MAIN LECTURES

ML-01
CURRENT AND NEXT GENERATION IN-MOULD COATINGS FOR AUTOMOTIVE EXTERIOR TRIM

W. (VOYTEK) S. GUTOWSKI, SHENG LI, GARY TOIKKA, and MARK SPICER

CSIRO Materials Science & Engineering, Functional, Interfaces & Coatings and Intelligent Materials, Graham Road (PO Box 56), Melbourne-Highett, Vic. 3190, Australia Voytek.Gutowski@csiro.au

Abstract

Currently, the most common method of surface finishing plastic automotive exterior trim components is post-mould painting which provides the desired aesthetic and functional attributes to the moulded product (colour, surface gloss, wear & weather resistance). If uncoated, plastics would exhibit sub-standard durability on exposure to environmental and service elements, e.g.: UV radiation, rain erosion, fuel residues, thus compromising product’s visual attributes.

Whilst post-mould coating adds value, improves aesthetics and extends the life of plastic components, it also adds significant costs and additional production steps. It also creates hazardous solid waste and VOCs. In the automotive industry, painting and associated operations account for 30% of the component’s cost, and are a significant source of defects and unrepairable rejects.

This paper addresses the followings:
1. Reviews alternative surface finishing techniques used by auto- and other industries focussing on feasible means for overcoming current challenges and attaining:
   - High-performance automotive quality exterior surface finish through a single-step ‘in-mould processing’ comprising coating co-cure with the moulded product, and
   - Single step ‘fusion & co-cure’ of surface finishing topcoat material with the substrate, i.e. simultaneous consolidation into a “coated plastic trim component”
2. Describes successful development of an in-mould coating process for plastics which offers the following advantages over the currently used wet-paint finishes:
   - Primer-less in-mould coating (ability to produce ‘service-ready’ parts),
   - Significantly reduced manufacturing time,
   - Total elimination of hazardous wastes (VOC’s and solid waste),
   - UV and wear protection to composite parts during transport and assembly.

REFERENCES

ML-02
SPECIAL-PURPOSE RUBBERS REQUIRE SPECIAL CROSS-LINKING SYSTEMS. AN OVERVIEW

HANS MAGG

C/o Lanxess Deutschland GmbH, Chempark, Building K 10 D-51369 Leverkusen, Germany hans.mag@lanxess.com

Abstract

This report will attempt to provide a brief review of the state-of-the-art in cross-linking systems for non-tire rubbers.

The most important conditions that cross-linking systems are required to meet are functional, process-related and generally "toxicological" in nature, and only to a limited extent economic.

The polymer backbone and cross-linking agent must be matched to one another.

Increased crosslink stability requires polymers with a backbone of increased stability, possibly achievable by the "hydrogenation" of the double bonds.

A classic example of this is the formal transition from IR (or NR) to EPM, being now cured by peroxides. However, since this means that the polymer suffers a significant loss of reactivity for the "classic" cross-linking agents and can therefore no longer be cross-linked sufficiently, new routes must be found to overcome the apparently contradictory effects. The problem is solved by reactive monomers ("cure site monomers). Peroxides are comparable to sulfur in terms of their versatility as cross-linking agents, since they are capable of reacting both with double bonds and with systems lacking double bonds, and are essential cross-linking agents for HNBR, FPM, EVM, CM and EPM. The mechanism of peroxide cross-linking systems are shown in detail.

Resin cross-linking is as the third variant of proven curing systems. This involves the use of resoles of p-octylphenol or p-tert-butylphenol as crosslinking agents, which selectively crosslink polymers with double bonds to form elastomers, with or without chlorine-containing activators depending on their structure.

Another possibility are cross-linking systems involving halogens, which are suitable hetero atoms for activating stable and polar or non-polar polymers of poor reactivity. When modified by these cure sites, such polymer become accessible.
for a variety of cross-linking agents since the carbon-halogen bond can readily be cleaved heterolytically or homolytically.

