# Design and Development of Poly (acrylonitrile-co-methyl methacrylate) Copolymer to Improve Viscoelastic and Surface Properties Critical to Scratch Resistance

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ARTICLE

# Design and Development of Poly (acrylonitrile-co-methyl methacrylate) Copolymer to Improve Viscoelastic and Surface Properties Critical to Scratch Resistance

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Scratch resistance has become one of the coveted properties for exterior applications as scratches not only reduce the life cycle and durability of a product but also affect its aesthetics. Poly(methyl methacrylate) [PMMA] based materials are often used for exterior applications despite their limited scratch resistance. This work focuses on the design, development and evaluation of methyl methacrylate (MMA) and acrylonitrile (AN) copolymers to improve viscoelastic and surface properties critical to scratch resistance. In this work, molecular modelling approach based on quantitative structure-property relationship (QSPR) was employed to predict the desired properties such as elastic (E)-modulus and shear yield stress at different copolymer composition. Thus, a series of poly (acrylonitrile-co-methyl methacrylate) [p(AN-co-MMA)] with increasing AN content (~35, 75 and 82% in copolymer) were prepared by solution polymerization and evaluated using a nano-indentation test to investigate surface hardness and E-modulus on compression moulded films. Tests revealed a significant increase in modulus and surface hardness for the copolymers compared with the homopolymer (E-modulus: 5.8 GPa and 4.5 GPa; surface hardness 0.32 GPa and 0.22 GPa respectively). The values increased with increasing AN content of the copolymers. Stress relaxation studies were also performed to validate the predictions of improved shear yield stress obtained from molecular modelling approach. It is suggested that the incorporation of AN imparts structural rigidity to the copolymers and thereby improving the scratch resistance of the p(AN-co-MMA) copolymers. Thus, p(AN-co-MMA) are good candidates for applications requiring improved scratch resistance.

## 1. Introduction

Poly methyl methacrylate (PMMA) exhibits excellent optical transmission, weather resistance, hardness, and an ability to be processed into various shapes and colours giving it attractive design flexibility.[1] Due to these favourable attributes, PMMA finds extensive use

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in exterior applications for electronic displays, over-the-hood automobile components - windshield and lighting components, medical as well as in architectural and construction applications.[2] However, scratching and abrasion of surfaces causes a drastic loss of optical and tribological performance. Moreover, scratches in plastic surfaces diminish the aesthetics of the product and may cause stress concentration, making them susceptible to premature failure. This results in a reduction in the durability of products,[3-10] which in turn limits the more widespread use of plastics. Thus, the scratch resistance of plastic surfaces is limiting the use of these materials, especially PMMA.

Extensive research has been carried out to understand the correlation between scratch resistance and the bulk material properties such as tensile modulus, yield stress, and elastic recovery as well as the coefficient of friction.[4,5] This work has resulted in varied approaches to improve the scratch resistance of PMMA by targeting improvements to the bulk and surface properties. Recent strategies for improving the scratch resistance of PMMA have largely involved blending with organo-modified layered aluminophosphates,[11] organoclays,[12] zirconia,[13] as well as their blends[14], to form nano-composites. Little focus has been given to the intrinsic scratch resistant behaviour of PMMA.[15]

Combining AN with MMA should increase the hardness[16] and thus the scratch resistance of PMMA but the melt blending of Polyacrylonitrile (PAN) and PMMA is not possible as PAN degrades before melting.[17] This paper concerns the improvement of the scratch resistance of PMMA by statistically copolymerizing MMA with AN. The p(AN-co-MMA) copolymers were synthesized as described elsewhere.[18] Copolymers of AN and MMA have been reported for various applications but mainly as PAN precursors for carbon fibre production.[19] As far as it is known, these polymers have not been explored for their scratch resistance.

