_M , depends on the content of plasticizer, which can be expressed by the following equation¹⁷:

$$1/T_M - 1/T_M^0 = RV_u(v_1 - \chi V_1^2) \Delta H_u V_1 \quad (1)$$

where ΔH_u is the enthalpy of melting per monomer unit, V_1 and V_u are the specific molar volumes of the plasticizer and monomer units, respectively, v_1

is the volume fraction of plasticizer, and χ is the Flory–Huggins interaction parameter of the system. For PVC–DOP systems χ is believed to be close to zero.^{17,18} Taking $v_1 \approx 0.36$ (40 phr DOP), the estimated decrease in melting point should be ca. 20°C (i.e., $T_M \approx 200^\circ\text{C}$). This value should, for example, be obtained for an indefinitely large crystal. The high temperature endotherm (peak 3) extends to a somewhat higher temperature, 208°C, in all cases (Fig. 7). Even if the mobility in the amorphous phase is decreased due to the introduction of crosslinks, the melting temperature should, however, not increase above T_M^0 . This can explain why peak 3, which is very broad in the noncrosslinked samples, becomes sharper with increasing degree of crosslinking (cf. DSC traces in Fig. 8).

The observed penetration properties are thus a result of two networks, one physical with crystallites as crosslinks and one deliberately introduced chemical based on covalent bonds. The introduction of the permanent network does not, however, decrease the flexibility at room temperature (cf. penetration up to 50°C in Fig. 1), which means that the physical network dominates. It has been stated that the distance between the physical crosslinks is 80–100 monomer units,¹⁹ (i.e., the same as the maximum density which could be obtained with 3 phr DB). The dominance of the physical network in the low temperature range indicates that conversion is not complete.

Melting of the crystallites corresponding to peak 1 causes increased penetration. If a chemical network is introduced, penetration becomes somewhat limited (cf. the broken and the solid lines in Fig. 1), but there is no marked effect of the amount of chemical crosslinks, except at high levels. Increasing the temperature above the second endotherm results in complete penetration, unless the total network is stabilized with chemical crosslinks (i.e., the latter becomes more and more dominating).

The rubberlike behavior of plasticized PVC is generally related to the presence of the crystallites. At temperatures above 50–60°C, however, plasticized PVC will flow under mechanical load, although different heat treatments such as processing and annealing have introduced crystallites melting at higher temperatures. The strength of the material is thus substantially decreased when a relatively small part of the crystallites is disintegrated. The high melting crystallites will, of course, influence the rheological behavior of the PVC–DOP “melt”.²⁰ If, on the other hand, a relatively dense chemical network is introduced as well, the load-bearing ability of the crystallites can be seen in a simple me-

chanical test as illustrated by the plateaus in Figure 4.

If a higher crosslinking temperature is used, the melting temperature of the crystallites formed by annealing will be higher. The physical network should thus contribute to decreased penetration in a larger temperature interval. The time to reach maximum degree of crystallinity is, however, almost independent of the temperature,¹ while the rate of the chemical crosslinking is strongly temperature dependent.¹¹ It must also be remembered that the relatively low thermal stability of PVC restricts the allowable time at high temperatures. At about 180°C complete crosslinking can be obtained in a few minutes,¹¹ while annealing demands ca. 1 h.¹ The latter would definitely involve a too heavy thermal load for a conventionally stabilized material. If the chemical crosslinks are introduced very rapidly at a high temperature, the crosslinking points will interfere with the crystallization. Furthermore, the attainable degree of crystallization shows a maximum at about 125°C.¹ In order to obtain the most efficient physical network complementing the chemical one, a relatively low crosslinking temperature should thus be advantageous.

CONCLUSIONS

This investigation shows that the physical network formed by crystallization is an important complement to the chemical network in plasticized PVC crosslinked with dithioltriazines. The effect of the physical network successively decreases with increasing temperature due to melting of the crystallites. The heat resistance of the physical network can, however, be substantially improved by annealing, which can be performed at temperatures suitable with respect to the crosslinking as well. A relatively dense chemical network will increase the heat resistance of the physical network furthermore.

Large improvements in the penetration properties up to relatively high temperatures can be obtained even without a thorough-going chemical crosslinking. After annealing at 90°C, PVC with increased molecular weight, or a normal quality with a few

chemical crosslinks, will show good resistance towards penetration up to about 110°C.

The financial support from the Swedish Board of Technical Development (STU) and Norsk Hydro a.s is gratefully acknowledged.

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Received October 3, 1989

Accepted February 26, 1990