The trick is to make it stick

A novel block copolymer has been developed for use in a waterborne primer for application on untreated PP or TPO plastics. It is designed for use on most of the common commercial or automotive specific substrates. Optimisation of the formulation parameters is an important factor in the properties of the resin and the subsequent coating performance.

Innovations in waterborne coatings for untreated PP and TPO plastics

Derrick Twene*
Mike Schellekens
Jeroen Donders

Plastic parts based on polypropylene (PP) and thermoplastic polyolefins (TPO) are very desirable due to costs related to manufacture and the ability to form complex objects. However, there are some disadvantages associated with their use for exterior applications, in that the surface can be easily damaged from wear, UV light or impact. To improve the longevity and the performance of the formed objects, it is necessary to protect them with a polymer-based coating material which acts as a barrier. Due to the inert nature of the plastic, coupled with low surface energy (30 mN/m for PP), it is extremely difficult to obtain direct adhesion to the surface of PP and TPO plastics without a pre-treatment stage to change the surface characteristics. Treatments such as plasma or in-line flaming are common in the automotive industry on exterior bumpers, facades and sidings. Chemical treatments involving the use of chlorinated polyolefins (CPOs) are also employed mainly for the North American and Asian markets. All these treatments have their drawbacks. Flame and plasma treatments, which effectively ionize the surface, are not long lasting and thus the coating has to be applied shortly afterwards. In addition getting the ionisation evenly around curves and holes can be difficult resulting in coating adhesion failure. CPO treatments are more robust, but expensive and pose an environmental risk.

The market is clearly looking for a simple elegant, easily applicable solution.

To meet this need, a chlorine-free waterbased polymer dispersion based on novel adhesion promoting block copolymer groups has been developed. These block copolymer groups are prepared by controlled radical polymerisation in solution; (2) (1) synthesis of amphiphilic acrylic acid (AA) - iBOA homopolymer block for interaction with untreated PP. [6], (2) pendant block copolymer groups with a high affinity for the surface of PP and TPOs. Tested using the well-known cross-cut adhesion test without the additional use of CPO or "PP swelling" solvents like toluene in the formulation.

Why adhesion onto untreated polyolefins is difficult

The problem associated with gaining good adhesion to polypropylene is the lack of adhesion onto untreated polyolefins [1]. This has been attributed to several aspects. Firstly, their chemical inertness, meaning it is difficult to get solvents to attack the surface to gain adhesion via mechanical mechanisms. And secondly, poor wetting caused by the low surface energy and lack of polar functionality [2] resulting in a high contact angle. Thus the main mechanism for gaining adhesion comes from forces of attraction better known as "van der Waals" forces. For these to be effective it is important to have good wetting of the surface allowing good contact of the anchoring groups.

When looking into the automotive industry, where a large amount of PP is employed on exterior parts, an additional dimension is encountered. To meet OEM automotive standards for toughness, flexibility strength and performance, their suppliers modify the PP with other plastics and additives. The compositions of these are generally trade secrets. One route to imparting toughness and flexibility is to blend the PP with rubber such as EPDM (ethylene propylene diene monomer) done at varying levels to obtain desired performance. The EPDM does improve the coating adhesion to the substrate as it has a higher permeability and mobility causing it to migrate to the surface. The EPDM on the surface makes the plastic more susceptible to solvents leading to enhanced mechanical adhesion [2]. There are, however, higher costs associated with compositions containing EPDM. This has resulted in alternative materials being used. This is depicted schematically for the bumper market in Figure 1 and shows geographical and automotive manufacturer preferences.