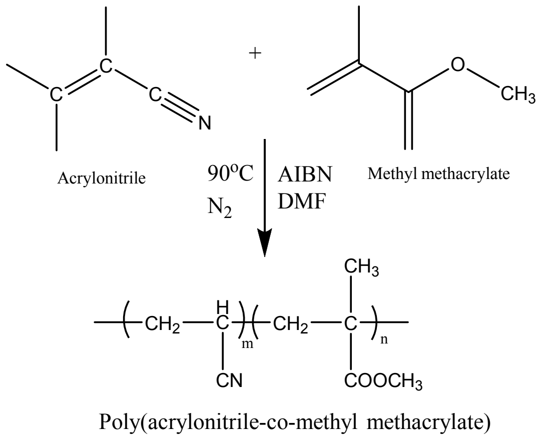
Nano-indentation tests were performed on compression-moulded films of the prepared copolymers and the results were correlated with the E-moduli obtained from predictive study. Since the introduction of stiffer segments into the polymer can also be expected to affect the viscoelastic behaviour of the copolymer,[20] the scratch resistance was also correlated with stress relaxation behaviour of copolymers.

## 2. Experimental

**(i) Materials:** All solvents and reagents were purchased from Sigma-Aldrich unless stated otherwise. Acrylonitrile (≥99%, contains 35-45 ppm monomethyl ether hydroquinone as inhibitor) was purified immediately prior to polymerization by passing over a column of basic activated alumina (Activated Basic Brockmann) to remove the inhibitor. Methyl methacrylate (MMA ≥98.5%) was also purified in the same way. 2,2′-Azobis(2-methyl propionitrile) (AIBN, Spectrochem (98%)) was used as the initiator. Dimethyl formamide (DMF, anhydrous, 99.8%) was used as the solvent for the polymerizations.

**(ii) Molecular Modelling Study**: The elastic modulus and shear yield stress were calculated at 298K using the Synthia module in Accelrys Materials Studio 6.1.[21] Synthia employs quantitative structure-property relationships (QSPR) using information about the topology for the calculation of polymer properties. The properties are expressed in terms of connectivity indices (derived from graph theory) combined with geometrical variables and other structural descriptors. This enables polymer property predictions, without being limited by an unavailability of group contributions for structural fragments.[21] The method performs very well for the prediction of the properties of isotropic amorphous linear polymers.[22] The method is also applicable to the amorphous phase of semi crystalline polymers and to properties not sensitive to percent crystallinity for highly crystalline polymers. In semi crystalline polymers, the crystalline phase is stiffer than the amorphous phase but the moduli of these phases differ only slightly when the temperature (T) is below the glass transition temperature ($T_g$).[21]

**(iii) Synthesis and Characterization of Copolymers:** The copolymers of MMA and AN were synthesized as described[18] and this synthesis is represented in scheme 1. The prepared copolymers were characterized using NMR, FTIR, DSC and TGA. The detailed procedures are given in the supplementary information. Table 1 shows the final compositions of homo- and co-polymers synthesized, as calculated from the $^1$H NMR spectra.



Scheme 1 Reaction Scheme for the Synthesis of p(AN-co-MMA) Copolymer

| Sample Code | Composition AN/MMA (wt.%) |
|---|---|
| A | 82/18 |
| B | 75/25 |
| C | 35/65 |
| D | 100 MMA |
| E | 100 AN |

Table 1 Composition analysis results of synthesized co-polymers by $^1$H NMR

**(iv) Preparation of Copolymer Films by Compression Moulding:** The p(AN-co-MMA) copolymers synthesized by solution polymerization techniques were isolated as powders. The polymer powders were compression moulded into films according to the processing curve given in Figure 1 (a). For PAN and PMMA homopolymers and the copolymers the temperature was 220°C to obtain clear films. Figure 1 (b) is a sketch of the moulding set-up.

