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Acrylic TPE approaching automotive

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Recently, Kuraray has developed a novel all (meth)acrylic block polymer named LA-Polymer by using its own polymerisation technologies. The structures of LA-Polymer are triblock copolymers. i. e. poly(methyl methacrylate)-block-poly(n-butyl acrylate)-block-poly(methyl methacrylate) [1]. LA-Polymer is processed in Kuraray's pilot plant at commercial level in Japan. In this paper, characteristics and some possible application examples of LA-Polymer and its modifications with engineering plastics for potential automotive use are shown.

1. Introduction

After Kuraray developed key technology for mass production of specialised PMMA-PnBA-PMMA triblock copolymers, **(fig. 1)** the use of flexibilised PMMA with no change in transparency was the first exiting characteristic feature. Furthermore, we found monomers and oligomers are absent which provides basically odourlessness in application. This is also supported by a very narrow molecular weight distribution **(fig. 2a)** [2]. Because of the intrinsic elastic part PnBA rubber, no additional plasticisers are needed to get flexibilisation of PMMA in broad hardness and elasticity ranges. The well-known weatherability aspects of PMMA were proofed also for LA-Polymer as well as a high level of transparency **(fig. 3)**.

In looking at the polar nature of LA-Polymer we found good compatibility and adhesion to other polar plastics like PC, ABS, SAN and even PVC. In fact the polarity seems also causal for good paintablity. With inorganic fillers we found a good dispersion effect beside good compatibility. Depending on the molecular weight and structure, LA-Polymer show a low to very low melt viscosity. This fact is used for adjusting well-set elastified PMMA modifications and for combinations of LA-Polymer with engineering plastic PBT for targeting automotive applications.

Figure 1 shows the molecular structure of LA-Polymer, which is fully (meth)acrylic triblock copolymer. It is sequentially prepared by using our living anionic polymerisation system. The LA-Polymer is built of two terminal hard PMMA blocks (T_g = 100 ~ 120 °C) and one inner soft rubbery PnBA block (T_g = -40 ~ -50 °C). In general LA-Polymer can be used as a thermoplastic elastomer.

The result of SEC (Size Exclusion Chromatography) and molecular weight distribution curves of LA-Polymer and conventionally made PMMA are depicted in **figure 2a.** The molecular weight distribution of LA-Polymer is more narrow than the one of a conventional acrylic polymer. Moreover, LA-Polymer has a well-defined structure and a very low content of monomers and oligomers. In **figure 2b** the grade map is shown with three grades, LA2140e, LA2250 and LA4285, being produced as pellets in different Shore hardnesses (A32-soft, A65-middle, A95-hard). Hardness generally depends on the content of PMMA blocks.

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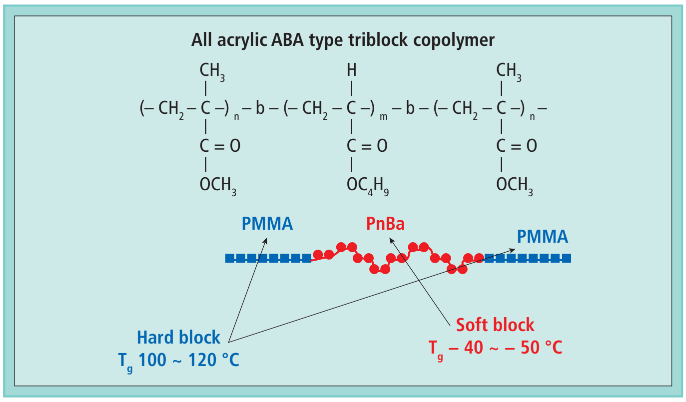


Fig. 1:
Structure of LA-Polymer - by using our living anionic polymerisation system, the acrylic block copolymers were sequentially polymerised.