Heterolytic cleavage is promoted by metal oxides (zinc oxide and/or magnesium oxide) or metal soaps, for example, enabling a consecutive reaction to take place with classic sulfur systems, thiourea derivatives and cross-linking agents derived from these, triazine thiols, thia diazoles and others.

With homolytic cleavage, the polymer can be cross-linked with peroxides. This reaction is similar to the cross-linking of EPM with peroxides outlined above.

Various routes lead to the halogen modification of polymers, i.e.

1. Halogens as randomly distributed ligands in the polymer backbone (CM, CSM, ECO, CO),
2. Halogens as cure sites which are formed statically during polymerization (CR),
3. Halogens as cure sites which are formed by polymerization (FPM, ACM).
4. Halogens as cure sites which are used as special comonomers during polymerization (IIR).

Further improves stability is generated by halogen-free systems and cross-linking via nucleophilic reaction steps. For carboxylated diene rubbers and for ethyl acrylate and acrylate rubbers (AEM, ACM) and FPM, acrylic acid or methacrylic acid are among the monomers used as cure site monomers. These create additional possibilities for cross-linking by reaction with metal oxides, preferably zinc oxide thus opening up new application opportunities for the elastomer thanks to improved tensile and wear properties.

There is a need for – naturally polyfunctional – crosslinking agents capable of building up a covalent bond to the polymers. Suitable examples include nucleophilic reactants for electrophilic cure sites or conversely electrophilic reactants for nucleophilic cure sites. A diamine derivative, hexamethylenediamine carbamate (Diak No. 1), has proved most suitable for this purpose.

In fluororubbers too, nucleophilic attack on a double bond activated in situ is utilized.

Copolymers of vinylidene fluoride (VDF) / hexafluoropropylene (HFP) can therefore also be cross-linked with hexamethylenediamine carbamate.

The cross-linking of FPM (VDF/HFP) with "alcohols" is largely replacing diamine cross-linking owing to its good processing safety and high degree of cross-linking. The only cross-linking agent used here is bisphenol AF, chemically 2,2-bis(4-hydroxyphenyl)hexafluoropropane.

Isocyanates, for example, react electrophilically with the double bonds of diene rubbers, thus forming stable cross-linking bridges.

Similar – "inverse" systems, as it were – are also possible in heat-resistant rubbers. For example, urethanes are formed under vulcanization conditions if blocked di- or polyisocyanates are present. Polyfunctional carboxylic acids could also conceivably be used as cross-linking agents for amine or hydroxyfunctional cure sites.

ML-03
NEW ASPECTS OF POLYMER ALLOYS AND TPEs REVEALED BY POLYMER NANOTECHNOLOGY

TOSHIQ NISHI**, KEN NAKAJIMA*, and HIROSHI JINNAI*

* WPI Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan,
** Department of Macromolecular Science and Engineering, Graduate School of Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, Japan
nishi.toshio@wpi-aimr.tohoku.ac.jp

1. Introduction

In order to satisfy industrial demands for various purpose, vigorous research and development have been done on polymer alloys, blends and polymer composites. Recently the characteristic sizes of phase structures of such materials can be as small as on nanometer scale. Especially in the case of thermoplastic elastomers (TPEs), nano-scale microphase-separated structures play an intrinsic role in controlling their mechanical properties. However, the relationship between macroscopic physical properties and microscopic morphological structures was still obscure. In order to boost efficient development and promote creation of novel materials, it is important to develop techniques to evaluate nano-distribution directly. We categorized the required methods into three; nano-three dimensional (3D) measurement, nano-physical properties evaluation systems and nano-spectroscopy. We introduce the first two techniques in this paper.

Transmission electron microtomography (TEM) is an ideal tool for characterization of polymer nanostructures1, as such, it has proven useful for providing high-resolution 3D information on a variety of polymeric structures, e.g., block copolymer nano-scale microphase-separated structures2-3, etc. Some of these studies provided not only clear 3D pictures but also quantitative structural information. In what follows, we briefly show some examples of structural studies carried out using TEM to show possible future applications of the methods in polymer science.

