

Acrylic Block Copolymers for Pressure Sensitive Adhesives

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Introduction

Acrylic polymers are widely used in Pressure Sensitive Adhesive (PSA) applications, in the form of emulsion, solvent or radiation-cured systems. They combine good UV resistance, transparency, tailored tack and stiffness thanks to a large choice of acrylic and methacrylic co-monomers.

Acrylic copolymers are produced through conventional free radical polymerisation processes that lead to random structures with broad polydispersities. Furthermore, free radical polymerization does not allow functional groups introduction at specific locations along the polymer chains. For adhesive applications, a key synthesis challenge is the optimization of the polymer composition and molecular weight to achieve low viscosities, good adhesiveness, and creep resistance. This balance of antagonistic tack/creep properties is generally achieved through extremely high molecular weights, often above 1 million g/mol, or partial cross-linking. However, both cases are detrimental for lamination properties and flow behavior. The extremely high molecular weights effectively prevent application as hot-melt adhesives, while cross-linking can require several days to be completed. UV curable acrylic adhesives are another alternative toward high performance adhesives, but their implementation requires significant equipment investments and expertise.

This paper deals with new acrylic copolymers having block structures and controlled functional group placement, thanks to a controlled radical polymerization process (CRP). These polymers are a part of Arkema's Nanostrength[®] line of acrylic block copolymers. They bring a good balance of tack and creep properties, in the absence of cross-linking, which enables their application as acrylic hot-melt or solvent borne adhesives. Additionally, these materials can be functionalised in a controlled manner. This paper focuses on the presentation of these new structures, with some examples of physical and chemical properties, and illustration of their application as adhesives.

1 Controlled Radical Polymerization

Products described in this presentation for PSA applications are block copolymers combining a low T_g acrylate block and at least one high T_g methacrylate block. Current products consist of a hard-soft-hard triblock structure, although diblocks and star-shaped structures can be readily produced. Achieving such new structures has been possible through Controlled Radical Polymerization (CRP), more precisely Nitroxide-Mediated Polymerization (NMP) and based on BlocBuilder[®] alkoxyamine, a commercially available molecule encompassing both the polymerization initiator and the radical trap. Radical stabilization, provided by the nitroxide "SG1", allows a first set of monomers to be polymerized into a copolymer A, followed by polymerization of a second set of B co-monomers onto A, leading to structures such as AB or BAB block (Figure 1). NMP process does not leave any metal residue in the polymers, contrary to other CRP technologies.

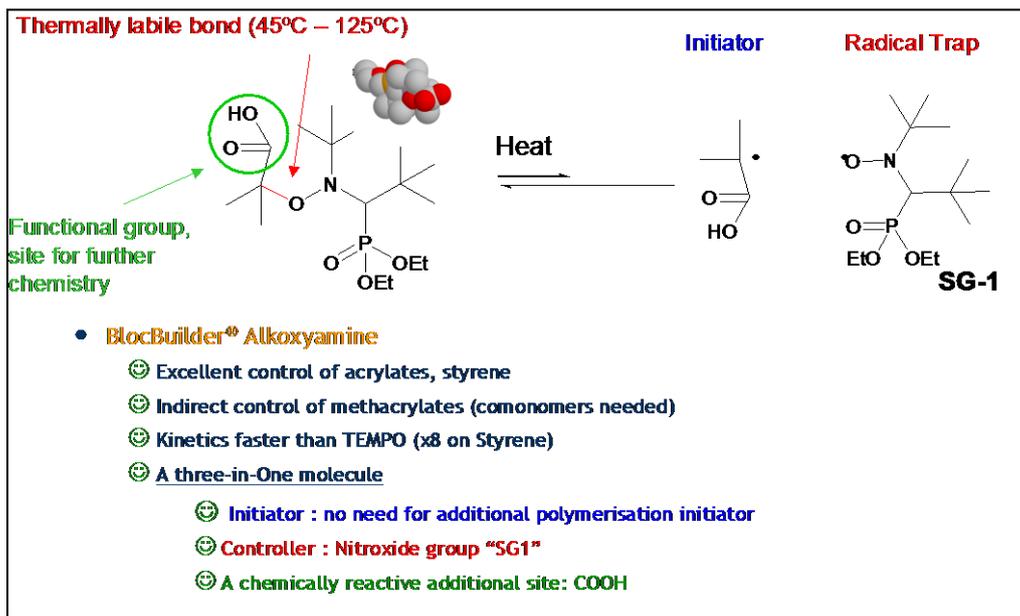


Figure 1: Description of Nitroxide Mediated Polymerization

BlocBuilder® is a versatile initiator/controller that can be used in bulk, emulsion, solvent, and suspension processes. It controls a broad range of monomer types including styrenics and almost all types of acrylates and methacrylates. The extremely large range of available functional acrylic and methacrylic monomers offers the possibility to selectively introduce specific functional groups into the blocks. Typical structures achievable with this technology are illustrated in Figure 2.