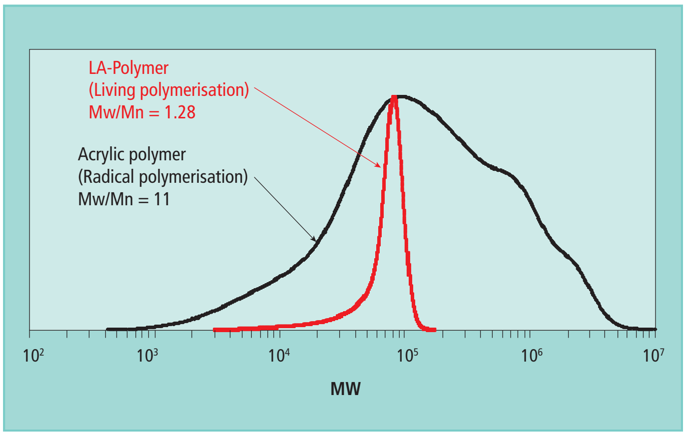
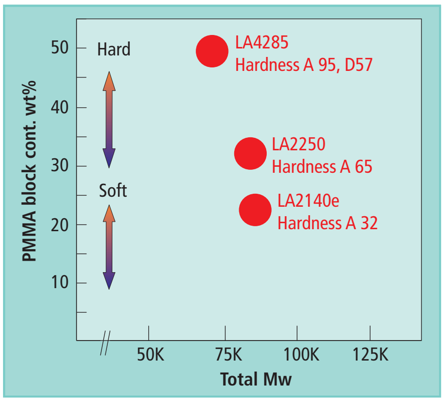


Fig. 2a:
SEC (Size Exclusion Chromatography) and molecular weight distribution curves of LA-Polymer and conventionally made PMMA

Fig. 2b: Grade map of different LA-Polymer types



2. Characteristics

2.1 Morphologies

By using Kuraray's specified staining method, an observation of LA-Polymer with TEM has become possible **(fig. 3)**.

The TEM photo also shows that LA-Polymer has a well-defined structure. The micro-phase separation is very clear and the sample shows cylindrically arranged dark PMMA micro-domains with an approximate diameter size of 10 – 20 nm in a light PnBA matrix.

For structure analysis, TEM micrographs of LA-Polymer are compiled in **figure 3.** Here the black parts represent the PMMA and white parts are the PnBA. The LA-Polymer have different micro-phase separated morphologies, which depend on the content ratio of PMMA block and PnBA block:

- LA2140e short cylindrical morphology
- LA2250 long cylindrical morphology
- LA4285 lamellar morphology.

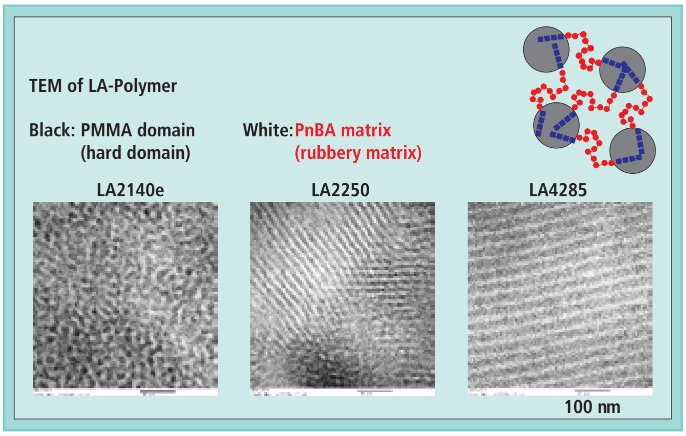


Fig. 3: Morphology investigation of LA-Polymer by TEM (Transmission Electron Microscopy)

2.2 Transparency and durability

The dependence of several resins' transmittance on wavelength has been measured **(fig. 4).** In the range of visible light wavelength (380 – 780 nm), LA-Polymer has excellent transparency (ca. 92 %). It is on the same level as polymethyl methacrylate, and it is suggested to be better than polycarbonate and polystyrene (ca. 90 %).

Fig. 4: Transparency of LA-Polymer compared to polycarbonate (PC) and polystyrene (PS)

