

Super high crystalline TPU's for the market of non-solvent based adhesives.

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INTRODUCTION

Merquinsa, a Spanish company located in Barcelona, has been devoted for 34 years to the research, development and production of polymers intended for the adhesives and coatings industries. At present, MERQUINSA is basically involved in thermoplastic polyurethanes, for the adhesives as well as a variety of processing industries, mainly extrusion, injection moulding and calendering. Aqueous polyurethane emulsions and prepolymers for the cork industry complement the company's range.

Merquinsa operates in accordance with a Total Quality philosophy, and was awarded an ISO 9001 Certificate in 1994 and an ISO 14001 Certificate in 1999.

The purpose of this paper is to describe a new family of Thermoplastic Polyurethanes, with two main special properties:

- Very high crystalline structure
- High thermoplasticity.

These important and specific properties, allow the application of these TPU's in a variety of different market segments in the field of adhesives, sometimes replacing other polymers or solvent-based urethanes and sometimes also water-based urethanes.

With this purpose in mind, the paper intends to offer first a general description of the specific nature of thermoplastic polyurethanes (TPUs), focusing on the characteristics of one of the components, namely the macrodiol or soft segment of a polyurethane. The whole TPU range that has been developed by MERQUINSA will also be summarised. Special attention will then be given to the speciality Super high crystalline TPUs for the market of non-solvent based adhesives, compared with other conventional products used in the market, such as thermoplastic copolyesters and polyamides. These new super high crystalline polymers developed by MERQUINSA are in a patent pending situation.

Among the most important advantages of this kind of TPU pellets, the paper underlines the "environmentally friendly" characteristics of the TPU's adhesives, as a consequence of the structure-properties relationship (very low melting point and high adhesion, in a wide variety of materials), and the different kinds of applications that we can find in the market, as shown in Table 1.

Table 1: Applications of the Super high crystalline TPU's in the market of non-solvent based adhesives.

- In powder form, in thermobonding processes.
- As a film, in foil lamination processes.
- In direct extrusion applications.
- In reactive hot melt adhesives, 100% active material.
- As a paste made of a water – based dispersion of the powdered TPU's.

All these advantages make of such products an important candidate for a substitute for solvent-based adhesives, and even also some water based adhesives, considering the costs of transport (which is higher for aqueous adhesives), of the water evaporation process, besides, in all cases, their strong contribution to the “sustained growth” tendency.

1. The market and the principles of application

During these last years, MERQUINSA has been developing a wide range of polyurethanes used as a raw material in the production of adhesives intended for the shoe, automotive and wood industries, as well as other industrial markets.

This continued development has covered all the application fields, processes and products. Thus, our company was a pioneer in the development of PU dispersions specifically intended for the production of adhesives. Our company was a pioneer as well, in offering ecological alternatives for the processes based on the use of solvents, which so far have no valid replacement in some markets, through reports and presentations on solvents that do not harm the environment (not listed in the T.R.I.).

With this idea in mind, MERQUINSA has developed products for film, powder or melting applications, which help this adhesives sector to keep a sustainable growth and, at the same time, are environmentally safe.

With this general background, the intention of this paper is to present a new range of highly crystalline TPUS developed by MERQUINSA and intended for solvent-free and water-free applications, for use as raw materials by adhesives makers.

Only in Europe, this speciality market moves the following amounts Europe (figures for the rest of the world are not yet available):

A	Thermobonding	350 T/y.
B	Reactive hot-melts	300 T/y.
C	Shoe stiffeners	2000 T/y.

The yearly growth of A and B sectors registers dramatically high rates: 15% and 30% respectively. Such expanding new markets will find in super high crystalline TPU's the ideal raw materials because the profile of these products meets all their requirements.

Fig. 1: Competitive products in the market

COPOLYOLEFINES	Relatively low cost.	Good stability. Bad stability to chemicals and washing if EAA's or EVA's are used.	Low to medium elasticity.	Not stable against plasticizers (soft PVC).
COPOLYESTERS	High cost and high performance.	Good chemical stability and good all-round-adhesive properties.	The standard products are rigid.	–
COPOLYAMIDES	High cost and high performance.	Good all-round-adhesive properties.	Very rigid.	Some types allowing adhesion to polyolefines.
POLYURETHANES (TPU's)	High cost and high performance.	<i>Very good all-round-adhesive properties.</i>	<i>High elasticity and softness, good for textile bonding, where a soft hand is needed.</i>	<i>High versatility.</i>

From this point of view, the analysis of Figure 1 will be of interest (cf. **Fig.1** Competitive products in the market). As we can see, the crystalline TPU's offer a very good package of competitive advantages in front of other alternative products.

