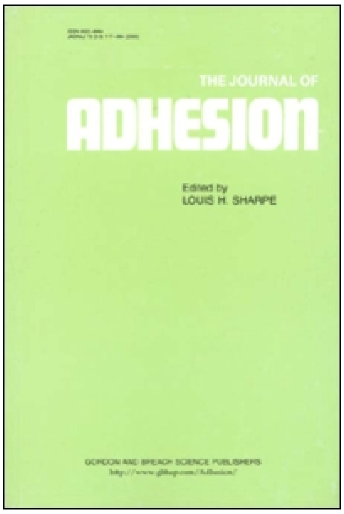

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Reactive Hot Melts on the Basis of Polyester and Polyamide†

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Hot melts show many advantages over other adhesives, for instance, their lack of solvent and their very short setting time just by cooling. The weak point of hot melts in comparison to thermosetting resins is their limited thermal resistance. There is no doubt that the high performance hot melts on the basis of polyester and polyamide show a better heat performance than the widely-used rubbery hot melts. Nevertheless, it is true that the thermal resistance is limited by the melting point of the hot melt. To improve the heat performance, without losing the favourable hot melt properties, crosslinkable hot melts have been created. For the example, copolyamide/blocked isocyanate blends, it can be shown that crosslinkable hot melts are achievable in a wide range of reactivities. After curing, which takes place during the bonding process, these hot melts withstand temperatures of over 220°C even if the melting point of the initial hot melt was 100°C.

KEY WORDS Crosslinked hot melt adhesives; blocked isocyanates; high performance; polyamides; polyesters; thermal resistance.

INTRODUCTION

Hot melt adhesives consist of thermoplastic polymers. Melting point and melt viscosity of hot melt adhesives are relatively low compared to those of thermoplastic materials in general. The bonding with hot melts is performed by wetting the substrate surfaces with the hot polymer melt while joining them. Final bond strength is achieved

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after cooling the hot melt. The main advantage of hot melts over other adhesives is their lack of solvent and their very short setting time.

The weak point of hot melts in comparison to thermosetting adhesives is their thermal resistance. There is no doubt that polyester and polyamide hot melts show a better heat performance than the widely used ethylene vinylacetate copolymers (EVA) or styrene diene block copolymers (SBS, SIS).[1,2] Nevertheless, it is true that the thermal resistance is limited by the melting point of the hot melt. The melting point on the other hand defines the processing temperature which itself is limited by the thermal stability of the substrates.

To overcome this problem we have created crosslinkable hot melts which hold the advantages of hot melts but show a better heat performance.

High performance hot melts

The so-called high performance hot melts are semicrystalline polymers on the basis of polyester or polyamide.[3] Melting points in the usual range of 80–200°C are achieved by copolymerizing different monomers. Figure 1 shows the chemical structure of a polyester hot melt. The usual monomers are terephthalic acid, isophthalic acid and several aliphatic diacids and glycols. The polymer contains hydroxyl and/or carboxyl endgroups. A typical copolyamide hot melt, as shown in Figure 2, is polymerized from caprolactam, laurinlactam and several aliphatic diacids and diamines.[4] The endgroups in this case are carboxyl and/or amine.

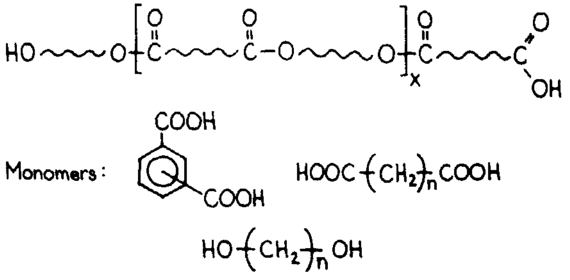


FIGURE 1 Chemical structure of a copolymer hot melt.

