Study of the healing process of polymers with different chemical structure and chain mobility

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A systematic study of the healing process of polymers with different chemical composition, structure and properties is carried out. It is shown that welding can be due to a number of physical and/or chemical factors. Diffusion alone leads to relatively weak welding under the selected conditions. A jump is observed in the temperature dependence of the shear stress of Kepton-H and Upilex-R. The increase of the activation energy is explained by chemical reactions taking place at the contacting surfaces. For the first time the healing process is carried out at temperatures below the glass transition temperature. In this way, the contribution of the physical processes to the healing is distinguished from that of the chemical processes.

(Keywords: chemical healing; chain mobility; diffusion; Kepton-H; Upilex-R)

INTRODUCTION

The process of joining two samples of bulk amorphous polymer which have been brought into good contact at a temperature above the glass transition point is called 'healing'. During the last decade the healing of polymers has been widely investigated since it is interesting both from a theoretical and a practical point of view[1–9]. On the basis of the healing process, new polymer composite materials can be obtained[10,11].

In contrast to the healing due to physical processes (diffusion)[12], it was recently suggested that healing can be the result of chemical reactions in the solid state. Such 'chemical healing' is supposed to be due to additional condensation and exchange (*trans*) reactions taking place at the polymer–polymer interface[13,14].

In order to distinguish the contribution of the solid state reactions between macromolecules located at the interface from that of diffusion-based healing, samples of polyamides with strongly restricted chain mobility (by crystallization and chemical crosslinking in the amorphous regions) were investigated[15]. It was concluded that the welding of crosslinked polyamides is due mainly to solid state chemical reactions at the interface because the diffusion was suppressed[15]. The same conclusion can be derived from the studies of the healing process in native cellulose[16] and in a liquid crystalline polymer[17], i.e. in polymers with an inherent strongly restricted chain mobility.

In this work, further evidence is sought for the existence of the chemical healing phenomenon using a series of polymers with different chemical structure and chain mobility.

EXPERIMENTAL

The polymers used are listed in *Table 1*. Commercial films of PBT, PTFE, Kepton-H (DuPont, USA) and Upilex-R (ICI Americas Inc., USA) were obtained. Films of PA-6,12 (Aldrich Chemical Co. Inc, USA), PPS and PP (Polysciences Inc., USA) were prepared by pressing at high temperature. Strips 0.5 cm wide and 3 cm long were cut from the polymer films. Samples of PA-6,12 and PBT with higher melting temperatures were obtained by previous annealing for 6 h at 200°C.

The thermal properties of the samples were studied by means of a Perkin-Elmer differential scanning calorimeter. Glass transition and melting temperatures, T_g and T_m, respectively, were determined. The healing procedure was carried out by placing two strips in a drill press vice with partial overlapping (~ 1 cm). The healing process was performed in a vacuum oven for 6 h at different healing temperatures, T_h, between 60°C and 250°C, T_h being always below the melting temperature.

The mechanical properties were measured using an Instron tester. The ends of the healed samples were fixed in the grips and drawn at a cross-head speed of $0.25\ \mathrm{cm\ min^{-1}}$. The shear stress, σ, was calculated, referring to the value of the bonded area.

RESULTS AND DISCUSSION

The polymers used and their T_g and T_m values are shown in *Table 1*. The polymers differ in composition and chemical structure which leads to different thermal properties. Since the T_h is selected to be always below T_m, the T_m is not so important in this case. Except for PA-6,12 and PBT, all other polymers have a high temperature resistance. The T_g of the polymers studied changes within a broad range, between -150°C (PTFE) and 410°C (Kepton-H). The chain mobility below T_g differs drastically from that above T_g. In case the healing process is a result of physical diffusion, it is of great importance to determine whether T_h is below or above T_g.

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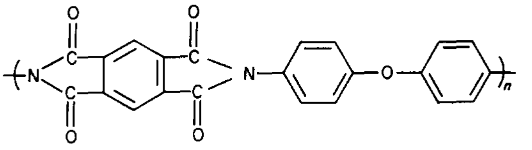
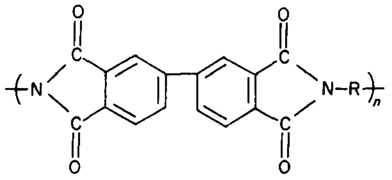
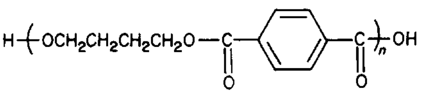
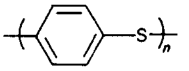
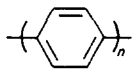
Table 1 Glass transition and melting temperatures of polymers with different chemical structure and chain mobility