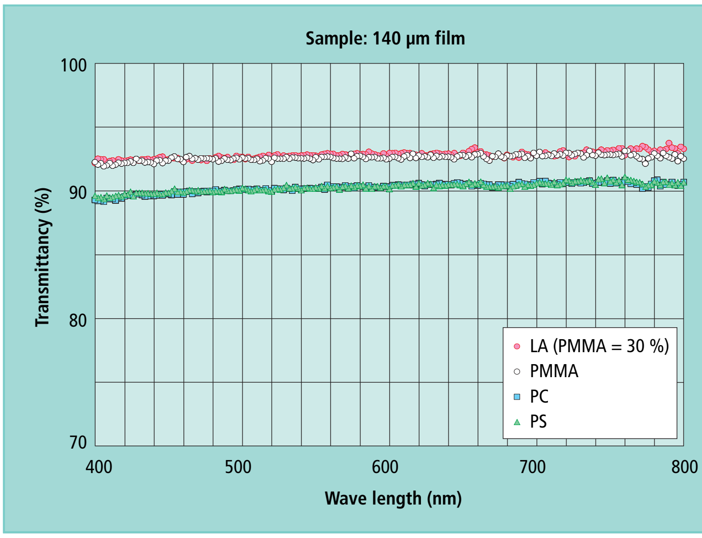
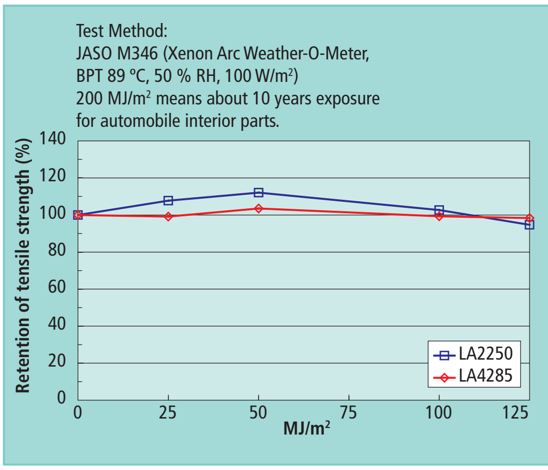
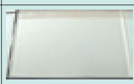
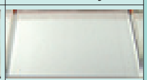
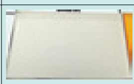
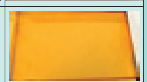
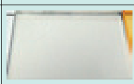
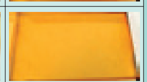
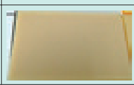
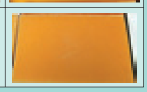


Figure 5 shows the weather resistance of LA-Polymer by Sunshine Weather-O-Meter (SWOM) with retention of tensile strength and colour stability. After the specimen (2 mm thickness injection moulded sheets) had been exposed, the values of factors (δa*,δb*,δYI) remained low with only little change. Suggesting that, the weather resistance of LA-Polymer is relatively stable with steady tensile strength and very low yellowing.

Fig. 5: Weather resistance test on tensile properties and colour change



Samples	Before irradiation	After irradiation (200 MJ/m²) = about 10 years
LA4285		
TPU polyester type		
TPU polyether type		
TPO		

TGA curves are shown in **figure 6.** The thermal stability is accounted by a temperature of 5 % loss which is 316 °C in N_2 atmosphere and 282 °C in air. As indicated above, LA-Polymer has good flow ability and it can be processed below the degrade temperature in injection moulding, extrusion moulding, compression moulding, hot-melt coating, etc. Blending with other polymers can be conducted in a mixer or kneader such as kneader-ruder, extruder, mixing-roll, Banbury mixer, etc.

2.3 Flow properties

Compared to an HSBC with equivalent molecular weight and hard block content, the LA-Polymer shows an extremely high melt fluidity (means low melt viscosities) and softness properties, caused by the PnBA block **(tab. 1).**

In a study on the dynamic mechanical properties it was also indicated that LA-Polymer is softer than SEBS, and has a good high temperature performance, caused by a higher glass transition temperature (T_g) of the syndiotactic PMMA block.

Because of their high flow and easy to paint properties, LA-Polymer can be effectively used in moulding materials, especially injection moulding. The melt viscosity as a function of shear rate at various temperatures is given in **figure 7.** This demonstrates the good processability of LA-Polymer without using plasticisers.

3. Adhesion to polar plastics

Adhesion to plastics is generally requested for all 2K applications. Conventional TPE based on HSBC has good adhesion to non-polar plastics (PP, PS, PPE, etc.) but it is difficult to bond to polar plastics such as PC, ABS, and PMMA. Recently, a TPV "bondable grade" was developed that shows improved adhesion to polar plastics. It is used here as reference material.

To investigate adhesion to polar plastics, an insert moulding system was prepared **(fig. 8).** The LA-Polymer shows high adhesion to polar plastics and PS, compared to the TPV bondable grade. In addition it maintains good transparency whereas the TPV gets turbid.