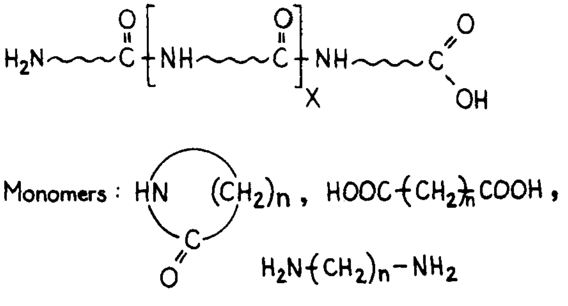


FIGURE 2 Chemical structure of a copolyamide hot melt.

Possibilities for crosslinking

Chemically these polyester or polyamide hot melts can be crosslinked *via* their functional endgroups. Possible crosslinking agents are multi-functional epoxies, isocyanates, oxazolines and so on. The crosslink density of the cured hot melt depends on the chain length of the polymer; it is relatively low compared to thermosetting resins.

Higher crosslink densities are achievable by using functionalized copolymers. In this way polymers with higher concentrations of hydroxyl, carboxyl or amine groups can be produced. Other functional groups, such as double bonds, can be introduced in the same manner.

The chemical possibilities in finding crosslinkable combinations with polyesters or polyamides are virtually unlimited. Unfortunately, the mixtures of the said reactive compounds with the hot melt are not storage stable; the reaction already starts during the blending process.

To combine the properties of long shelf life and fast crosslinking, the reactivity has to be inhibited. Possibilities are a chemical masking of functional groups or a physical microseparation of the components. Another consideration is crosslinking with humidity. It is not possible to expand on all these possibilities in this paper; however, a chemically-blocked system will be concentrated on. It will be shown that the boundaries with physically-inhibited systems or humidity-reactive systems are smooth.

Blocked isocyanates

A well known example of the chemical masking of reactive compounds is the blocking of isocyanates.[5] The reaction of isocyanates with proton donors, H-B, like phenols, lactams, malonic esters and so on is an equilibrium reaction as illustrated in Figure 3. The equilibrium shifts to the left side of the equation at elevated temperaures. In other words, blocked isocyanates form free isocyanates when heated. The cleaving temperature depends on the chemistry of the isocyanate and the blocking agent. In the presence of a crosslinkable polymer the crosslinking reaction starts as soon as free isocyanate has been formed.

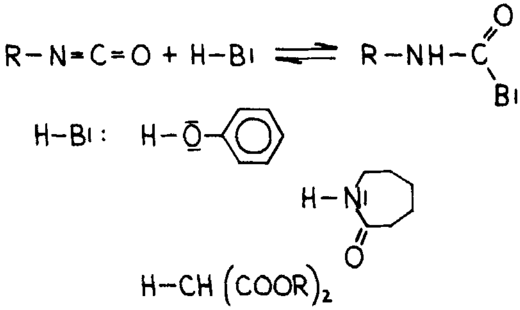


FIGURE 3 Chemistry of blocked isocyanates.

The reaction kinetics of isocyanates or blocked isocyanates with hydroxyl, carboxyl or amine groups can be investigated by differential scanning calorimetry (DSC). Unfortunately, these experiments can be only conducted on low molecular weight model compounds as, for instance, hexane diol, adipinic acid or hexamethylene diamine. In the case of polymeric hot melts with molecular weights in the range of 10,000 to 15,000 g/Mole the concentration of reacting groups is too small to be detected by DSC. Nevertheless, the DSC measurements on low molecular model compounds give useful information about the kinetics of polymeric systems as well.

RESULTS AND DISCUSSION

Table I shows the reaction temperatures of variously blocked MDIs, which have been stochiometrically mixed with different reaction partners. The given reaction temperatures are the onset and the maximum of the reaction exotherm measured by DSC at a heating rate of 20°C/min.