Polymer	T_g (°C)	T_m (°C)
Polytetrafluoroethylene (PTFE, Teflon) $-(CF_2-CF_2)_n-$	−150	327
Polypyromellitimide (Kepton-H) 	360–410	-
Polyimide (Upilex-R) 	285	-
Polyamide-6,12 (PA-6,12) $-(NH-(CH_2)_6NH-OC-(CH_2)_{10}CO)_n-$	45	225
Poly(butylene terephthalate) (PBT) 	25	229
Poly(*p*-phenylene sulfide) (PPS) 	85	282
Poly(*p*-phenylene) (PP) 	232	-

The chemical composition and structure of the polymers are related to the chain flexibility and chain mobility.

During the healing procedure, the following processes can take place between molecules on the contacting polymer surfaces:

1. van der Waals intermolecular interaction;
2. formation of hydrogen bonds;
3. intermolecular interaction based on the specific overlapping of π-electron orbitals of polymers with conjugated bonds;
4. physical diffusion of molecules through the contacting surfaces;
5. intermolecular solid state exchange (*trans*) reactions or post-polycondensation.

When two polymer samples are bonded together as a result of healing, the following question arises: which of the above processes represents the main reason for the welding?

In the case of PTFE, only van der Waals interactions and diffusion are possible. The temperature dependence of σ for PTFE, PA-6,12, PBT, Upilex-R and Kepton-H are shown in *Figure 1*. One can see that the interaction at the contacting surfaces which is reflected in the value of σ is lower in the case of PTFE. Since the diffusion process is rather slow, it is to be supposed that within 6 h of healing, van der Waals interactions between macromolecules at the contacting surfaces are predominant, especially at lower temperatures.

Welding of PA-6,12 and PBT films can be due to most of the processes mentioned above, excluding the interaction between conjugated systems of neighbouring macrochains. The shear stress strongly increases with the rise in T_h (*Figure 1*). If the overlapping area is larger than the critical contact length[13] the shear force is so high that instead of debonding, breaking of the samples is observed (at $T_h > 180$°C). Since the rise of the temperature favours all possible processes it is rather difficult to distinguish the contribution of each of them. On the basis of investigations with crosslinked polyamides[15] and polymers with inherent low molecular mobility such as cellulose[16] and liquid crystalline polymers[17], it has already been shown that welding is observed even at suppressed diffusion. It should be noted that both PA-6,12 and PBT form a great number of strong hydrogen bonds. In addition to the possible chemical interactions between neighbouring macromolecules, such hydrogen bonds should lead to a very strong welding of the healing components.

An interesting effect of T_h on σ is observed with Upilex-R and Kepton-H (*Figure 1*). As seen in *Table 1*, the chemical structures of these polymers, in addition to low molecular mobility, suggest a specific intermolecular

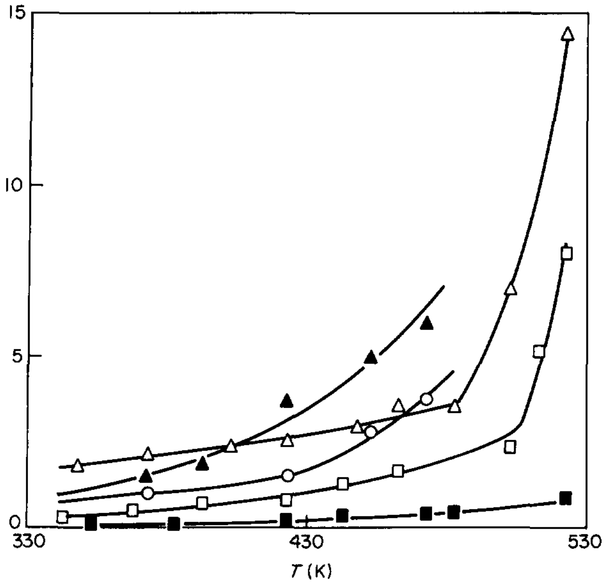


Figure 1 Dependence of the shear stress σ on the temperature of the healing process for different polymers: (■) PTFE; (□) Kepton-H; (△) Upilex-R; (○) PBT; (▲) PA-6,12