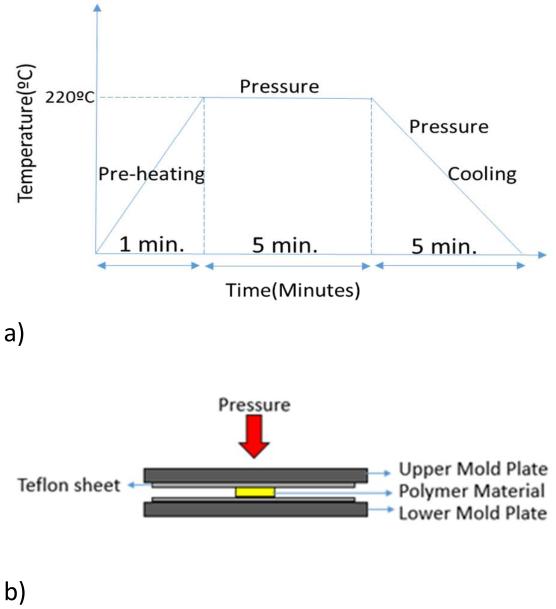


Figure 1(a) Processing Curve for film preparation. (b) Sketch of the Moulding Set-up

**(v) Nano-Indentation:** Nano-indentation experiments were conducted using the Nano-Indenter® XP (Keysight Technologies, Inc., Santa Rosa, CA) with depth control method at fixed depth of 1000 nm. In this nano-indenter, the maximum distance allowed for the tip to travel, normal to the sample surface, is about 1.5 mm. Over the entire range, displacement resolution is better than 0.1 nm. The maximum load capacity for this system is 500 mN with a precision of better than 1μN. The load and displacement data obtained in the nano-indentation tests were analysed according to the model developed by Oliver and Pharr.[23] Indentations were made with a constant strain rate of 0.05 $s^{-1}$. The properties of the film alone were calculated by averaging over an appropriate displacement range and the range depended on the thickness of the film. On each sample 5 indents were made and average values were calculated. Figure 2 illustrates the Nano-indentation process.

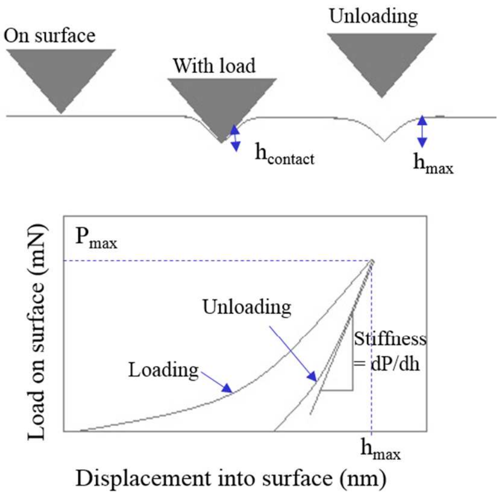


Figure 2: Nano-Indentation Process. $P_{max}$ is the maximum indentation load and $h_{max}$ is the depth at maximum load.

The tangent to the unloading curve at maximum load is a measure of stiffness of the material. The nano-indentation test was not performed for sample B.

**(vi) Stress Relaxation:** Stress relaxation experiments with all polymer samples were done in ARES instrument using the cone and plate attachment (25 mm dia. plate and 0.1 radian cone angle) in the transient mode. PMMA homopolymer and all p(AN-co-MMA) copolymers were tested at 240$^{o}$C whereas the PAN homopolymer was tested at 300$^{o}$C as measurements were not possible at lower temperatures and due to the short duration of the experiment, it can be assumed that no decomposition of the PAN occurred. A constant shear rate lasting only for a brief time interval is imposed to the sample and the decay of the stress that was generated by this sudden small displacement was monitored. The stress typically decreased monotonically as the polymer continued relaxation with time.