The highly crystalline TPU's find their main applications in the market of industrial adhesives. For a better understanding of such applications, they can be split into several market segments, which will allow to show the variety of requirements TPUs have to meet in each of them.

A) Additives for reactive hot melts

B) Thermobonding (heat-sealing)

Shoe stiffeners (toe-boxes, counters)

Applications in the textile industry

Applications in the automotive industry.

Fig. 2: Range of MERQUINSA'S PU raw materials

		CHARACTERISTICS	REMARKS
LIQUIDS <i>(PEARLSTICK QUILASTIC)</i>	SOLVENT-BASED	<ul style="list-style-type: none"> • Polymer molecules dissolved in solvents 	<ul style="list-style-type: none"> • Hazard, solvent vapours, toxic and flammable
	AQUEOUS DISPERSION	<ul style="list-style-type: none"> • Polymer particles dispersed in water 	<ul style="list-style-type: none"> • Slower drying than for solvent-based
	REACTIVE	1-COMPONENT <ul style="list-style-type: none"> • Reactive NCO/OH groups • Crosslink after application 	<ul style="list-style-type: none"> • Low initial adhesion (green tack) • Need moisture
		2-COMPONENTS <ul style="list-style-type: none"> • Reactive NCO/OH groups • Crosslinking starts when mixed 	<ul style="list-style-type: none"> • Low initial adhesion (green tack)
SOLIDS <i>PEARLSTICK PEARLBOND</i>	REACTIVE HOT MELTS	<ul style="list-style-type: none"> • In thick liquid form when heated • Crosslink after application 	<ul style="list-style-type: none"> • Melt at lower t° than EVA • Need moisture • Special equipm. for application
	HOT MELTS	<ul style="list-style-type: none"> • In thick liquid form when heated 	<ul style="list-style-type: none"> • Relativ. high melting visc. • Low penetration in porous surf.
FILMS <i>PEARLTHANE</i>	CRYSTALLINE TPUs	<ul style="list-style-type: none"> • High melting t°, not requested • Slightly opaque appear. of film 	<ul style="list-style-type: none"> • Low solvent-resistance
	NON CRYSTALLINE TPUs	<ul style="list-style-type: none"> • High melting t° requested • Transparent film appearance 	<ul style="list-style-type: none"> • Good resistance to solvents and chemicals

A) Additives for reactive hot melts (Fig. 2)

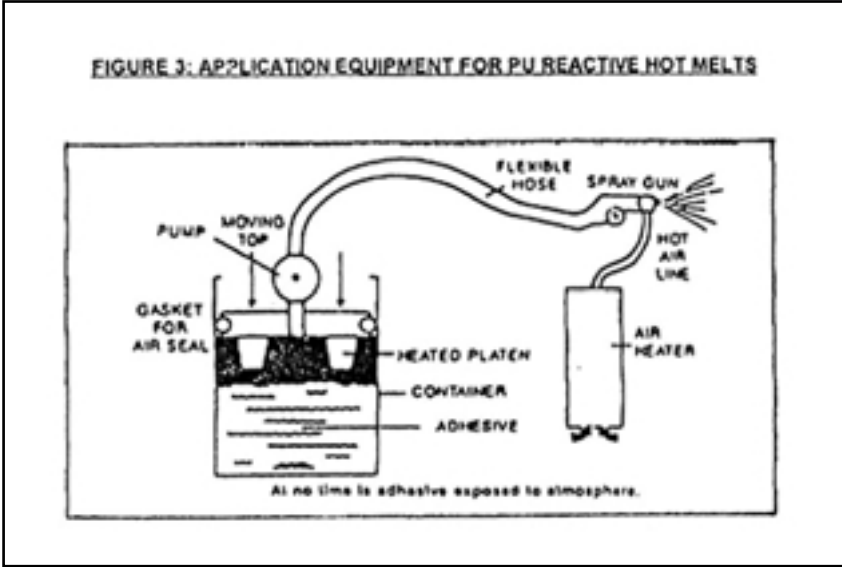
Basically, the purpose of TPU's is to modify some of the properties which are inherent to reactive hot melts, that are based on urethane polyol prepolymers of polyester type, as it is well known.