The first experiments (1–3) indicate decreasing affinity of the isocyanate in the grading: alcohol > acid > amine. The poor reactivity of the hexane diamine seems not to be dependent on the chain lengths.[4] Small amounts (0.1%) of triethylamine as a catalyst, on the other hand, decrease the reaction exotherm by 30°C.[5]

Because none of these mixtures with unblocked MDI is storage stable, the following measurements will refer to blocked species. From the literature, it is known that lactam-blocked isocyanates are less reactive than phenol-blocked isocyanates; and the latter are less reactive than free isocyanates.[5] The experimentation data on that topic[6–9] are, at first glance, disappointing. Nearly no difference is

TABLE I
Reaction temperatures of differently blocked MDIs measured by DSC (heating rate: 20°C/min)

	Blocking agent	Reaction partner	Reaction temperature/°C onset	Reaction temperature/°C maximum
1	unblocked	hexane diol	70	90
2	unblocked	adipinic acid	130	155
3	unblocked	hexane diamine	170	185
4	unblocked	dodecane diamine	170	185
5	unblocked	hexane diamine/cat.	145	155
6	caprolactam	hexane diol	175	190
7	caprolactam	adipinic acid	185	220
8	caprolactam	hexane diamine	170	185
9	phenol	hexane diol	180	190
10	caprolactam[a]	hexane diol	150	190
11	caprolactam[a]	adipinic acid	180	210
12	caprolactam[a]	hexane diamine	155	180
13	caprolactam[a]	hexane diamine/cat.	145	160

[a] amorphous

visible between the reaction temperatures in respect to blocking agents and reaction partners. The explanation for this behavior can be given by experiments 10–13, which have been conducted using a different, caprolactam-capped MDI.

The first measurements have been carried out with a pure, crystalline material with a melting point of 197°C (caprolactam-capped, Grilbond® IL-6 (EMS-CHEMIE AG)), respectively 186°C (phenol-capped, Grilbond® IPH). The last measurements have been made with a nearly amorphous, caprolactam-blocked MDI. In the case of the amorphous, capped MDI the reactivities depend upon the reaction partner. Therefore, it seems that both the cleaving temperature of the blocked isocyanate and its melting point have to be exceeded in order to initiate the reaction. What is present is a combination of a chemical and a physical inhibition.

Bonding with hot melts

Before transferring the kinetic results from the DSC-measurements to polymers, something must be mentioned about the basic properties of the hot melts themselves. Otherwise, there would be a risk of creating a crosslinkable polymer which is no longer a hot melt.

Provided that the chemical structure is adapted to the required chemical resistance, the most important properties of the hot melt are the melting point and the temperature dependence of the melt viscosity. These properties define the processing temperature and the apparatus to be used for processing, the optimum bonding temperature and the wetting of the substrates and, last but not least, the thermal resistance of the finally-bonded structure.

Figure 4 shows the viscosity-temperature relationship of a copolyester hot melt with a melting point of 130°C. The hot melt in this example has an optimum temperature range for bonding of 140–180°C. At temperatures lower than 140°C the viscosity is too high to be able to wet the substrate or *vice versa*: this temperature marks the thermal resistance of the finally-bonded structure. The upper temperature limit for bonding is determined by the type of substrates. With textile materials there is a substantial risk of seepage if the temperature increases too much, that is, if the viscosity decreases too much. Also, the thermal stability of the substrates has to be taken into account.