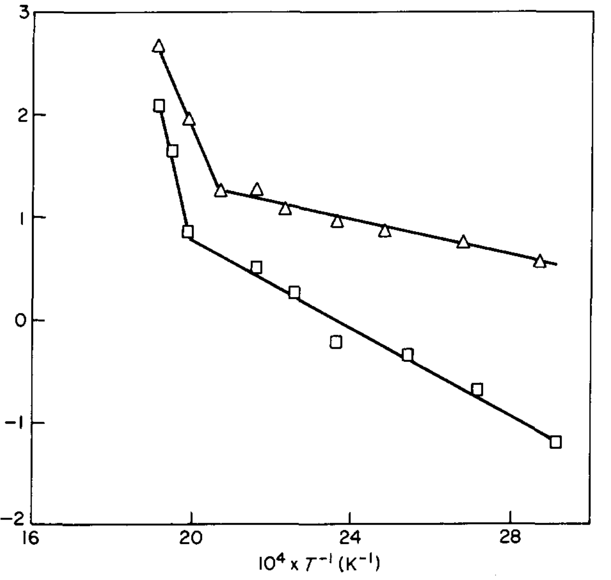


Figure 2 Arrhenius plot of the temperature dependence of the shear stress σ of Kepton-H (□) and Upilex-R (△)

interaction between conjugated π-electron systems. Such an interaction is possible between neighbouring macrochains from contacting surfaces.

Upilex-R and Kepton-H are characterized by very high T_gs (*Table 1*) so that the highest T_h (250°C) is much lower than T_g. It is clear that diffusion is practically impossible over the entire range of T_h. For that reason the observed welding of Kepton-H and Upilex-R films is due to other factors — mainly to intermolecular interactions (including hydrogen bonding) and possibly to chemical reactions on the contacting surfaces. The problem is how to estimate the contribution of each process to the welding.

The σ against temperature dependence of Upilex-R and Kepton-H is presented in an Arrhenius plot in *Figure 2.* Two straight lines are observed for each polymer with slopes leading to different values of the activation energy, E_a, of the welding processes:

Upilex-R	7.1 kJ mol^{-1}	for $T_h < 210°C$
	74.6 kJ mol^{-1}	for $T_h > 210°C$
Kepton-H	17.6 kJ mol^{-1}	for $T_h < 230°C$
	134.5 kJ mol^{-1}	for $T_h > 230°C$

The lower values of E_a (7.1 and 17.6 kJ mol^{-1}) can be related to the hydrogen bonding. The higher values (74.6 and 134.5 kJ mol^{-1}) do not correlate with any type of intermolecular interaction except for chemical reactions between molecules at the contacting surfaces. In other words, in the cases of Upilex-R and Kepton-H when T_h is lower than 210 and 230°C, respectively, the bonding can be due to intermolecular interactions (hydrogen-bonds and possibly interchain interactions of delocalized π-orbitals). When T_h is higher than 210°C, welding can be related to chemical reactions between neighbouring molecules at the contact area. This is most likely the reason for the observed jump in E_a (*Figure 2*).

The E_a value for Kepton-H (134.5 kJ mol^{-1}) is identical with the reported E_a values for thermal weight loss of Kepton-H film in air over the temperature range 442–485°C (129.9 and 138.3 kJ mol^{-1})[18]. This is in agreement with our assumption that the higher E_a value should be related to the chemical processes.

In order to find direct evidence for chemical reactions leading to welding, investigations were carried out by i.r. and electron spin resonance (e.s.r.) spectroscopy. The i.r. spectra of Kepton-H films taken from the contact area and outside the overlapping are identical and independent of T_h. Hence, the healing process is not related to a new type of chemical bonds between macromolecules.

The e.s.r. spectra of Kepton-H films subjected to healing at 65 and 240°C are shown in *Figure 3.* The narrow signals without superfine structure demonstrate the existence of unpaired electrons. The number of unpaired electrons is proportional to the integral intensity of the e.s.r. signal, i.e. to the area under the peak. The peak area/sample weight ratio is given in *Table 2.*

As can be seen from *Table 2*, the number of unpaired electrons is higher at higher T_h. On the other hand, the healing process at contacting surfaces leads to a further increase in the e.s.r. signal. This can be considered as proof of chemical processes taking place at the polymer–polymer interface. It is well known that other polyazo compounds, such as Schiff base polymers, fail to show e.s.r.[19]. The higher molecular weight of the polymer leads to a higher signal. When the chain length is increased from low to high values, this is reflected in the orbital delocalization of the conjugated π-electron system[19].

Most likely, the healing process of Kepton-H films can be considered as the overlapping and delocalization of molecular orbitals of neighbouring macrochains from contacting surfaces. This is equivalent to creating new chemical bonds and increasing the chain length which leads to increasing the e.s.r. signal.