The addition of TPU's is expected to give the following benefits:

- increased crystallisation rate and final crystallinity of the product,
- increased initial adhesion, with the improvement of green strength (initial peeling resistance)
- viscosity control
- they perform as a set point modifier

The application process is shown in Fig. 3.

Such products are basically intended for the furniture industry, where they are used in edge bonding with ABS/PVC and wood substrates as well as for the car industry, for the lamination of automotive parts. They must be compatible with EVA, PU and PVC.



B) Thermobonding (Heat-Sealing) (Fig. 4)

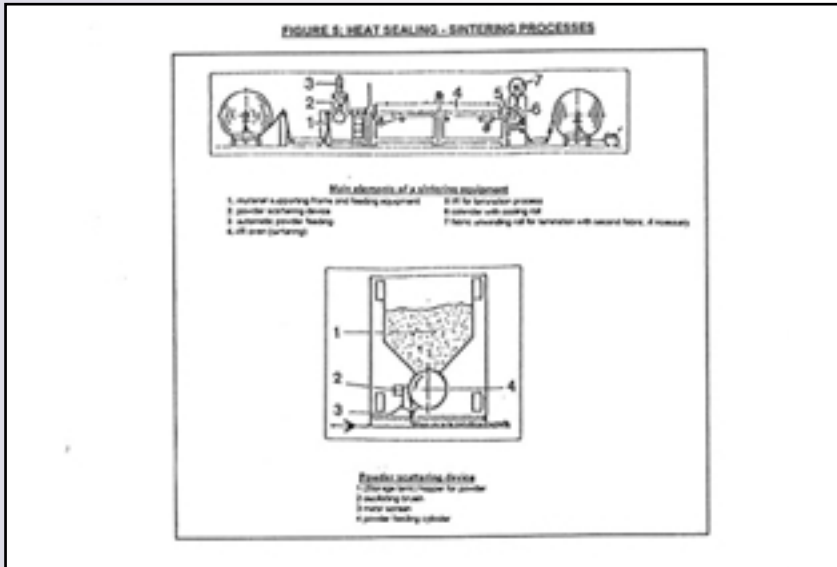
Another important application of these crystalline TPU's is for thermobonding (heat-sealing) processes, by which the adhesive is laid on a series of substrates (mostly fabrics), then treated with heat and pressure so as to bond them. In some cases, TPU's don't compete with other items such as EVA, Copolyester, polyamide, SBR, etc., as they are used as an additive for such products, so as to achieve the performances that each application requires.

FIGURE 4: CRYSTALLINE TPUS FOR HEAT-SEALING - MAIN APPLICATIONS

HEAT SEALING (THERMOBONDING)	SHOE STIFFENERS	Toe-boxes, Counters, etc.
	TEXTILE APPLICATIONS	Textile/PUF Foam bonding Bonding of carpet car - fittings Uniforms and raincoats PVC lamination Linings for leathergoods • Clothing • Footwear

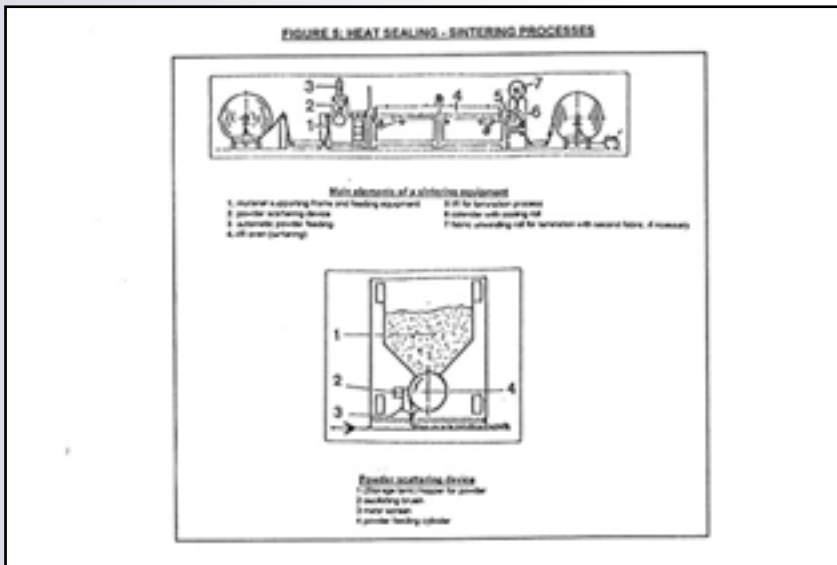
Highly crystalline TPU's confer good mechanical, physical and chemical properties within a wide range of temperatures and, most of all, due to their good polarity, they enable very good bonds with a variety of substrates.