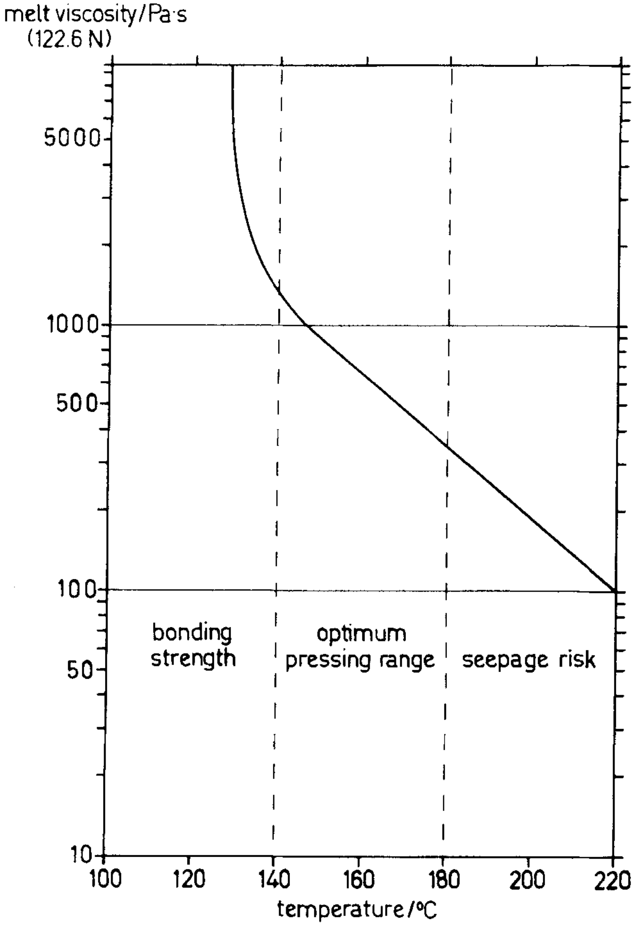


FIGURE 4 Viscosity-temperature relationship of the copolyester hot melt Griltex® 6 (EMS-CHEMIE AG) with a melting point of 130°C.

Crosslinking hot melts

In the case of crosslinkable hot melts the viscosity depends not only on the temperature but also on the time at a given temperature. An illustration for this additional time dependence is given in Figure 5. shown are melt viscosities of a copolyamide hot melt blended with 5 and 10% by weight of a caprolactam-blocked isocyanate. Unfortunately, this type of measurement gives only poorly reproducible

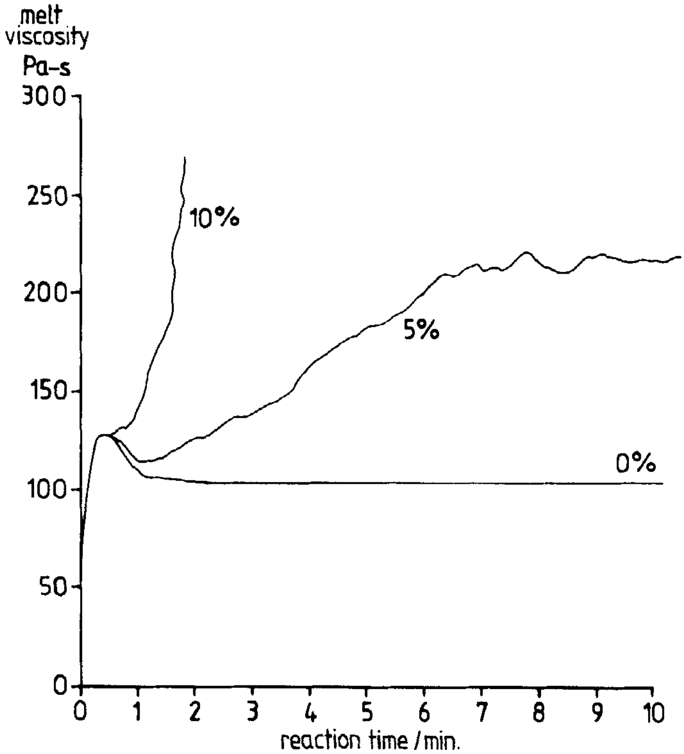


FIGURE 5 Viscosity increase of reactive copolyamide hot melts measured with a cone-plate viscosimeter at 200°C.

results in the case of highly reactive systems. But it is extremely useful to give an idea of the complexity of the viscosity-time-temperature dependence of reactive hot melts.

First, the latent reactive system has to be storage-stable for as long as possible. Then it has to be heated above its melting point, retaining a low viscosity until the substrates which are to be bonded are wetted. Afterwards, in the last step, the crosslinking reaction has to occur as quickly as possible.

The crosslinking kinetics of hot melts which are blended with blocked isocyanates depend upon several factors. The following discussion is based on discontinuous measurements of the relative viscosity. The reactive mixtures have been heat-treated for a fixed time and, afterwards, the viscosity has been measured in solution (0.5% in m-cresol).