4. Paintability

Because of the adhesion properties the idea of over painting seemed reasonable. Therefore the interesting process of coloration was studied and other useful plastics have been checked in the same manner. The result is depicted in **figure 9,** where solvent-based and water-based acrylic paints have been used versus LA-Polymer, PVC, EMMA, and TPO. The adhesion was checked by pulling a tape.

5. Physical properties

The hardness and mechanical properties of the LA-Polymer can be easily controlled by mixing. A mix of LA2250 and LA4285 was done without loss of transparency. **Table 2** shows properties of the injection-moulding grades LA2250 and LA4285 and a 1:1 mix of both.

6. Comparison to TPO and TPU

When looking at the key properties of LA-Polymer, it is useful to check the standard materials in these applications, thermoplas-

Tab. 1:
Flow properties of LA-Polymer and HSBC (SEBS)

	Molecular characteristics		Hardness	MFR [g/10 min]	
	Mw	Hard block content	[Shore A]	190 °C, 2.16kg	230 °C, 2.16kg
LA-Polymer	77,000	30 wt.%	60	7.0	110
SEBS	80,000	30 wt.%	80	0.04	0.46

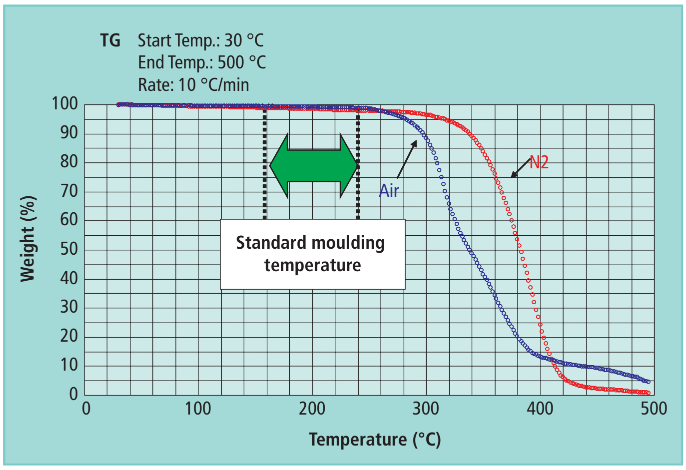
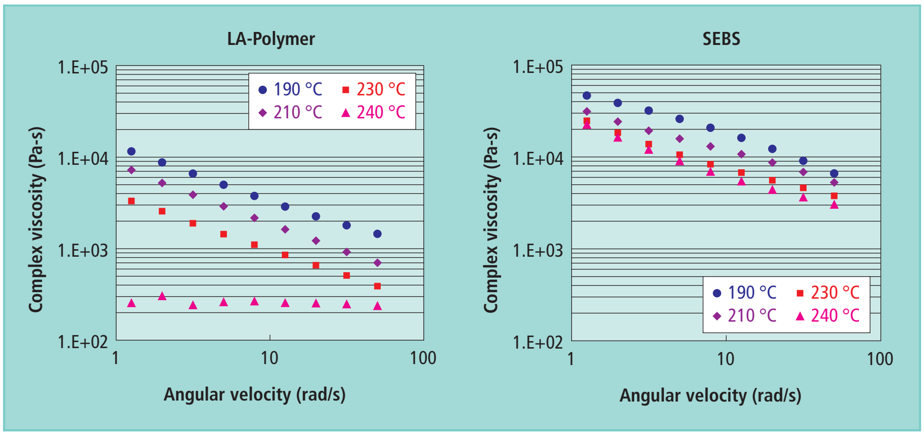


Fig. 6:
Thermal stability analysed by TGA in air and nitrogen. Measurement condition: The sample was heated from 30 °C to 500 °C at a rate of 10 °C/min.

Fig. 7: Melt viscosity of LA-Polymer (MnBM) as a function of shear rate at various temperatures



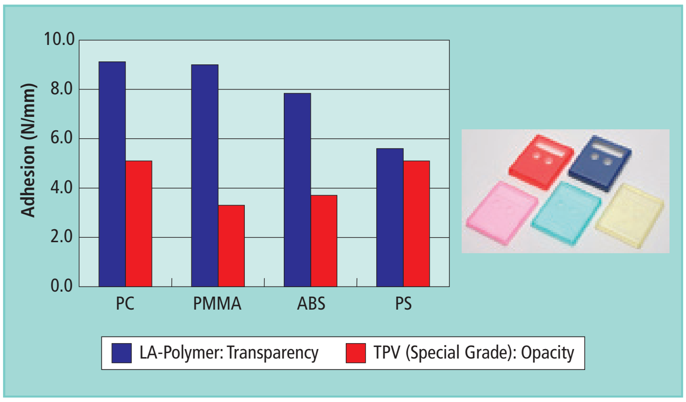


Fig. 8:
Adhesion to polar plastics in peel test; photograph shows double moulded samples.