For the purpose of evaluating local physical properties, atomic force microscopy (AFM) has a great advantage. While AFM can capture surface morphology on nanometer-scale lateral resolution, it can detect interactive force, which works between a sample and a probe. AFM is mostly used in intermittent contact mode in order to observe surface morphology and phase image was thought to be responses of mechanical properties. However, to derive some physical properties from a phase image is quite difficult4. On the other hand, force-distance curve measurement has an advantage that it can obtain quantitative mechanical properties such as Young’s modulus. A force mapping measurement is a method to measure force-distance curves at each point after dividing a sample surface into a grid. We combined force mapping measurement with force-distance curve analysis and succeeded in visualizing distribution of various properties such as Young’s modulus, adhesive energy on high lateral resolution5-15. We show the recent progress on the application of this technique...
to block copolymer nano-scale microphase-separated structures.

2. TEMT on block copolymers

Following the classic study carried out by Spontak et al.\(^{1,2}\), a couple of morphological studies were carried out in the 1990s (ref.\(^{3,4,6,11}\)). The numbers of studies using TEMT on block copolymers are increasing rapidly, especially in the past couple of years. This technique has been mainly used for structural investigations due to its 3D visualization capability\(^{6,7}\).

An interesting example of visualizing complex 3D morphology by TEMT is the double-helical structure of poly(ethylene-co-butylene-b-styrene)-block-polybutadiene-block-poly(methyl methacrylate) triblock terpolymer (SBM)\(^{5}\). Since the discovery of the double-helical structure of DNA, the helix has been an attractive subject for investigations of molecular structure\(^{18,19}\). In materials science, numerous studies have investigated the artificial creation and control of helical structures. Because of their sophisticated self-assembling capabilities, block copolymers have been used to mimic the well-known biological architecture, the helix\(^ {8,10}\).

Fig. 1 shows TEM micrographs of the SBM triblock terpolymer, in which the dark gray regions correspond to the OsO\(_4\)-stained PB micro domains. The white and light gray regions are the poly(methyl methacrylate) (PMMA) and PS micro domains, respectively. The TEM images reveal that the PS cylinders along with the PB helical micro domains are hexagonally packed in the PMMA matrix. The PS cylindrical micro domains are not completely covered by the PB micro domains, as shown in Fig. 1a. Although the nanostructure of the SBM triblock terpolymer is quite interesting, the 2D projection of the 3D structure did not provide adequate structural information.

Both left- and right-handed double-helical structures could be clearly visualized by TEMT (Fig. 1a). Contrary to the previous report on the same triblock copolymer by Krappe et al.\(^{18}\), it was found that the SBM triblock terpolymer has a simple “double”-helical structure and not a four-stranded (i.e., “double double”) helical structure. Interestingly, the number of left- and right-handed helical structures was the same. Although the structural order in terms of the helical sense appears to be random, at least at first glance, it is likely that an adjacent pair takes opposing helical configurations (see Fig. 1a). Such detailed but important features of the helical structures can be obtained only by TEMT. It appears that with helical “mesoscale” structures are becoming popular, TEMT will be one of the essential tools for studying the helical morphology as well as complex microphase-separated structures in general.

The TEM and TEMT 3D observations were carried out using a JEM-2200FS (JEOL Co., Ltd., Japan) operated at 200 kV. A series of TEM images were acquired at tilt angles ranging from ±75 at an angular interval of 1°. The experimental details can be found elsewhere\(^1\).

3. Nanomechanical mapping on block copolymers

Block copolymers have attracted increased interest in recent years. The highly ordered nanostructures formed by self-assembly can be found in a wide range of promising applications\(^{20-23}\). To date, most of the studies on their nanostructures have been done using small angle X-ray scattering (SAXS) and electron microscopy with proper staining techniques\(^{24}\). However, each of these techniques has limitations. The radiation and staining of electron microscopy may damage and change the delicate structure of these Block copolymers, while neither SAXS nor electron microscopy techniques can be used to determine mechanical information on such materials. In order to understand and develop advanced block copolymer-related materials, there is great importance to investigate these samples for identifying phase separated topography, composition, and mechanical properties of individual blocks.