The first parameter to be investigated is the ratio of the reactive component in the hot melt. Figure 6 shows viscosity-time relationships of a copolyamide hot melt (Griltex® 4) which contains various percentages of a caprolactam-capped MDI (Grilbond® IL-6). For a one-to-one stochiometry the isocyanate amounts to 5.9%. The continuous acceleration of the viscosity increase from 5% to 15% crosslinking agent indicates that there must be a side reaction in addition to the endgroup reaction. Possible, but still unproven, is a coupling of the isocyanate with the amide groups in the polymer chain, or a reaction of isocyanate with urea groups which are formed through the amino endgroup reaction.

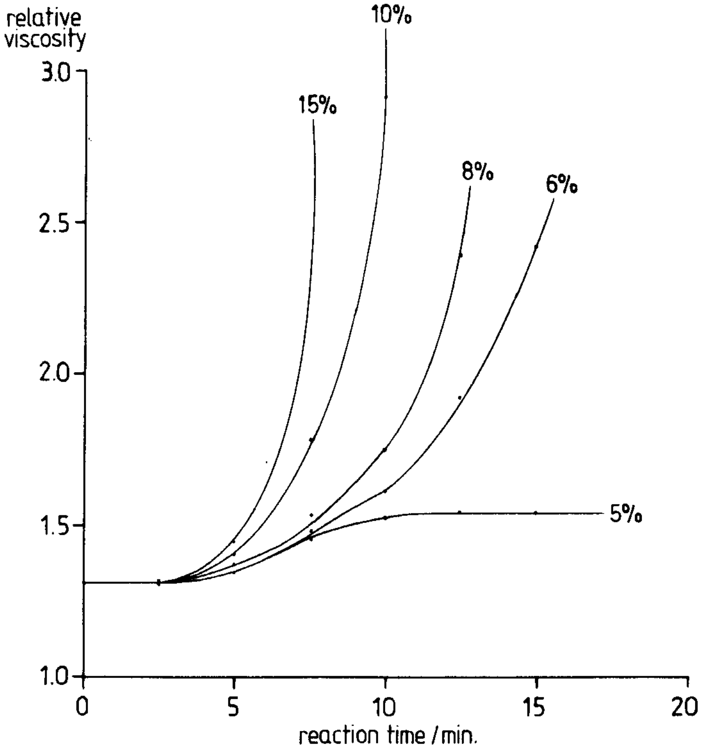


FIGURE 6 Viscosity-time dependence of copolyamides with different amounts of caprolactam-capped MDI, measured at 200°C.

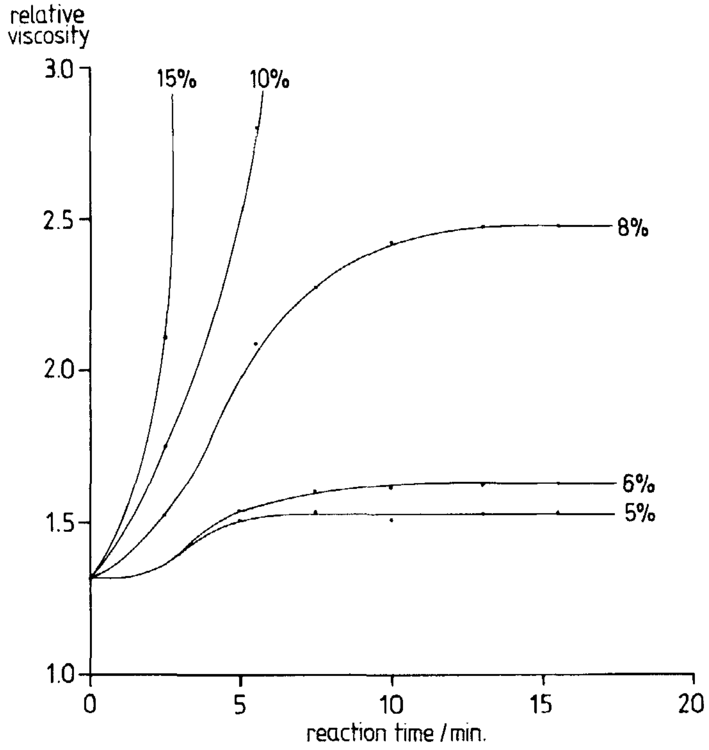


FIGURE 7 Viscosity-time dependence of copolyamides with different amounts of caprolactam-capped MDI, measured at 250°C.