How to tailor polymer structures

Controlled radical polymerisation (CRP) techniques have given greater opportunities for the polymer chemist to design specific polymer structures such as block, graft or star shaped polymers with specific functionality control. Block copolymers with tailored composition can, for example, be used to improve the adhesion to a difficult substrate such as untreated polypropylene. The best known and most widely studied CRP techniques are nitroxide mediated polymerisation (NMP) [3], atom transfer radical polymerisation (ATRP) [4] and reversible addition-fragmentation chain transfer (RAFT) polymerization [5] The strength of these CRP techniques lies in the ultimate combination of the desired chain growth control in ionic polymerisation with the versatility and robustness of conventional free radical polymerization. Simplification of the polymer chain growth process in CRP versus classical free radical polymerization (FRP) is shown in Figure 2. The approach in designing polymer dispersions with pendant block copolymer groups with a high affinity for the surface of PP and TPOs makes use of the RAFT polymerisation technology. RAFT polymerisation is particularly suited for the preparation of a water-dispersible block copolymer containing an isobornyl acrylate (iBOA) homopolymer block for interaction with untreated PP. [6], [7] The synthesis in designing water-based polymer dispersions with the pendant adhesion promoting groups is performed according to a three step process as outlined in Figure 3: (1) synthesis of amphiphilic acrylic acid (AA) - iBOA block copolymers via RAFT polymerisation in solution; (2)
dispersion of the block copolymers in water by aid of a suitable base (optionally followed by solvent removal); and (3) subsequent use of the dispersed block copolymers in an emulsion polymerization process for preparation of a film forming polymer binder. To obtain a good balance of desired coating properties, the block copolymer level was set at 20 wt% on total emulsion monomers. The Tg of the emulsion polymer binder (BMA/BA) was set at 0 °C to obtain good film formation.

Tailor made is not enough

Even though the polymer dispersion has been tailor made to adhere to PP and TPOs, it is important to ensure the groups responsible for the anchoring to the surface and thus supplying the adhesion via attraction forces are in contact with that surface. To do this, the correct substrate wetter must be selected. In the study, commercially available substrate-wetting agents, used at their recommended levels, were investigated by means of measuring the adhesives forces of clear films on untreated PP using the well known cross-hatch method, performed in accordance with ASTM D3002/D3359 and DIN EN ISO 2409. According this method, a series of straight cuts are made onto the coated substrate using a special blade horizontally and vertically crossing each other resulting in small boxes. A tape is applied to the cut area and firmly pressed in place to ensure good contact. The tape is then quickly removed in one swift motion. The process is repeated and areas in the boxes examined for any loss of coating. No loss of the coating is rated as a “0” and complete removal given a value of “5”. Figure 4 shows the application conditions of the clear lacquer and the results for dry and wet adhesion with respect to variation in chemistry of the substrate wetting agents. Good wet adhesion means that good coating adhesion was obtained after having exposed the cross-cut area to a water-droplet for four hours at 20 °C prior to performing the tape test. The best performance in both wet and dry adhesion to untreated PP tended to favour polysiloxane based wetting agents. Fluoro-based wetting agents tended to perform less well in the dry adhesion measurements. An explanation could be they cover the surface of the substrate, thereby hindering the contact of the adhering groups of the block-copolymer based dispersion. The polysiloxane based wetting agent “S1” was selected and amount needed optimised.

Test results demonstrate better adhesion

Solvantbased resins with elastomeric urethane backbones are deemed to be the best commercial materials in primer formulations for use on exterior automotive parts. To ensure good adhesion, these resin systems are combined with CPOs either in a primer or a wash pretreatment step. This ensures that the surface of the substrate is suitably modified allowing adhesion of the subsequent layers. Figure 5 shows a comparison of an optimized clear formulation with that of a market reference containing the recommended amount of CPO for the more critical dry adhesion on PP as well as other more commonly used plastic substrates namely, PC, ABS, PA and PVC. The testing was done using the standard procedure of applying a wet film of 100µm, dried 10min at room temperature and after 16hrs at 50C. The results for dry adhesion using the cross-cut method show better adhesion on all substrates compared to the solventbased standard containing CPO. It should be noted that the solvent-based system with CPO is designed specifically for TPOs. However, the fact that the water-based block copolymer lacquer also has good adhesion to these substrates is an encouraging result.

Finally, the performance of the block copolymer-based dispersion as a primer coated on three different untreated commercial grades of plastic and an untreated PP/EPDM bumper part was tested. This took into consideration the variation in the composition of the plastic substrates and determined if the primer based on the block copolymer has adequate adhesion. Often the adhesion to the plastic can be compromised when the applicator prepares the total finished system. This is caused by the combination of upper layers of solid colour topcoat or (metallic/effect pigment basecoat - clear topcoat). They could contain specific solvents which ingress into the primer and soften the polymer matrix, or interfere with the adhesive forces coming from the block copolymer. The substrates were coated in three layers as outlined in Figure 6 using: (1) a pigmented primer based on the block copolymer dispersion; (2) a metallic basecoat; (3) a two-component commercial clear, cross linked with isocyanate (NCO), used in automotive plastic coating. In Figure 7 shows photos of primer adhesion measurements for the various substrates, where it was determined if the system is affected by the subsequent layers resulting in poor inter-coat adhesion or total adhesion failure. In Figure 8, results are shown for adhesion tests performed on the EPDM bumper, including results for a simulated impact “stone chip effects” test, done by direct and indirect impact.