In this work, we report a quantitative method to obtain nanomechanical mapping data of poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) triblock copolymers. Our method emphasizes the AFM force volume imaging technique together with Johnson-Kendall-Robert (JKR)\(^{25}\) analysis. With our technique, high-resolution maps of Young’s modulus, adhesive energy, and topography can be obtained simultaneously in a single scan. In addition, we introduce a procedure to rebuild a true height image by which the real surface topography of samples can be determined.

A SEBS sample was supplied by Asahi KASEI Corp. without further treatment. The number average molecular weight, Mn, and the weight fraction of polystyrene (PS) are 50 000 and 0.30, respectively. The film samples with thickness about 10 \(\mu\)m were prepared by solvent-casting a 0.04 g mL\(^{-1}\) SEBS toluene solution onto cleaned glass slides. The as-prepared films were first dried in a fume hood for 1 day and then in vacuum at room temperature for another 3 days to remove residual solvent.
Nanomechanical measurements were operated in force volume (FV) mode on a commercial AFM system (Multi-Mode with a NanoScope V controller) under ambient conditions. The samples were scanned at constant force using an E scanner and triangular Si$_3$N$_4$ cantilevers with nominal spring constant of 0.32 N m$^{-1}$ (SNL-10, Veecoprobes). An actual spring constant of 0.397 ± 0.005 N m$^{-1}$ was measured by the thermal tune method. Force curves were collected over selected surface areas of 1 μm × 1 μm at a resolution of 128 × 128 pixels. In order to eliminate the effect of substrate stiffness, the value of the trigger set point (3.0 nm) was far less than the 1 % of the film thickness. The obtained force curves were analyzed using JKR contact mechanics to obtain mappings of Young’s modulus $E$ and adhesive energy $\omega$ (ref.11,12).

Fig. 2 shows the generated original height, sample deformation, and true height images. Shown in Fig. 2a is the original height image directly obtained from the FV mode. It contains artifacts due to the low elastic modulus of rubbery poly (ethylene-co-butylene) (PEB) component. The sample contains artifacts due to the low elastic modulus of rubbery PEB component. The sample height image and the sample deformation image. The weak contrast of the true height image is due to large compensation of the deformation at soft PEB regions. Even though, it reveals the real surface topography of the SEBS films prepared by solvent casting technique. By comparing the section analysis of the original height and true height images, it is found that the topography is totally reversed. The higher and lower regions in the original height image become lower and higher regions in the true height image. The height contrast reverses is due to the large deformation caused by the force between the probe tip and the sample.

Fig. 3 shows simultaneously generated maps of the Young’s modulus and adhesive energy. Both the Young’s modulus and adhesive energy distribution images show phase-separated lamellar morphology. The corresponding modulus and adhesive energy profile across a section reveals the two chemical blocks have a large difference in modulus and adhesive energy values. In the Young’s modulus image, the light green areas with higher Young’s modulus are considered to be the hard PS blocks, while the red areas with lower Young’s modulus are considered to be the soft PEB blocks. The Young’s modulus is calculated as 53.3 ± 5.4 MPa for white circle and 10.6 ± 3.2 MPa for dark circle. We thus further demonstrate that the light green areas correspond to PS blocks and the red areas to PEB blocks. Using the same evaluation method, we also investigate the Young’s modulus of bulk PS and PEB films. The measured modulus value of glassy PS and rubbery PEB is 2.23 ± 0.51 GPa and 13.64 ± 0.68 MPa, respectively. Therefore, the observed modulus on PEB block agrees with bulk value, while PS block’s demonstrates a dramatic decrease in stiffness. This decrease may be due to the microstructure effect that the soft PEB blocks surround and support the PS blocks underneath. Other possibilities are that there are some uncertain factors such as the contact area, tip geometry, and the local value of Poisson’s ratio.