tic poly olefins (TPO) and thermoplastic polyurethanes (TPU). The superior features of LA-Polymer are highlighted in **table 3.**

7. Modifier for polar plastics (LC-Series)

As commonly known HSBC are used as impact modifiers of non-polar polymers and blends (PP, PS, PPE, etc.). As mentioned above, LA-Polymer is more flexible than HSBC and it is a polar material. The behaviour of LA-Polymer as an impact modifier for polar plastics (PC/PBT blend) was studied and compared to SEBS **(tab. 4).** Impact strength is improved without losing flow ability and HDT. The effect at low temperatures is especially good.

Certainly important in fact is the change of transparency into translucent or turbid while mixing polar plastics LA-Polymer with PBT, PVC, etc. which is dependent on the matching of the refractive indices. Nevertheless, the combination of good scratch and oil resistance was found as a main requirement of the automotive industry. A set of formulations **(tab. 5)** was established and the blending of LA-Polymer with engineering plastics like PBT under a new product name "LC-Series" was defined.

8. Abrasion resistance

Abrasion tests were carried out under conditions described in JASO M312 with cotton cloth and steel wool rubbing **(fig. 10).** LC150B is between TPUs (ester and ether type) and TPOs which are generally worse.

Tab. 2: General properties of LA-Polymer injection-moulding grades

		Test method	LA2250	LA2250/LA4285 = 50/50	LA4285
Hardness [type A]	(-)	ISO 7619-1	65	78	95
Specific gravity	(-)	ISO 1183	1.08	1.10	1.11
Modulus at 100 %	(MPa)	ISO 37	3.7	9.1	19
Tensile strength	(MPa)	ISO 37	9.0	12	19
Tensile elongation	(%)	ISO 37	380	190	120
MFR [190 °C 2.16 kg]	(g/10 min)	ISO 1133	25	3.8	1.5
MFR [230 °C 2.16 kg]	(g/10 min)	ISO 1133	330	68	31
Transmittance [3 mm]	(%)	ISO 13468-1	91	91	91
Haze [3 mm]	(%)	ISO 14782	2	2	2
Table shows typical values which are not specific values.					

9. Oil resistance

Various fats, oils and lubricants are either used in cars or are part of dirt that cars are exposed to. Therefore information on oil resistance is important, mainly for automotive interior applications. The assessment was done according to ISO 1817; volume change and weight change (uptake) were investigated. The results show a better performance of the LC-Series which is a 50:50 LA/PBT blend **(tab. 6).**

Tab. 3: Performance map of LA-Polymer versus TPO and TPU

	LA-Polymer	TPO (non-DV)	TPU
Polar/non-polar	Polar	Non-polar	Polar
Melt viscosity	Excellent	Good	Not good
Transparency	Excellent	Bad	Not good
Weatherability	Excellent	Not good	Bad (yellowish)
Softness	Excellent	Not good	Bad
Colouring/paintability	Excellent/excellent	Good/not good	Good/excellent
Elasticity	Not good	Not good	Excellent
Tensile strength	Not good	Good	Excellent
Heat resistance	Good	Good	Good
Oil resistance	Good	Not good	Excellent
Alcohol resistance	Bad	Good	Good
Abrasion resistance	Not good	Good	Excellent

Tab. 4: Properties of PC/PBT/LA-Polymer blend

	1	Ref. 1	Ref. 2
[Formulation]			
PC	60	60	60
PBT	40	40	40
LA-Polymer triblock, PMMA=23 %, MW=80,000	10	–	–
SEBS triblock	–	10	–
[Charpy notched impact strength]			
23 °C [KJ/m^2]	85	68	11
-40 °C [KJ/m^2]	21	9	10
[MFR] 250 °C, 2.16 kg [g/10 min]	12	11	10
[HDT] 1.82 MPa	84	89	80
[Flexible modulus] 23 °C [MPa]	1610	1530	1760

Tab. 5: Examples of LA/PBT formulations

			1	2	3	4	5
LA2250			25	33	50	67	75
PBT Novaduran 5010L (MEP)			75	67	50	33	25
Hardness	(Type A)	ISO 7619-1	91	88	80	78	76
Tensile strength	(MPa)	ISO 37	30	23	16	10	9.0
Tensile elongation	(%)	ISO 37	40	40	90	170	250
MFR (230 °C, 2.16 kg)	(g/10 min)	ISO 1133	17	32	70	140	180
Flammability	–	(UL94)	HB	HB	HB	HB	HB
Table shows typical values which are not specific values.							