The influence of the temperature on the curing time is illustrated in Figure 7. The measurements are conducted on the same uncatalysed blends of copolyamide with caprolactam-capped MDI as above. What is different is the reaction temperature of 250°C instead of 200°C. This rise in temperature quickens the reaction by at least a factor of two, but the 6 and 8% samples do not crosslink as before.

The effect of the type of blocking agent is shown in Figure 8. The phenol-blocked MDI (Grilbond® IPH) reacts much quicker than the caprolactam-blocked MDI. An uncapped MDI cannot be blended with the copolyamide without increasing the viscosity during the blending process.

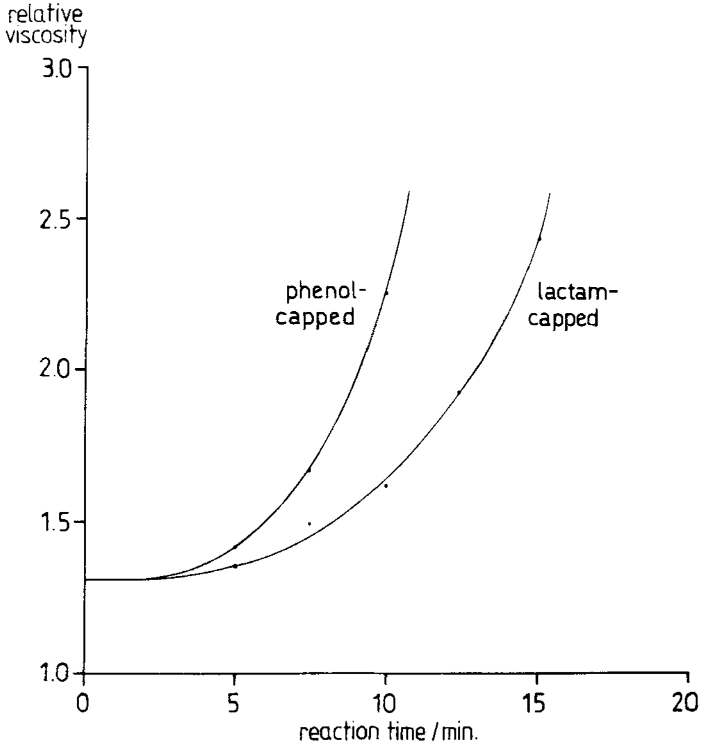


FIGURE 8 Comparison of the reactivities of caprolactam- and phenol-blocked MDI both 6% blended into copolyamide.

An accelerating effect on the increase of the viscosity is to be expected when the number of functional groups per molecule is increased. The corresponding experiments cover a three-functional caprolactam-blocked isocyanate, and a triamino copolyamide. The multi-functional isocyanate is a more highly condensed MDI-type isocyanate with an average functionality of 2.9, which has been capped with caprolactam. The multi-functional copolyamide has been synthesized using a small amount of triamine comonomer. The viscosity data of the mixtures containing multi-functional components are given in Figures 9 and 10. Besides the different functionalities Figure 10 contains data of hot melts with different