Another possibility is related to the high electrostatic interaction between delocalized π-orbitals of molecules at contacting surfaces. Usually, the weak interactions are associated with physical processes, while the strong interactions are related to chemical ones. Since both processes can take place at the polymer–polymer

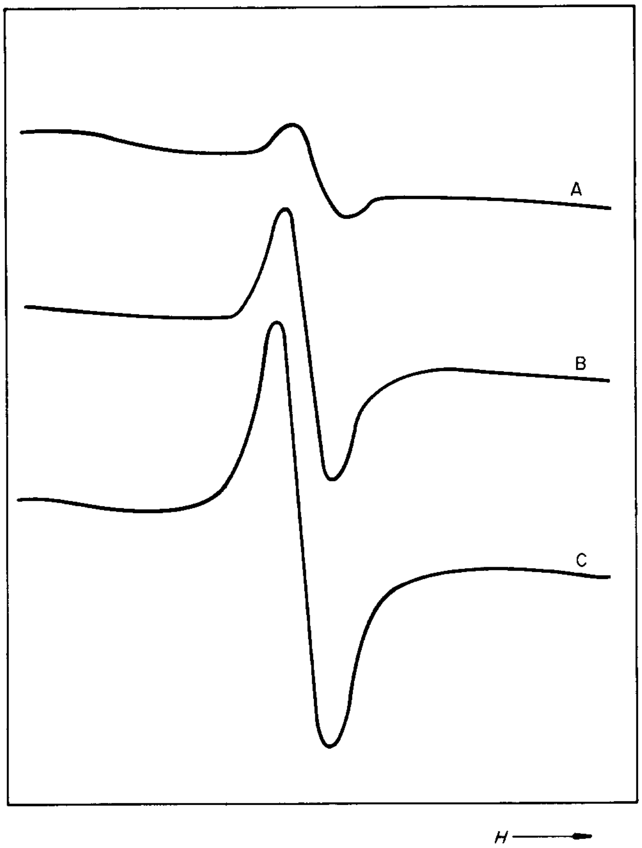


Figure 3 E.s.r. spectra of Kepton-H film subjected to healing: (A) at $T_h = 65°C$; (B) at $T_h = 240°C$ (spectrum taken outside the overlapping area); (C) $T_h = 240°C$ (spectrum taken from the healing area)

Table 2 E.s.r. data for Kepton-H film subjected to healing

T_h (°C)	Peak area/sample weight ($cm^2 g^{-1}$)
65	190.0
240 (outside the healing area)	373.5
240 (from the healing area)	484.7

interface, there is no sharp boundary between them. However, it is logical to suppose that at $T_h > 210°C$ the welding is due mostly to interchain σ-bond formation at the contacting surfaces, i.e. to chemical healing. It is known that other polymers with delocalized π-orbitals possess interchain σ-bonds[20]. The jump in the E_a with increasing temperature is proof of the change in nature of the healing from a physical to a chemical process.

The results of the healing experiments with PPS and PP can be considered as further confirmation of this concept. These polymers are characterized by intrinsic chemical and thermal resistance[21,22]. The PPS films were subjected to the healing procedure but bonding was not achieved after 6 h of healing at 250°C. PP films behaved in the same manner.

During the healing procedure of PPS and PP films diffusion is practically excluded because of the low molecular mobility. Chemical reaction between macromolecules as well as the formation of hydrogen bonds are impossible and healing was not observed. It can be concluded that van der Waals interaction alone is not sufficient for the strong welding.

In other words bonding can be due to:

1. diffusion when the formation of hydrogen bonds and chemical reactions are excluded (PTFE);
2. diffusion, hydrogen bond formation and chemical reactions (PA-6,12 and PBT);
3. chemical reactions when T_h is sufficiently high but below T_g so that diffusion could be restricted (Kepton-H, Upilex-R).

If none of these processes takes place at the contacting polymer surfaces welding is not observed (PPS and PP).

CONCLUSIONS

The systematic study of the healing process at different temperatures for polymers with different chemical composition, structure and properties shows that welding can be due to a number of physical and/or chemical factors. In some cases the physical interaction is predominant but for selected healing conditions it leads to relatively weak welding. Some chemical processes cause welding when diffusion is excluded. High E_a values and high debonding stresses are observed in this case. An intermediate situation is observed in the cases when hydrogen bonding can take place. In fact, hydrogen bonds can be considered either as physical or as chemical bonds according to their intermediate energy value.

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