The different applications and markets can be synthesised as follows:

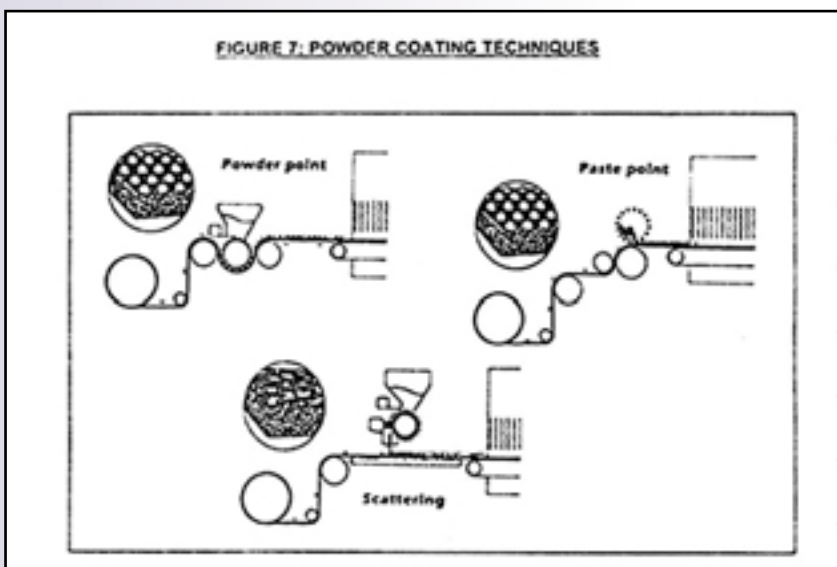


B1: Shoe stiffeners (toe-boxes and counters).

Highly crystalline TPU's are used as hot melts. Their main market is the shoe industry. The most usual application processes which are followed are:
Sintering: TPU's are used in powder form, as shown in **Fig. 5**.



Extrusion: The pellets are extruded directly on the substrate, as shown in **Fig. 6**



B2: General textile applications.

This covers several applications. The usual processes are shown in **Fig.7**.

The following applications can be mentioned (TPU's are generally used in powder form):
Carpet back-coating
Carpet inner car-fitting
Bonding of textile/PUR foam
Carpetbonding
Uniforms, raincoats,
PVC Lamination
Linings for leather goods, clothing and footwear.

TPU's must be compatible with ABS, EVA, SBR and PVC when they are used in combination with such items, with the purpose of enhancing them. In this market, TPU's have to compete basically with Copolyesters, EVA, Polyamide, Polyethylene and others.

These products can be used in other markets, as adhesives for the footwear industry and for foil lamination processes, either in powder paste or as a very thin film.

1. Powder paste. Besides some applications in the textile industry, MERQUINSA is now working on the development of water dispersions of such crystalline TPU's, as an alternative to the solvent-based adhesives, for the shoe automotive and furniture industries.
2. Film applications: MERQUINSA can supply super high crystalline TPU's, film grade, that means gel-free, for producing very thin films for foil-lamination processes, in the shoe and automotive industries. This is a very interesting development, also in the path of the environment-friendly TPU's adhesives.