Good adhesion on all plastics tested

This test showed that the variation in plastic compositions did not affect the performance of the primer. The anchoring groups of the block copolymer have a very strong affinity for the surface of the TPOs ensuring that good adhesion is maintained. The spray applied, waterbased metallic basecoat had a low enough surface tension and wetted the primer surface sufficiently to give a uniform appearance with no defects. Tests on the total system with the solventbased commercial clear coat showed that the solvents coming from the topcoat partial penetrate into the coating. This did not affect the performance of the total system nor the intercoat adhesion between the layers rated as “0” for all the three substrates. On the untreated PP/EPDM bumpers depicted in Figure 8, we obtain good adhesion of the primer to the substrate. It is as yet unknown if the adhesive forces of the block copolymer on the different substrates vary in strength depending on the composition of the TPOs or PP blends with EPDM, thus tailoring the polymer architecture further. If so, this could result in added performance to specific grades. The simulation testing using direct and indirect impact did not cause adhesion failure in the primer or the total system. The variation in commercial metallic basecoats showed inter-coat adhesion failure between the solvent-based basecoat and primer. The primer formulation will have to be optimised to improve its performance with the commercial solvent based metallic basecoat.

Acknowledgements
The authors would like to thank Theo Braams for all the synthesis work.

References

Results at a glance
The use of a novel designed iBOA based block copolymer via RAFT polymerisation provides the possibility to gain good coating adhesion onto very hydrophobic untreated plastics PP and TPOs as well as other common types without the need of additional treatments such as flame, plasma or environmentally unfriendly CPOs. Due to the varied nature of composition of PP substrates used for exterior automotive parts, finding a universal system applicable to most of the common commercial or automotive specific substrates is still a challenge for the industry. A novel block copolymer based dispersion is clearly a route which fulfills these requirements and offers a water-based, environmentally friendly solution. Test results indicate that the specific block copolymer design is paramount to getting the overall adhesive performance. It is equally important to select the correct combination of solvents and wetting additives to ensure good contact of the anchoring groups with the surface of the substrate. There are some differences in the total system as seen in the failure of inter-coat adhesion when using a solvent based basecoat. It should be possible to resolve this by optimising the formulation of the primer to have a higher surface energy to promote better wetting of basecoat. This new type of polymer design based on RAFT polymerisation is a novel way to tailor-make water-based dispersion with specific functionality to perform as an adhesion promoting binder for use on PP and TPO based plastic substrates.

* Corresponding author:
Derrick Twene
DSM NeoResins+
T +31 416 689-943
Derrick.Twene@dsm.com
Figure 1; PP bumpers and manufacturers composition split.

Expanding (30-40 %) -> e.g. French OEMS minimal EPDM addition for impact, low price

Car bumpers (60-70 % PP)

Non-expanding: compounding with EPDM and talcum (60-70%)

-> e.g. JPN OEMs special “secret“ grades e.g. “Toyota Super Olefinic Plastics”
Figure 2: Schematic representation of the polymer propagation via FRP and CRP
Figure 3: Schematic representation of the synthesis of the water-based polymer dispersion with pendant adhesion promoting groups.
Figure 4: Applications condition and the wet and dry adhesion of the block copolymer based dispersion to untreated PP with various commercial wetting agents.

F = fluoro based wetting agents  
S = polysiloxane based wetting agents  
P = polymeric wetting agent  
A = alkyne based wetting agent
Figure 5: Dry adhesion of the block copolymer based clear lacquer against solvent based commercial reference containing CPO.
Figure 6: Schematic of coating layers applied on substrates
Figure 7: Cross-cut dry adhesion on commercial untreated substrates
Figure 8: Comparing the adhesion and impact resistance on an untreated PP/EPDM bumper part using a solvent based and water based commercial metallic basecoats