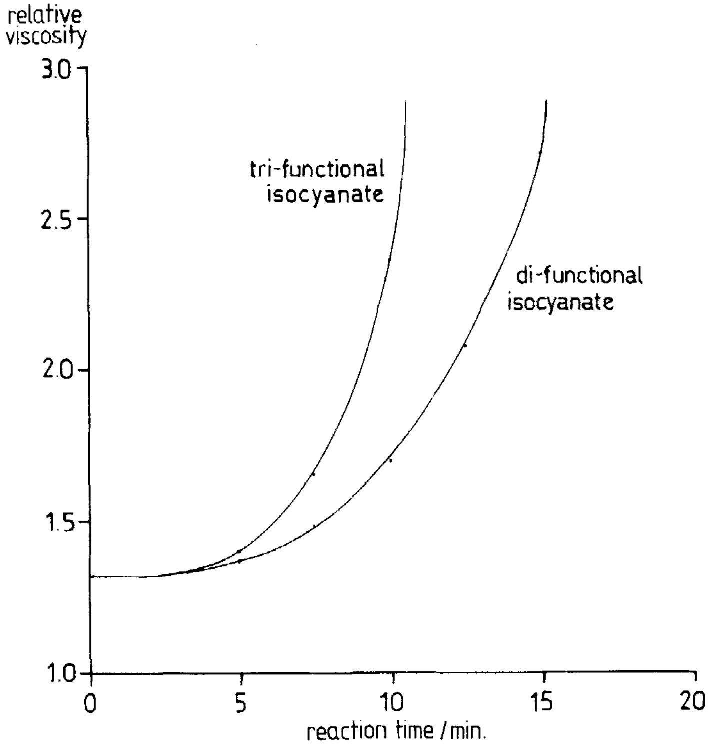
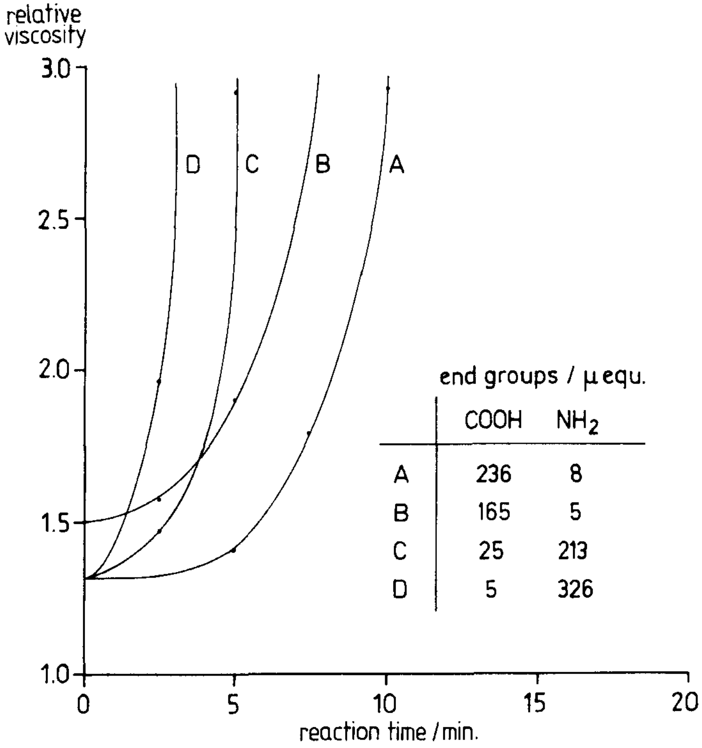


FIGURE 9 Comparison of the viscosity increase of di- and tri-functional caprolactam-blocked MDI, both 7% blended into copolyamide.

endgroups and different initial viscosities. Curve A is the copolyamide with mainly carboxyl endgroups (Griltex® 4) discussed above. Curve C shows an analogous copolyamide with amino endgroups which happens to react in about half of the time. D represents a trifunctional copolyamide of about the same molecular weight as A and C. The B-data are measured on a higher molecular weight hot melt.

Upon summarizing the kinetic data, it can be said that copolyamide hot melts can be crosslinked with capped isocyanates and the velocity of the reaction can be varied *via* the chemistry of the hot melt and the blocked isocyanate over a wide range, without losing the storage stability of the system.



	COOH	NH_2
A	236	8
B	165	5
C	25	213
D	5	326

FIGURE 10 Reactivities of copolyamides with different endgroups in mixtures with 10% caprolactam-blocked MDI.