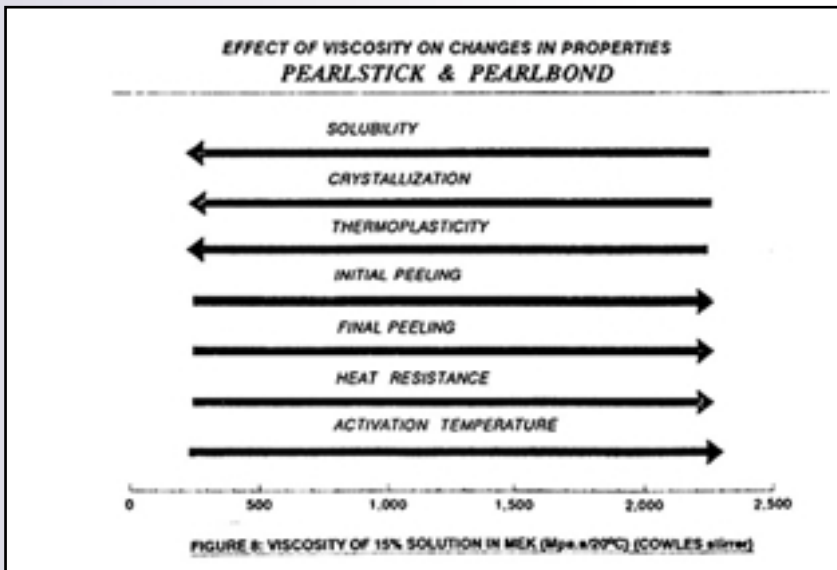
2. Requirements of the market

All the applications that we have shown so far require a product profile with some critical parameters that can be summarised as follows:

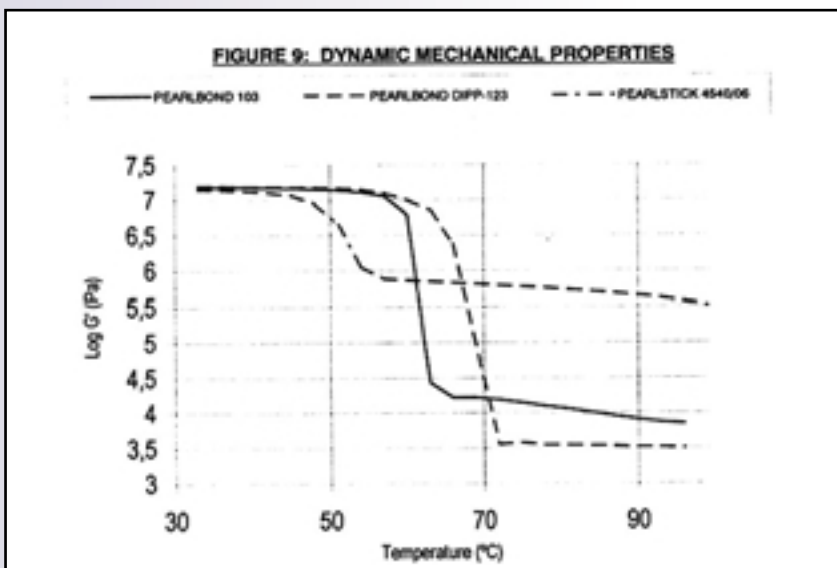
- High crystallisation rate
- High crystallinity level
- High thermoplasticity
- Melting temperature within a rather well defined range
- Good heat and hydrolysis resistance
- Melting viscosity values adequate for a variety of applications
- Possibility of adapting the product to the specific conditions of any applications.

We can state that these products meet the basic requirements. Indeed, the main advantage of the super high crystalline TPU's compared with other conventional products that are found on the market is their elastomeric nature, within a wide range of temperatures, from their T_g (glass transition temperature) to temperatures at which the crystals almost melt. This confers them, among other advantages, higher elasticity and flexibility properties at low temperature as well as within a broad range of working conditions, over standard items, which are completely crystalline and thermoplastic, but have not such elastomeric ingredient.

MERQUINSA makes in a continuous production system, a wide range of linear polyurethane elastomers, which have been especially developed for use as raw materials to make adhesives. Since most of them are made from copolyester polyols, mainly based on polycaprolactone and special polyadipates, the end-products have higher hydrolysis resistance and better mechanical properties than other ones, based on simple polyadipates.



The adhesive properties in connection with the molecular weight are described in **Fig. 8**, for all these product-families. MERQUINSA offers several types of PEARLSTICK® and PEARLBOND® highly crystalline TPU's. The differences between the PEARLSTICK® and PEARLBOND® families of products can be defined by the relationship between their rigid and soft segments, their molecular weights and the type of polyol they are based on. A wide range of options is thus made available, in terms of desired end-properties, for all the requirements of these markets.



3. Recent development: The super high crystalline TPU's (Fig.9)

Super high crystalline TPU's can be defined as those products that are characterised by their high linearity, very high crystallisation rate and thermoplasticity. This is basically due to their high molecular weight and a specific structure of their polyol component.

These TPU's can be compared with the conventional products presently found on the market, such as polyamides, copolyesters, however they have some added advantages, derived from their chemical nature. They are

unique products and in a patent pending situation. The peculiarity of such super high crystalline TPU's is that their soft segments are made of polyols that form a high molecular weight copolymer.