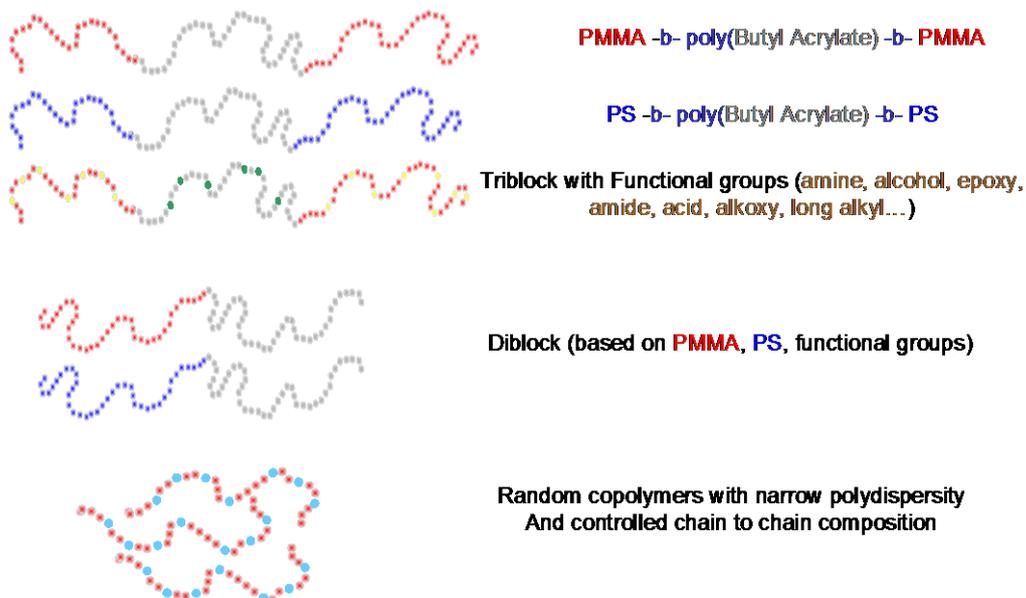


Figure 2: Illustration of some achievable polymer structures

Due to the immiscibility between the two types of blocks, the block copolymer nanostructures into soft domains providing tack and low temperature elasticity, and hard domains behaving as physical cross-links, bringing cohesiveness and mechanical properties. The morphology of the various phases depends on the ratio between hard and soft blocks, length of the blocks, and temperature. Figure 3 illustrates two types of morphologies achieved with p(MMA-bBA-bMMA) triblock copolymers (hereafter referred as “MAM”, for MMA-Acrylate-MMA).

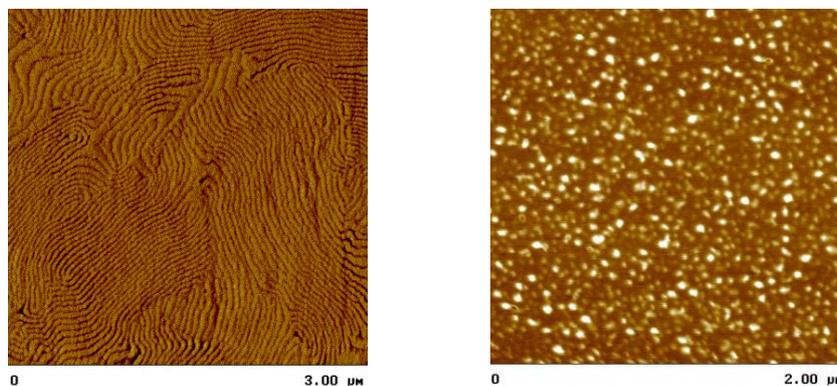


Figure 3: Atomic force microscopy pictures of two types of morphologies obtained with a block copolymer having 60% of soft mid block (left), and 85% of soft mid block (right)

2 Copolymer structures

The softest copolymers have been synthesized in two versions, a non-functional version, and a version modified with acid groups in the hard end-blocks. The presence of acid raises T_g of the end-block and improves performance at elevated temperature, as illustrated in Figure 4 by the higher $G' - G''$ cross-over temperature of SM8590XM5 as compared to SM8590. Acid also enhances the phase separation between soft acrylate and hard PMMA domains. Finally, these acid groups can also be used as reactive sites for further chemical reactions, for example controlled cross-linking through addition of molecules containing epoxy groups, amines, etc. Product characteristics are given in Figure 4.