10. Comparison of LA-Polymer and LC-Series

As a result of our development we were able to show key properties for potential automotive applications. The main benefits of these materials are their durability and weatherability. Properties and features of the materials can further be adjusted to specific OEM design standards.

The following collection is to be seen as an initial study on applications: For LA-Polymer we focus on their superior combination of transparency and elasticity leading to light guiding applications in illumination of switches, safety guards or optical communication parts. Application requirements in touch and feel can be supported because of the wide hardness range of LA-Polymer. Soft LA-Polymer are more tacky than harder ones. Because of their fully miscibility with each other and with PMMA all soft-touch nuances can be adjusted by simple mix.

In the harder and more rigid ranges, combinations of LA-Polymer with engineering plastics deliver improved oil and abrasion resistance. LA-Polymer/PBT combination was found to show good adhesion to ABS. In general the adhesion to polar plastics in 2K applications is promoted at higher content of LA-Polymer in the blend. In addition, parts made of neat LA-Polymer or in combination with other plastics obtain improved paintability on top. This results in improved cost efficiency, i. e. in grip or protecting applications, where colour varieties of the plastic parts are required. An overview is shown in **table 7.**

11. Possible applications

Potential applications in automotive interior are i. e. in instrument panels, dash board skins, inner door grips, parking levers, shift grips, steering wheel covers, assist grips, switches and many others more in system parts. An exemplary map and demonstration examples are depicted in **figures 11** and **12.**

Fig. 9:
Paintability test of LA-Polymer compared to PVC, EMMA, and TPO

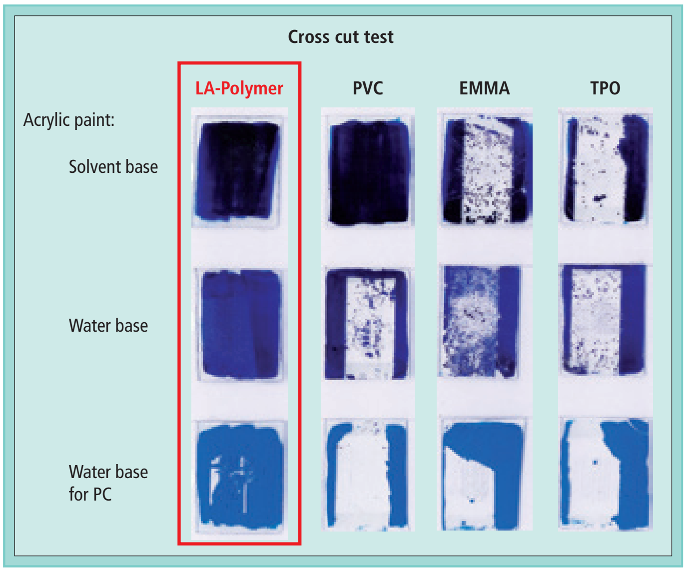
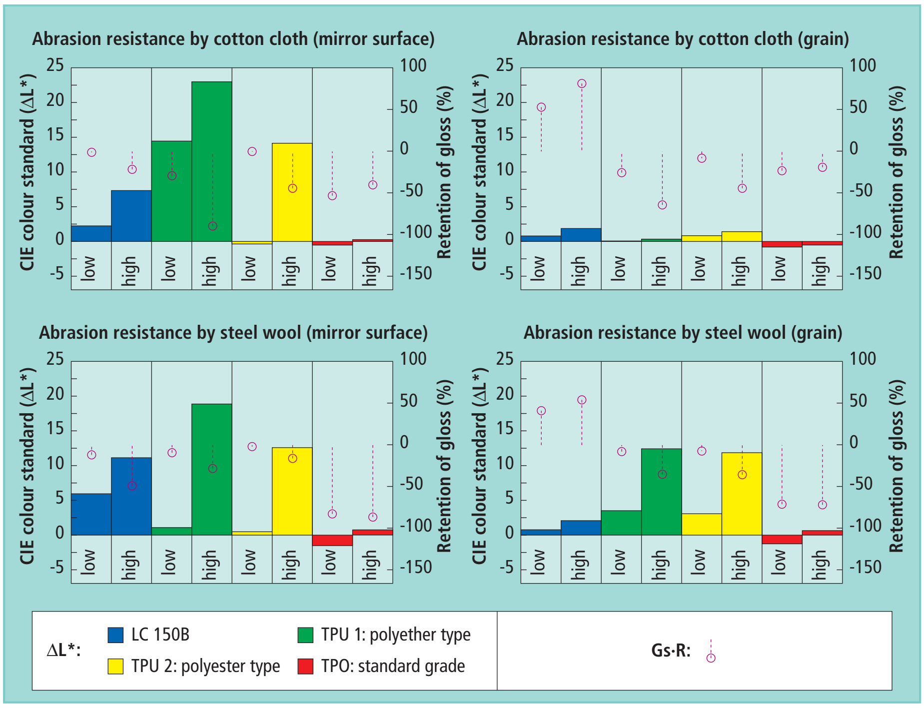