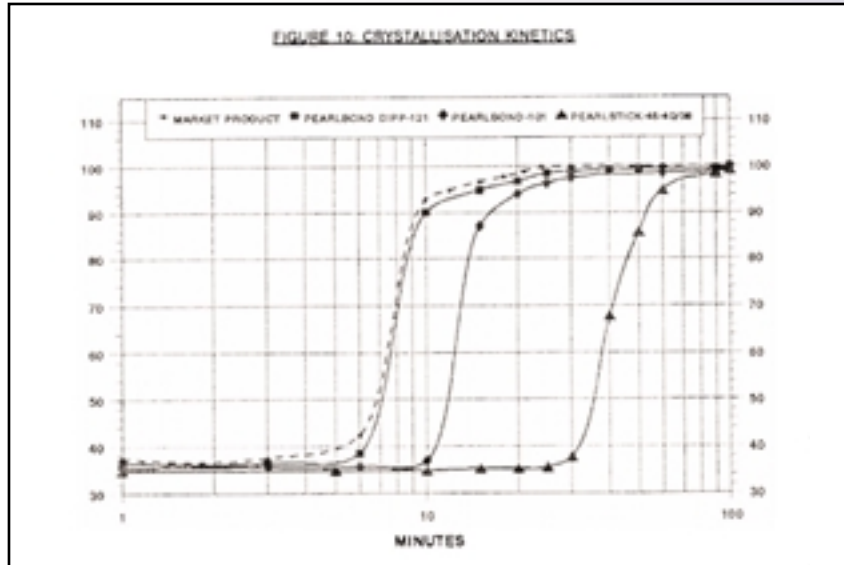
The high molecular weight and the structure of the copolymer are such, that they have a meaningful influence on the resulting polyurethane, to which they impart high crystallinity and thermoplasticity.

Fig. 9 shows an analysis of dynamic mechanical properties (DMA) that illustrates the mentioned characteristics, in comparison with a conventional crystalline TPU, used as a raw material for making adhesives. One of the curves corresponds to a well-known product of MERQUINSA: PEARLSTICK® 45-40, used in adhesives for the footwear industry. The other curve belongs to PEARLBOND® 103, one of the TPU's belonging to the highly crystalline range and PEARLBOND® DIPP 123, belonging to the new family, with a medium molecular weight. We can observe the strong influence of the polyol

component (in this case, polycaprolactone-polyester copolymer), due to its molecular weight, but also its structure, on the melting of the crystalline areas and the higher thermoplasticity. This latter is reflected by a G' module which is lower as from 60°C. This figure shows very well the differences between those products within a wide range of temperatures.

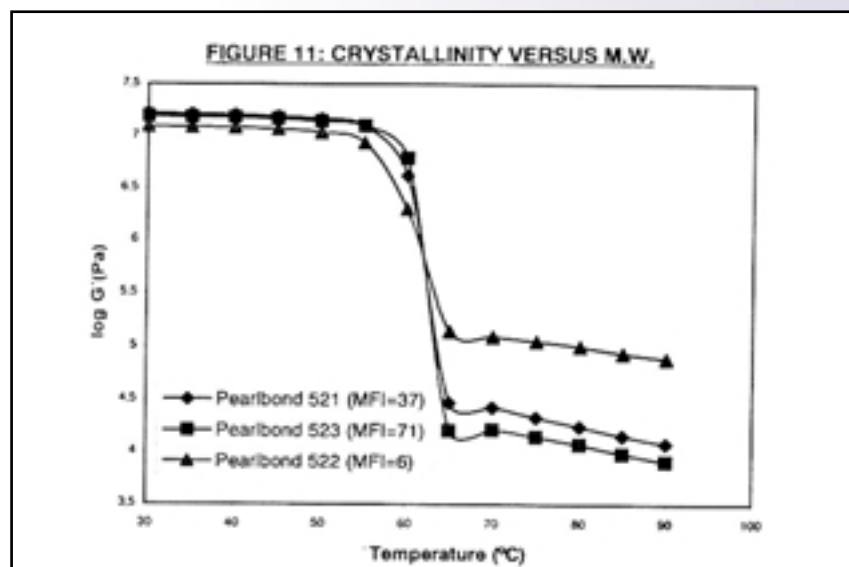
The super high crystalline products have a more defined melting range than conventional crystalline TPU'S. This characteristic is very important and requested by the users in the mentioned application fields.