Product	Form	% BA	Functional groups	T_g soft block, °C (max G'')	G' @ 25°C kPa	G' @ 150°C kPa	$G' - G''$ cross T°
SM6290	Granules	60%	/	-40	5950	360	> 250°C
SM7090	Sticky granules	70%	/	-42	350	60	> 250°C
SM7090XM5	Sticky granules	70%	Methacrylic acid in end block	-42	330	65	>250°C
SM8590	Rod / mass	85%	/	-41	130	2	137
SM8590XM5	Rod / mass	85%	Methacrylic acid in end block	-42	130	5	160-190

Figure 4: Block copolymers description

Due to their nanostructuration, these polymers have excellent transparencies even when used as a non-formulated material (Figure 5), and have good elastomeric properties with high stress at break values even for the softest grades (Figure 6).

Styrene-Acrylate-Styrene triblock copolymer (SAS) can also be obtained.

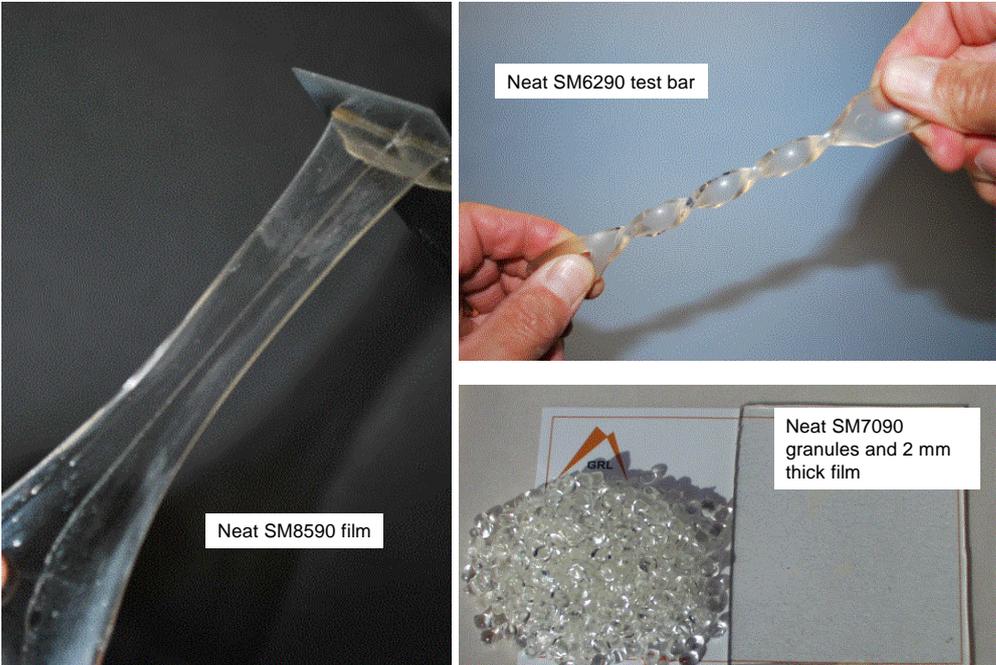


Figure 5: Illustrations of soft MAM copolymers transparency, softness, and tack

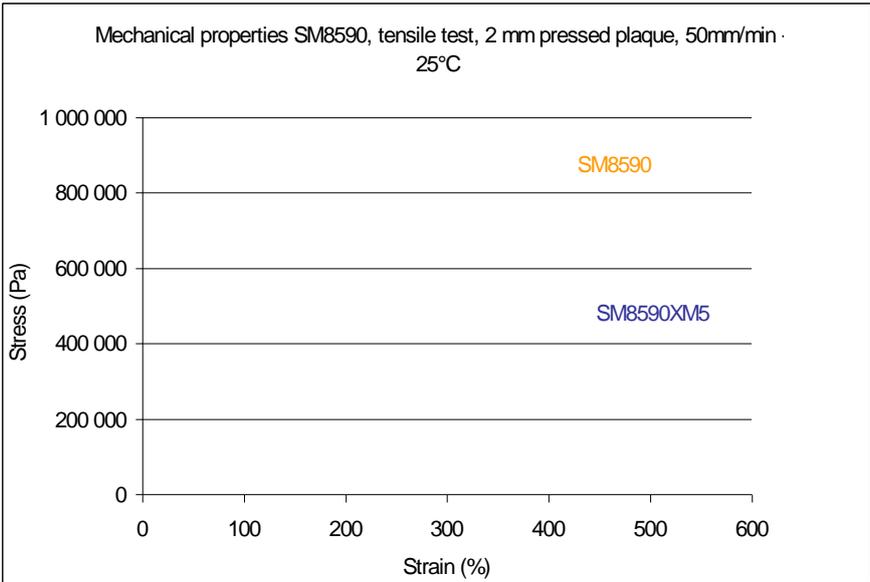


Figure 6: Tensile elongation curves of the softest MAM copolymers (85% BA)