Thermal resistance

So far the discussion has concentrated on the velocity of cross-linking and consequent viscosity increase. What is left to be demonstrated is that a hot melt which has been modified in the described manner shows an improved thermal resistance. The experiments which have been conducted to reveal the heat performance are shown in Figure 11.

The first test related to the resistance of the hot melt material itself. For this test a hot melt foil (0.5 mm) was heated at a rate of 1°C/min under a stress of $1 N/mm^2$ until it failed. The result of this series of experiments can be summarized very easily. In all cases

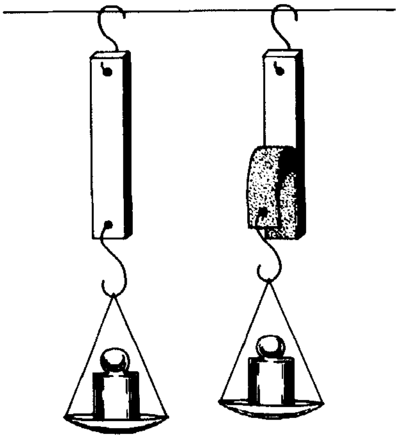


FIGURE 11 Left: test of the heat resistance of hot melt foils, right: heat peel test of hot melt bonded laminates.

where the insolubility in m-cresol indicates a crosslinked system, the hot melts withstand more than 220°C, even when the melting point of the basis polymer was 100°C. The not-completely-crosslinked systems fail in a range of 5–20°C above their melting point.

For characterizing the thermal resistance of bonded structures peel tests under a load of 1N/5 cm have been carried out. For this test, polyester carpet which was scatter-coated on its reverse side with 100 g/m^2 of hot melt powder (200–500 μm) was heat-pressed to phenolic-resin-cured backings. Laminates of this type are in use for door trims and rear shelves in car interiors.[6]

The experimentation data confirm the necessity of completely crosslinking the hot melt to get an essential rise in the heat stability. In the cases where the adhesive is crosslinked the bond remains intact until the carpet starts to degrade at about 220°C.

But the interdependencies between pressing temperature and time, hot melt reactivity and wetting behavior increase the complexity. The data in Table II may illustrate the influencing factors. The first three columns represent measurements on a low-viscosity, fast-reacting hot melt. Under the bonding conditions 100°C/30s a good wetting is achieved, resulting in a high peel strength. As visible from the thermal resistance, crosslinking has not occurred. A rise in the bonding temperature up to 140°C results in crosslinking.

TABLE II
Application properties of different crosslinking hot melts

Melting point/°C	80			120		
Initial melt viscosity (122.6 N, 160°C), Pa · s	25			1000		
pressing temperature/°C	100	140	180	130	150	200
pressing time/s	30	30	30	30	30	30
thermal resistance/°C	85	>190	>190	130	>190	>190
peel strength/N/5 cm	>25*	15	3	13	>25*	>25*

* substrate failure

The thermal stability increases to more than 190°C. In parallel, the peel strength decreases because the hot melt has soaked into the carpet. This effect is amplified at a bonding temperature of 180°C.

On the right side of Table II, bonding data of a high-viscosity, medium-reactive hot melt are shown. In this case, there is no decrease in the peel strength with increasing bonding temperature. On the other hand, the minimum bonding temperature is shifted to about 150°C because of the poorer wetting effect and the slower crosslinking reaction.

This short excursion into the application properties shows that crosslinked hot melts offer many possibilities. But it also shows that the type of hot melt and the bonding parameters have to be carefully selected with regard to each specific bonding problem.

CONCLUSION

Crosslinkable hot melts are a new class of adhesives. They are created to improve the heat performance of hot melts without losing the advantages of hot melts, for instance, their lack of solvent and their very short setting time. As shown, crosslinkable hot melts tremendously exceed their uncrosslinked counterparts in respect to thermal resistance. Only time will tell whether the requirement of more closely observing the application conditions will be accepted for achieving the described advantage.

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