The adhesive energy image also differentiates the two chemical blocks of the copolymer. However, the adhesive energy contrast between the hard PS and soft PEB blocks is inverted in comparison to the Young’s modulus map. The stiffer PS blocks provide lower adhesive energy than the soft PEB blocks. The calculated adhesive energy of PS and PEB components corresponding to the two areas indicated in the Young’s modulus image is 0.210 ± 0.004 and 0.243 ± 0.006 J m$^{-2}$, and for PEB (1.942 ± 0.094 J m$^{-2}$), the big discrepancy may relate to the interaction between tip and sample surface. The determined adhesive energy in this work includes all interactions between the tip and sample surface, such as capillary force, which makes the measured adhesive energy very high.

4. Conclusion

We showed several example studies of polymer nanotechnology for TPEs. We will show more examples at the site including TEMT observation of interfacial structure during the well-known order-order phase transitions. Nanomechanical mapping of SEBS with the different composition, with the different process condition as shown in Fig. 4.
Fig. 4. Nanomechanical mapping results: (a) Young’s modulus distribution image of spin-cast thin film specimen and (b) that of high-shear treated specimen with twin-screw extruder

The authors thank Dr. Kazuya Nagata of the Asahi Kasei Chemicals Corp. for technical assistance.

REFERENCES


ML-04

OVERVIEW OF BIOFOAMS FOR LIGHTWEIGHT AUTO PARTS

MOHINI SAIN*

Centre for Biocomposites and Biomaterials Processing, Faculty of Forestry, University of Toronto, 33 Willcocks Street, Toronto, Canada M5S 3B3
m.sain@utoronto.ca

More lightweight auto parts help save fossil fuels. Biofoams are moving into the mainstream for the auto industry recently because renewable biomasses replace for petrochemicals to make vehicles more environmentally friendly. Biofoams are entirely new sustainable and biologically degradable polymer made from renewable bio-sources. In addition, biomass consumes less energy associated with the energy required for the fabrication process and reduces CO₂ emissions by absorbing greenhouse gas during the plant lifecycle. In the auto parts market, biofoams are mostly biopolyurethane foam with increased content of biomass due to its good quality. The foamed PLA only gains a small proportion.

Bio-polyl is pursued to fabricate polyurethane foam by a foaming process. Most bio-polyl is derived from the production of plant seeds, which is refined to oil. The large output of soybean oil is motivating the use of soy-based polyol, typically in polyurethane foam. Soy-based polyol is made from soybean oil by adding hydroxyl groups at the unsaturated sites. Thus, it has very similar structures to petroleum-based polyol and could react with isocyanates to produce foam (Fig. 1).
High performance polyurethane biofoam could be used to replace traditional petroleum-based polyurethane foams in automotive parts (over 20 kg each car), including seat system, panel, under the hood parts, bumper fascia, and other interior parts etc.

In Canada, the Woodbridge Group has developed soy-based polyurethane foam used in automotive seat cushions, head restraints and arm rests of several popular vehicles, such as 2009 Ford Escape. Biofoam developed by Woodbridge offers up to 25% bio-based content. We have achieved 100% bio-polyol substitution with acceptable tensile strength in laboratory trials. Ford is weeding out petroleum-based foams in favor of bio-based alternative helping reduce the environmental impacts of its vehicles.

The Ontario BioAuto Council is committing a 4-year, $18 million program to support the research and commercialization of bio-based auto parts, including $1 million in polyurethane automotive seats and interior pieces. There are also more efforts to get bio-based isocyanates to produce absolutely bio-based polyurethane foam. The ongoing project of soy-based isocyanates is funded by Michigan Soybean Promotion Committee to substitute for traditional isocyanates. All the efforts lead to green vehicles in the future with a great win-win situation both for agriculture and the auto industry.

Still, natural fiber containing hydroxyl groups can also be introduced in foaming reaction mixtures for reinforcement and gains better biodegradation.

The authors would thank the NSERC and BioCar for their financial support. Air Products and Chemical Inc. and Urethane Soy Systems are also acknowledged for their cooperation.