3 A new class of elastomeric adhesives ?

So-called “electrometric adhesives”, “elastomeric hot-melts”, often refer to formulations based on styrenic block copolymers like SIS (Styrene-Isoprene-Styrene), SEBS (Styrene-EthyleneButylene-Styrene), and their combinations with their diblock forms. The nanostructuring of such materials is well known, based again on hard and soft blocks immiscibility. Since the neat polymers are not tacky, SIS and SEBS adhesives are formulated with combinations of tackifiers, plasticizers, as well as other additives. As opposed to isoprene or ethylenebutylene mid-blocks, soft acrylates like butyl acrylate, 2-ethylhexylacrylate, and octylacrylate, have a higher mass between entanglements, leading to lower modulus and inherent tackiness. The softest MAM copolymers can thus be used as elastomeric adhesives with little or no formulation. This can be of particular benefit in applications such as removable adhesive, where the adhesive must be removed without leaving any residue on the substrate surface. Major points of differentiation between SIS and MAM adhesives are summarized in Figure 7.

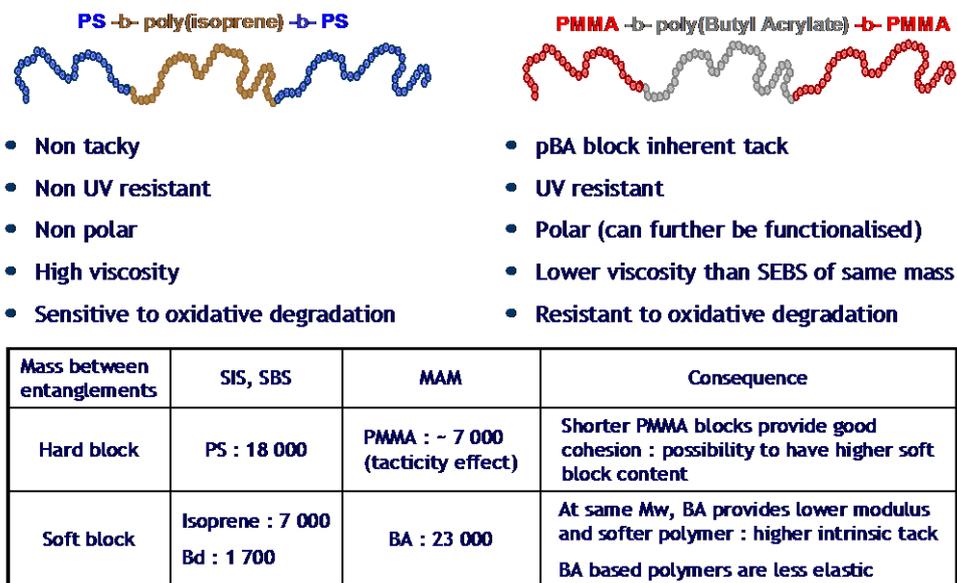


Figure 7: Major differences between SIS and MAM based adhesives

4 Adhesion properties and processing of neat MAM copolymers

Adhesion and creep behavior of MAM copolymers are directly related to the ratio between soft and hard blocks. The softest products like SM8590, SM8590XM5, offer a fair adhesion to a large variety of supports. Shear resistance is much higher than what can be achieved with acrylic random copolymers of similar composition and similar molecular weight. Figure 8 shows a comparison of MAM copolymers with commercial acrylic random copolymers developed for hot melt applications. It can be noticed that both tack properties and creep resistance are improved with block copolymers. This can be achieved without any formulation, which is a great advantage for maintaining excellent optical properties, UV resistance, and being able to remove the adhesive cleanly.

Due to their relatively high viscosities in the molten stage (Figure 9), preferred application systems are solution-based or extrusion. Many solvents can be used to dissolve MAM block copolymers including ketones, toluene, xylene, acetates, and chlorinated solvents.