Fig. 10: Abrasion assessment according to JASO M312 test with cotton cloth and steel wool. Delta of colour change (left) and gloss (right) is measured. Specimen are 200 x 50 x 2 mm. (JASO M312 = Test method of plastics parts for automobiles, Japanese Automobile Standard Organisation).



Tab. 6: Oil resistance assessment according to ISO 1817.
Data show delta V (volume change) and delta W (weight change).
Specimen are 200 x 50 x 2 mm.

		Δ V (%) / Δ W (%)	
		LA/PBT = 50/50	TPEE
Machine lubricant	65 °C, 24 h	1.3 / 5.8	4.2 / 8.6
Castor oil	Room temperature, 168 h	0.5 / 1.8	2.3 / 3.0
50 vol.% aqueous ethanol	Room temperature, 168 h	7.1 / 5.3	10 / 7.7
Hand cream	Room temperature, 168 h	1.1 / 1.4	1.4 / 1.5
Table shows typical values which are not specific values.			

Tab. 7: Overview of key properties of LA-Polymer and LC-Series with regard to automotive applications

Properties	LA (/ LA)	LC-Series
Transparency	++	--
Printability	++	++
Oil resistance	+	++
Heat resistance	+	++
Stickiness	Yes	Dry touch
Adhesion to polar plastics (2K moulding)	++	+
Hardness (Shore)	> 65A	> 80A
High flow (thin parts moulding)	++	++

12. Conclusion

The new materials LA-Polymer and LC-Series have been presented and an overview on key properties for potential automotive application has been given. We showed the characteristics of materials ascribed as novel (meth)acrylic thermoplastic elastomers, containing no monomers and oligomers, nor plasticisers. Because of the low melt viscosity, good weatherability, transparency, paintability, adhesion to polar plastics, compatibility with fillers, combined with transparency or oil/abrasion resistance they show the strong ability for high class applications.

In addition some outline for applications was given. For a combination of LA-Polymer with PBT we showed resistivity against mechanical forces and oils. If this is used in combination with downstream colouration it may dedicate these compounds to grip and protection applications. In general transparent flexible applications are able to take a benefit in this material. But also more tough requirements in surface skins for automotive are possible and already tested.

13. References

[1] LA-Polymer Brochure, Kuraray 2006

[2] Details are shown in patents (United States Patent 6,329,480, United States Patent 6,555,637).

Fig. 11: Exemplary field map for potential automotive interior application

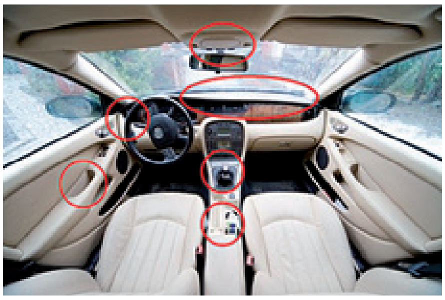


Fig. 12: Demonstration samples: Light guide in LED demonstration socket of 6 mm diameter (LA-Polymer) and gear grip application in three colours (LC-Series)