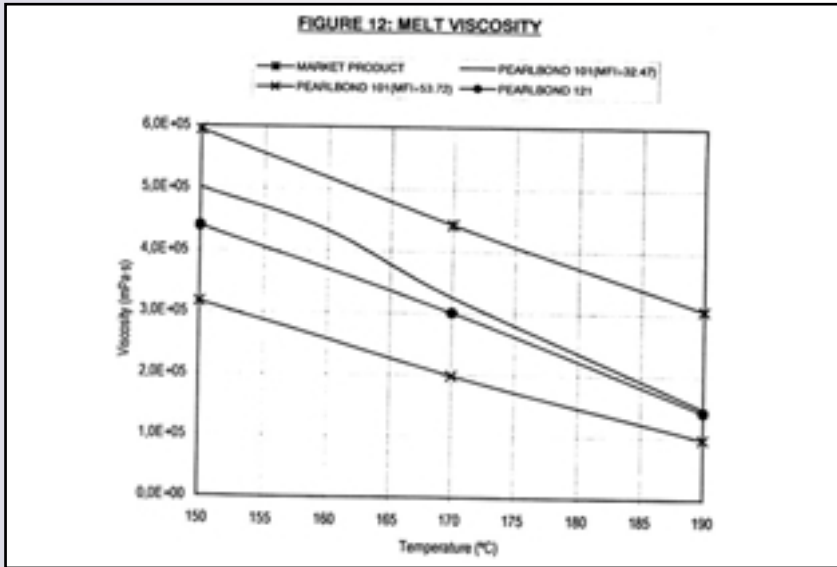
Fig. 10 describes the crystallisation rate of these new TPU's and the final crystallisation level reached at the end of the process. The graph includes products belonging to several, new developed families, as well as classical, well-known products. Two items can be taken as a reference: a highly crystalline, conventional one, already used in the mentioned markets, and another one, that has already been mentioned: PEARLSTICK® 45-40. As we can see, the crystallisation rate of the grade PEARLBOND®



DIPP121 belongs to the super high crystalline TPU line, developed with the purpose of offering a series with even higher crystallinity and thermoplasticity than the PEARLBOND® 101 series. Their respective polyol components, structures and molecular weights account for the differences of these recent developments, although the molecular weights of all the TPU polymers are rather similar. The crystallinity of these TPU's differs also in function of the molecular weight of the polymer they are based on.

Fig. 11 shows different products of this new series, with different molecular weights. The measurements intended to obtain the variation of module G' have been taken under a controlled temperature decrease, and specific moisture and temperature conditions. As a result, we can say that the crystallinity and the rate of crystallisation increase when the molecular weight decrease. The variety of crystallinity levels that are available, enable to respond satisfactorily, in a wide range of applications for which this parameter is determinant





The third figure (**Fig. 12**) is a graph showing the viscosity of the melt products at different temperatures. Here again, we can observe the variety of products, which make it possible to meet any requirements about viscosity levels of melt TPU's at different temperatures. The products used in the previous figures appear again, together with other items that are representative of the new families. The TPU's are: PEARLBOND® 101 with different molecular weights reflected in the MFI values and PEARLBOND® 121, representing the new family, based on a copolymer with a very high molecular

weight, higher thermoplasticity when compared with polymers having the same molecular weight but similar viscosity behaviour under the action of temperature.

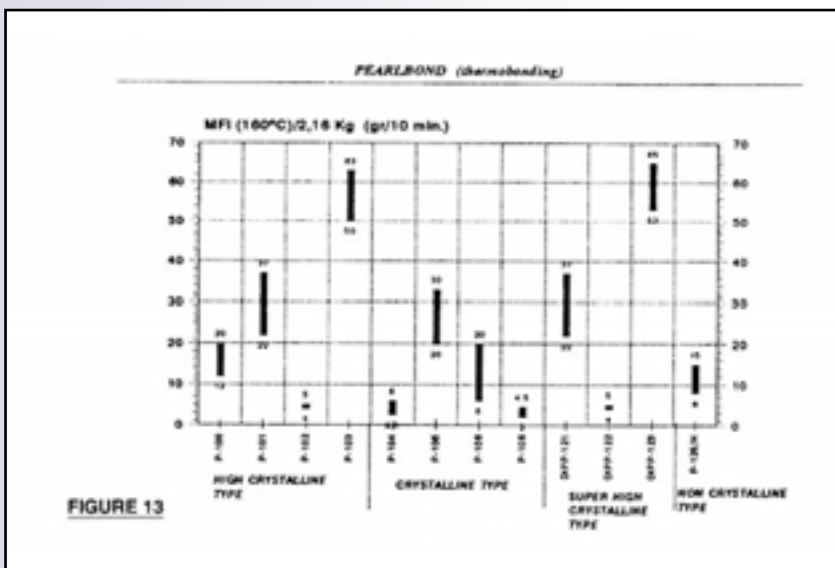


Fig. 13 details the MFI range or MW range of all the TPU's offered by MERQUINSA for this market. It is interesting to underline that the MW ranges of the super high crystalline types meet the market needs in terms of MFI or viscosity.