Measurement	FINAT test method	SM8590	SM8590XM5	Commercial acrylic hot melt adhesives ¹	
Weight (g/m ²)	FTM 12	21,05 (2)	22.6 (1.2)	25	25
180° Peel (20mn), N/25 mm	FTM 1	12,42 (0,6)	13.9 (0.3)	8.4	9.2
Type of failure		Clean plate	Clean plate		
180° Peel (24h), N/25 mm	FTM 1	17,12 (0,4)	18.1 (0.6)	11	9.2
Type of failure		Clean plate	Clean plate		
Loop Tack (N)	FTM 9	6.9	7.2	4.7	5.3
Lap shear, 25x25 mm, 1 Kg (mn)	FTM 8	> 11 000	> 11 000	> 3000 h	> 3000 h
SAFT 25x25 mm, 1Kg (°C)	ASTM 4498	85.6	94.1	79*	78*

¹: Commercial hydrophobic acrylic adhesive. Data from tech data sheet *: 500 g load only

- Coating on PET film from acetone solution (35%), 70 µm blade. Adhesion evaluated on stainless steel

Figure 8: Adhesion properties of the pure soft MAM block copolymers

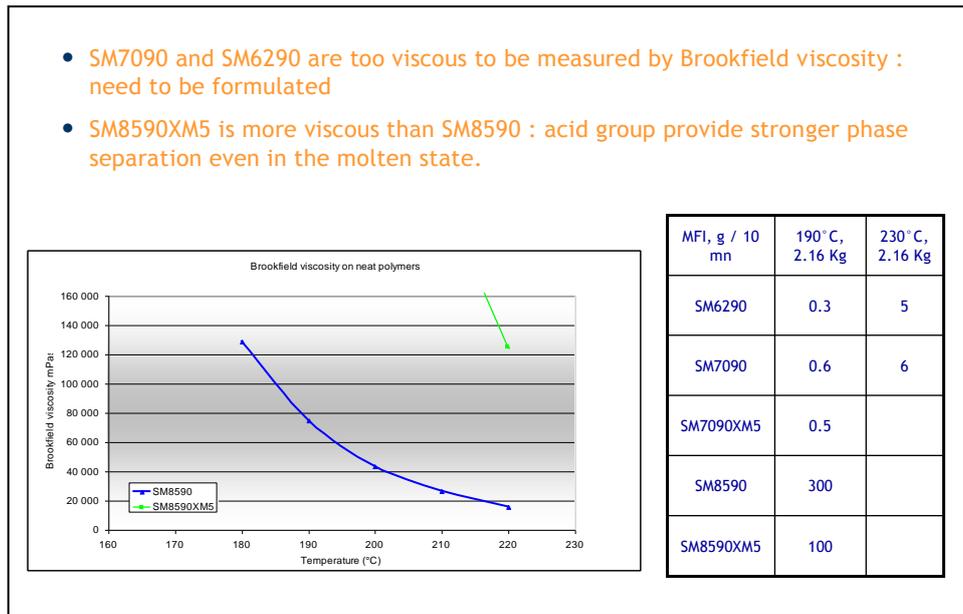


Figure 9: Viscosities or MFI values of neat MAM block copolymers

When the ratio between the soft and hard phase is decreased, tack becomes marginal, but mechanical and high temperature properties increase (see cross-over temperatures in Figure 4). A grade like SM6290 has almost no tack: the neat polymer can be used as non-slippery material, coextruded on a large variety of supports thanks to PMMA's compatibility with many other polymers (e.g., PVC, polyurethanes, PC, ABS) but not really as an adhesive. It will need to be formulated for adhesive applications.

5 Formulated adhesives based on MAM block copolymers

The choice of tackifiers for MAM copolymers is more challenging than it is for SIS systems. Many tackifiers are non-polar molecules and have only limited or very limited compatibility with the polar acrylates. Furthermore an ideal tackifier should be selective of the mid-block and not affect the hard structuring block. The gap in solubility parameters between polyacrylates and PMMA is not as high as it is for styrene and isoprene, making tackifier selection more complex.

Various tackifiers and plasticizers for soft block compatibility have been screened. Trends are given below, but this must be considered as a very rough indication, requiring double check with each commercial additive and each MAM copolymer.

