Plasma polymers and adhesion

Jörg Florian Friedrich TU Berlin

Different interface design of polymer composites



Structure of classic and plasma polymers

Classic radical chain-growth polymerization to linear polymer molecules



Random recombination of fragments in the plasma state to crosslinked networks



Functionalizations of polyolefin surfaces



Survival of NH₂-functional groups in the allylamine plasma polymer (used for adhesion-promotion to Cu)





OH- and COOH-functional groups in the allyl alcohol and acrylic acid plasma polymer (adhesion-promotion to Al)



Measurement of adhesion



Tensile shear strength test



Types of covalent linking of AI to polymer









covalently bonded by spacer molecules

covalently bonded by plasma polymers

Peel strength of AI films to gas-plasma modified PTFE and PP surfaces



Types of covalent linking of AI to polymer



Adhesion of AI to polypropylene promoted by spacers



- 1. the longer and more flexible the spacer the higher the peel strength
- 2. COOH end groups generate highest adhesion, OH groups act moderately

Interface design of polypropylene with special spacer molecules for non-peelable AI films



1. **covalent bonds** instead of physical interactions 2. introduction of **flexibilizing spacer** molecules

3. introduction of
spacers with
different chain
lengths

4. water-repellent hydrophobic Si-O-Si elements in spacers 5. water-repellent and **barriere-forming elements** with spacers (blocking ion diffusion, redox reactions)

- 1. **MOST EFFICIENT INTERFACE DESIGN** between polyolefins and aluminium.
- 2. It results in long-term (1 YEAR) durable NON-PEELABLE metal-polymer composites !!!

Types of covalent linking of AI to polymer



Many weak physical vs. a few strong chemical forces?

physical forces	energy (kJ/mol)	energy (eV) s	striking distance (nm)
van der Waals forces			weak bonds
dipole-dipole (Keesom)	20	0.2	0.3 - 0.5
dipole-induced dipole (Debye)	2	0.02	0.3 - 0.5
dispersion forces (Heitler-London)	0.08-40	0.008-0.4	0.3 - 0.5
hydrogen bonds	50	0.5	0.3 - 0.5
chemical bonds			strong bonds
ionic	560-1000	5.6-10.0	0.1 - 0.2
covalent (carbon)	300-750	3.0-7.5	0.1 - 0.2
metal	110-260	1.1-2.6	0.1 - 0.2

1.) The density of physically interacting polysort groups is approximately equal to that of chemical bonds for plasma polymers with monosort functional groups.

2.) Chemical bonds (monosort) are stronger by a factor of $\approx 200 \rightarrow$ higher adhesion.



Peel strength σ of thin Al layers from polypropylene vs. type and concentration of functional groups of plasma polymers



σ: -COOH>OH>>>NH₂

carboxyl and hydroxyl groups most efficient

bidentate bonds (AI-O)₂**C** (acrylic acid plasma polymer) $\sigma~\sim \textbf{C}_{\text{OH}}$

peel strength increases with concentration of OH groups linearly

monodentate bonds AI-O-C (allyl alcohol plasma polymer)

Peel strength of AI from plasma polymer coated PTFE





Mechanism of adhesion using plasma polymers

Covalent bonding between plasma polymer and polymer coating and/or substrate



(Schiff's base, esterification, addition to urethanes, substititution...)

chemical bonding between polymer substrate and thin plasma polymer layer

19

chemical bonding between

plasma polymer layer and

polymer coating

Problems with adhesion promotion using plasma polymers

Stormy and smoky oxidation of trapped radicals

1) Post-plasma oxidation of plasma polymers on exposure to air (auto-oxidation, "ageing")



Internal stress in plasma polymer layer caused by by surface oxidation and crosslinking leading to self-peeling



- # internal stress in the plasma polxmer layer by peroxy-induced crosslinking within the surface layer if exposed to oxygen from air
- # in the inner of layer only a few C-C recombination occur

comparable with the deflection of bimetals

3) Stress caused by different thermal expansion coefficients

material	thermal expansion coefficient α in 10-6K ⁻¹	
aramid fibre	-4.1	
carbon fibre	-0.5	
Si	²⁻⁴ inorganics	
ceramics	3	
diamond	1.3	
AI	23.2	
Au	^{14.2} metals	
Cu	16.5	
polyamide 6	120	
polymetylmethyacrylate	⁸⁵ polymers	
polyvinylchloride	80	



Quenching of any post-plasma oxidation of plasma polymers on exposure to air

Suppressing and quenching of post-plasma oxidation (auto-oxidation) using immediate (in situ) gassing with Br₂, B₂H₆ and NO



Conclusions



Advantages of plasma polymer

- 1. 50-90% dominance of 1 sort functional group (monosort)
- 2. form covalent bond to coating or substrate
- 3. concentration of monosort groups is high
- 4. concentration can be variied by copolymerization
- 5. thickness can be selected freely
- 6. layers are reactive (trapped radicals)
- 7. moderate to high improvement of adhesion
- 8. elimination of ageing by NO or Br_2 gassing
- 9. pinhole-free layers



Drawbacks of plasma polymer

- 1. freshly produced plasma polymers react strongly with oxygen from air (peroxy group formation and auto-oxidation)
- 2. plasma polymers undergo ageing
- 3. one sort of groups dominates but considerable amounts of side products are produced (not selective)
- 4. plasma polymers are crosslinked and hard
- 5. plasma polymers contain low-molecular weight components
- 6. plasma polymers cannot completely balance different thermal expansion coefficients of substrate and coating (self-peeling)
- 7. maximum thickness is limited to about 1 μm