The figures that come next (**Fig. 14 and 15**) show the new families of products, the markets they are intended for and the application processes.

Fig. 14 gives the main characteristics of these items, such as MFI, Hydroxyl number, crystallisation rate and the added-value they impart to reactive hot melts, with amounts between 5 and 10%, for the markets mentioned at the lower end of the table.

FIGURE 14

		PEARLBOND			
		DIPP-521	DIPP-522	DIPP-523	508
MFI (3 min)	Condition gr / 10 min	50 - 60	85 - 125	70 - 90	40 - 90
OH VALUE	mgAOH/g	4.3	4.3	4.8	4.3
SOLUBILITY	1% MEK	NI - 100	100 - 600	10 - 60	100 - 600
	1% CHCl ₃	400 - 600	1,000 - 4,000	100 - 100	NOT SOLUBLE
(in Pa ADPDC)	10% XLEH	100 - 600	1,000 - 11,000	100 - 600	NOT SOLUBLE
	Water (%)	65 ± 2	69 ± 2	62 ± 2	75 ± 2
THERMOPLASTICITY	RATING	VERY HIGH	VERY HIGH	VERY HIGH	NEUTRAL
WELT VISCOSITY (Pa.s)	170°C	280 ± 70	1,050 ± 200	120 ± 20	1,910 ± 100
CRYSTALLIZATION	Delta (part) 10%	9.2	9.5	9.1	60.8
RECOMMENDED AMOUNT		5 - 10%	5 - 10%	5 - 10%	5 - 10%
BENEFITS OF USE		Increased crystallisation rate	Increased crystallisation rate	Increased crystallisation rate	Improve adhesion on problematic surfaces
MAIN APPLICATION		FURNITURE INDUSTRY	FURNITURE INDUSTRY	FURNITURE INDUSTRY	PROFILE ENCAPSULATION
		EDGE BONDING (ABS/PVC)	EDGE BONDING (WOOD)	EDGE BONDING (ABS/PVC)	(METAL/PVC)

Fig. 15, related to thermobonding (heat sealing) applications, underlines characteristics such as hardness, melting viscosity, crystallisation and compatibility with other polymers, for different application processes used in the markets that have already been described.

FIGURE 15 THERMOBONDING

		PEARLBOND					
		102	106	DIPP-121	DIPP-122	DIPP-123	125W
SHORE HARDNESS	51 D	92 A	94 D	94 D	94 D	95 A	95 A
	52 D	100	100	100	100	100	100
WELT VISCOSITY at 170°C (Pa.s)	Min.	1,200	2,640	280	1,200	100	460
	Max.	48.70	71.77	62.67	61.69	60.64	145.916
CRYSTALLIZATION	Initial (part)	15.5	46.8	9.2	9.2	9.1	...
COMPATIBILITY	ABS	*	*	*	*	*	*
	EVA	*	*	*	*	*	*
	PVC	*	*	*	*	*	*
APPLICATION METHOD	Folder joint	*	*	*	*	*	*
	Face joint	*	*	*	*	*	*
	Scarfing	*	*	*	*	*	*
SHOE INDUSTRY	Insertion						
AUTOMOTIVE	Leather		X	X		X	
	PVC film		X	X		X	
TEXTILE	Non	X	X	X	X	X	X

4. Conclusion

For over 32 years, MERQUINSA has been supplying polyurethanes to the adhesives industry, for use as raw materials, either solvent-based, or in aqueous dispersion, liquid form, etc.

The presentation of these new TPU'S, intended for applications without solvent, are intended to invite to the development of these new end-products where polyurethane adhesives can compete very favourably with other items that are already available on the market.

New applications can still be developed, taking into account the possibility of crosslinking the TPU's, thanks to the addition of blocked isocyanates, and blending in an homogeneous phase, prior to the application process.