- Compatible tackifiers : (hydrogenated) rosin esters, (hydrogenated) aromatic hydrocarbon resins, aromatic modified hydrocarbon resins, aromatic modified polyterpene resins
- Non compatible tackifiers : terpene-styrene, polyterpene resins, aliphatic and cycloaliphatic resins
- Compatible plasticizers : phtalates, adipates, citrates, trioctyltrimellitate, polyethers, fatty acid esters
- Non compatible plasticizers : mineral oils, paraffin

Figure 10 illustrates some adhesive properties obtained with a set of formulations using various MAM block copolymers. It is clear that formulations could be significantly modified, but the aim of this table is simply to highlight that playing on the formulation allows for:

- Very high adhesion strength, with marginal effect of consolidation time (180° peel values after 1 and 24 h)
- Melt viscosities suitable for e.g. nozzle application in hot melt systems
- Polymer contents that could certainly be increased as compared to what has been done here in order to improve shear and SAFT values.
- Excellent compromise of properties in some cases.

Test Methods	SM8590 DERTOPHENE T CATENEX T145	SM8590XM5 DERTOPHENE T CATENEX T145	SM7090 DERTOPHENE T + DERTOLINE DEG 2 + 10% Hexamol DINCH	SM7090 DERTOPHENE T + DERTOLINE DEG 2 + 5% Hexamol DINCH	SM6290 DERTOPHENE T + DERTOLINE DEG 2 + 10% Hexamol DINCH
Coating weight (g/m ²)	23,82 (1,2)	21,77 (1,7)	26,29 (1,4)	26,37 (0,9)	26,95 (1,9)
Peel 180° after 20min (N-25mm) type of failure	20,21 (1,2) cohesive	20,29 (0,9) cohesive	17,86 (0,3) cohesive	around 23N cohesive & Slip stick	18,42 (0,4) cohesive
Peel 180° after 24h (N-25mm) type of failure	19,97 (0,4) cohesive	18,69 (2,6) cohesive	17,65 (0,3) cohesive	around 24N cohesive	18,96 (0,7) cohesive
Peel 90° after 20min (N-25mm) type of failure	19,32 (0,9) cohesive	18,59 (0,7) cohesive & Slip stick	13,32 (0,3) cohesive	/ Slip stick	around 17N cohesive & Slip stick
Peel 90° after 24h (N-25mm) type of failure	20,26 (0,9) Slip stick	/ cohesive & Slip stick	15,08 (0,6) cohesive	around 22 - 23 cohesive & Slip stick	16,62 cohesive & slight slip stick
Loop Tack (N)	2 to 5	32,30 (0,5)	21,14 (3,2)	5,60 (2)	19,35 (3,1)
Static shear (min)	> 7000	463 (27)	2923 (120)	> 11000	3197
SAFT (°C)	60 (2,2)	48,03 (0,6)	56,63 (0,4)	65,92 (0,4)	55,66 (0,5)
Brookfield viscosity @170°C - mPas	3540	15275	6635	6660	10140

Formulations with SM8590 and SM8590XM5	Formulations with SM7090 and SM6290
<i>Polymer : 30 Dertophene T : 49 Catenex T145 : 31 Irganox 1010 : 0.1</i>	<i>Polymer : 20 Dertophene T : 33 Dertoline DEG2 : 37 Hexamol DINCH : 10 Irganox 1010 : 0.1</i>

Test methods

FMT 1 (FINAT) : Peel Adhesion 180° (after 20min and 24h)
 FTM 2 (FINAT) : Peel Adhesion 90° (after 20min and 24h)
 FMT 8 (FINAT) : Resistance to shear from a standard surface
 FMT 9 (FINAT) : Loop tack
 ASTM 4498 : SAFT (Shear Adhesion Failure Temperature)

Basic material : stainless steel
 Substrate : PET film 50µ

Figure 10: Some formulations designed for MAM block copolymers

Figure 11 is another illustration of the potential adhesive properties achievable through formulation. In this case, SM8590 is used and formulated with varied amounts of copolymer versus tackifier + plasticizer. It is clear that a broad spectrum of adhesion / creep values could be covered. Higher creep could still be achieved with higher levels of polymers, as viscosities in all cases remain reasonably low (not tested).

Product	Polymer ratio	Adhesives properties					Brookfield viscosity in mPas	
		Peel 180° N/25mm	Type of failure	Tack, N	Shear resistance	SAFT, °C	170°C	160°C
SM 8590	30	23	Cohesive	30	-	53	625	885
SM 8590	40	26	Cohesive	26	-	52	1315	1920
SM 8590	50	18	Adhesive	18	-	57	2595	4055
SM 8590	60	10	Adhesive	11	+ / -	60	4675	7510

MAM Block copolymer: x %
 Hydrogenated rosin ester (KE311, Arakawa) : 90-x %
 Diisodecyladipate (DIDA): 10%

Basic material : stainless steel
 Substrate : PET film 50µ

Figure 11: Formulations with variable amounts of SM8590

6 Hydrophilic block copolymers

6.1 Structure description

The strength of the CRP technology used in this study is the ease of introducing specialty comonomers into selected blocks. For applications where the adhesive material needs to have an ability to absorb water and moisture, a hydrophilic block copolymer has been designed. The mid-block combines hydrophobic low Tg monomers and hydrophilic monomers, while the hard end-block is still hydrophobic and based on PMMA. Phase separation between the hard and soft blocks still applies and mechanical properties comparable to the standard MAM presented above are obtained.

When placed in contact with water, the soft block absorbs water and swells, while the hydrophobic hard block remains as isolated structured domains, thus maintaining cohesion and strength, as illustrated in Figure 12.

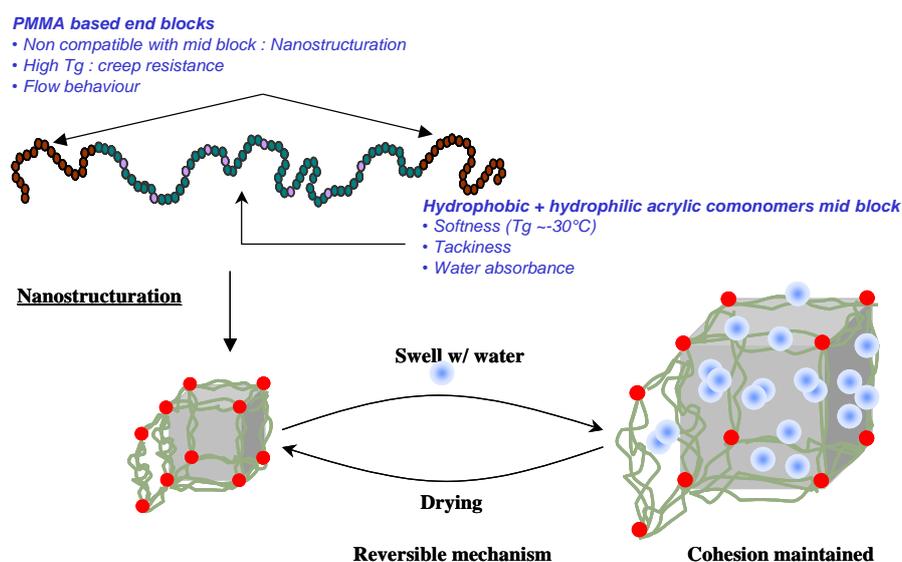


Figure 12: Design and water absorption-desorption behaviour of hydrophilic block copolymer

6.2 Hydrophilic block copolymer properties

Due to its fine nanostructure, the block copolymer remains clear and transparent even through thick layers. An illustration of some water absorption, retention of mechanical properties, transparency, and reversibility is observable in Figure 13. In this figure, the discs are 4 mm thick and the material is still very transparent.

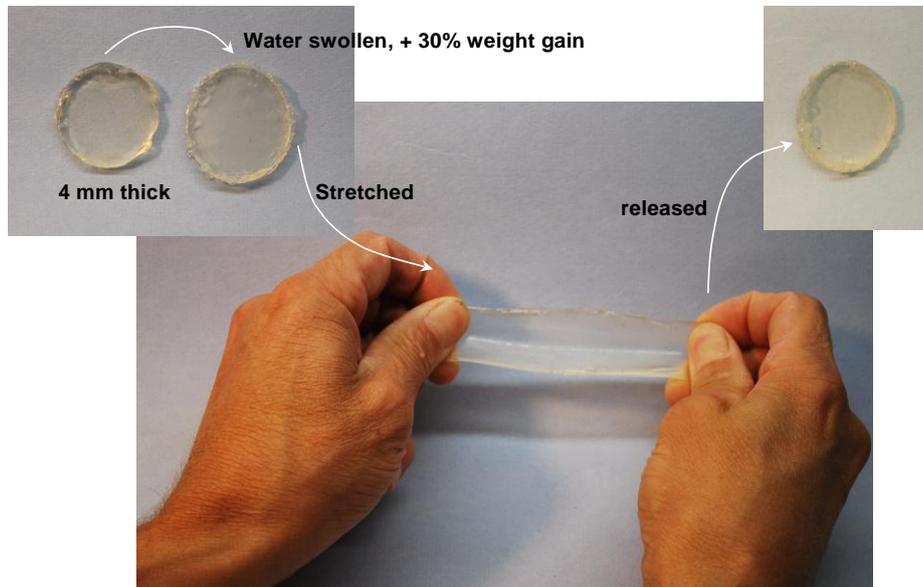
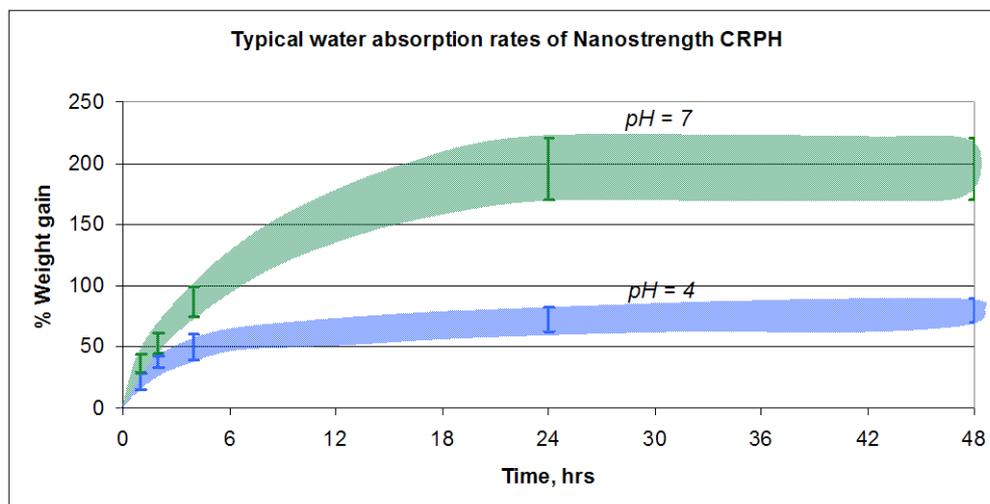


Figure 13: Water absorption, retention of mechanical properties, and reversible behavior

Since the mid block is hydrophilic, adhesives can be designed without the need to add hydrocolloid fillers as frequently done in the industry with current technologies. Water absorption rate and level is pH dependant. It typically can reach 100% water absorption at pH 4, and up to 200% at pH 7 and above. Water absorption rates are illustrated in Figure 14. Kinetics can significantly be increased through addition of small fractions of organic or mineral bases to the formulation.



Full immersion in water

Figure 14: Typical water absorption rate of hydrophilic copolymer

This polymer can be processed by extrusion and can be formulated to increase tack. It can also be applied after dilution in solvents such as ketones, toluene, acetates, and chloroform.

Tack values and creep resistance are comparable to what has been reported for SM8590 (Figure 15).

- Dissolution in acetone, enduction on PET film, adhesion to stainless steel
- Tack values comparable to (hydrophobic) acrylic polymers designed for medical applications

Measurement	FINAT test method	Hydrophilic block copolymer	Commercial acrylic medical adhesives ¹	
Weight (g/m ²)	FTM 12	19,2 (1)	25	25
180° Peel (20mn) <i>Type of failure</i>	FTM 1	8,6 (1,6) <i>Clean plaque</i>	8,4	9,2
180° Peel (24h) <i>Type of failure</i>	FTM 1	10,85 (1,4) <i>Clean plaque</i>	11	9,2
Loop Tack (N)	FTM 9	5,20 (0,9)	4,7	5,3
Lap shear, 25x25 mm, 1 Kg (mn)	FTM 8	> 11 000 mn	> 3000 h	> 3000 h
SAFT 25x25mm, 1Kg (°C)	ASTM 4498	82,4 (5,6)	79*	78*

¹: hydrophobic acrylic adhesive. Data from technical data sheet *: 500 g load only

Figure 15: Tack values of hydrophilic block copolymer

Finally, the unique set of properties offered by this new polymer is illustrated in Figure 16.

<ul style="list-style-type: none"> • Transparent • Fully thermoplastic • Fast water absorption rate • 80 – 200 w% water absorption • Water absorption rate and maximum uptake can be monitored with addition of bases • Intrinsically tacky • Soft (Tg mid block around -50°C) • UV resistant (acrylic structure) • No need for hydrocolloid fillers • Removable without residues • Can be coloured for innovative designs • Recyclable • Simplified formulation, less raw materials 	
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Figure 16: Summary of hydrophilic block copolymer properties

Conclusion

Thanks to controlled radical polymerization, block copolymers with interesting adhesive properties can be obtained. Their block structures allow the use in hot-melt adhesive applications. They can also be used in solvent-based systems, without need for cross-linking to achieve good creep resistance. The softest grades already provide an efficient tackiness/creep resistance combination, allowing their use without any formulation, thus avoiding the risks of small molecules migration or residues when used as removable or repositionable adhesives.

New structures having specialty groups in specified blocks, like hydrophilic behavior, are also presented.

Acknowledgements

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