## 3. Results and Discussion

**(i) Molecular modelling:** It is generally accepted that bulk material properties such as tensile modulus, shear yield stress, elastic recovery as well as surface hardness and the coefficient of friction affect the scratch behaviour of polymers. In polymers, which show shear dominated deformation, an approximate linear correlation between hardness and yield stress is observed.[24] Shear yield stress is also roughly proportional to elastic modulus.[21] Therefore, as an initial approach, some of these properties were predicted using the Synthia software as mentioned above for various compositions of copolymers of AN and MMA. The AN moiety is expected to introduce hardness in the copolymers[15]. Figure 3 shows the calculated E-moduli and shear yield stresses of p(AN-co-MMA) copolymers . Both the modulus and the shear yield stress increase as AN content in the copolymer system increases. This suggests that the hardness of PMMA can be improved by incorporation of AN into the MMA backbone. This study is in agreement with the hypothesis by Xiang et al[25] that shear yielding is the main cause of the plastic flow scratch pattern, based on a scratch model proposed by Hamilton & Goodman. [25]

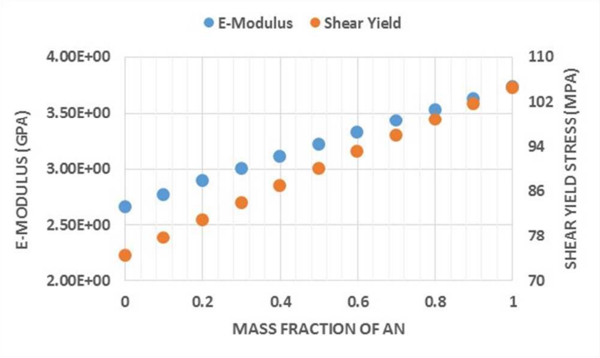


Figure 3: Calculated E-Modulus and Shear Yield Stress *vs* the AN Mass Fraction in the Copolymer (From Molecular Modelling Study.)

(i) **Nano-Indentation:** Nano-indentation is a commonly used technique to evaluate the surface-mechanical properties of polymer systems.[26] The test yields load-displacement curves, surface hardness and E-modulus data for the samples tested. Representative load-displacement curves obtained during nano-indentation tests of copolymers with different AN contents are shown in Figure 4. It can be seen from the figure that for the same penetration depth, maximum load increased with increasing AN content. As higher load indicates higher stiffness and resistance to plastic deformation, it is evident that copolymers with higher AN content have greater surface hardness.

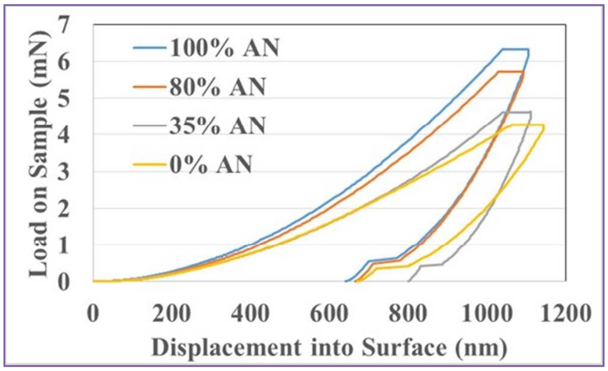


Figure 4: Load-displacement curves of samples with different AN content.

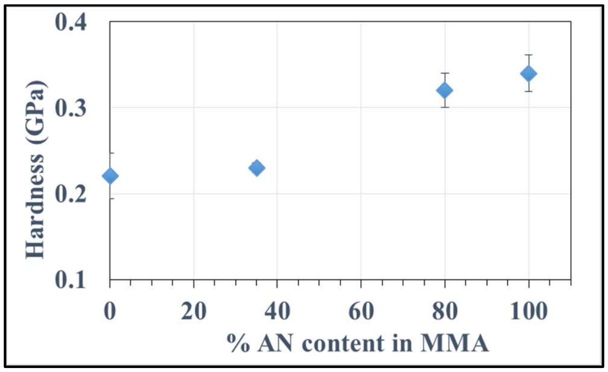


Figure 5: Surface hardness as a function of Acrylonitrile (Wt-%) in Copolymer

Figure 5 shows the surface hardness values for both the samples with different %AN content in the copolymer.

Surface hardness gives a good indication of the rigidity of materials and hence has been widely adopted to predict relative scratch resistance of the materials[27]. Therefore, an increasing hardness with increased AN content indicates that the copolymers may have better scratch resistance than neat PMMA. The trend was also expected from load-displacement curves as discussed earlier (cf. Figure 4).

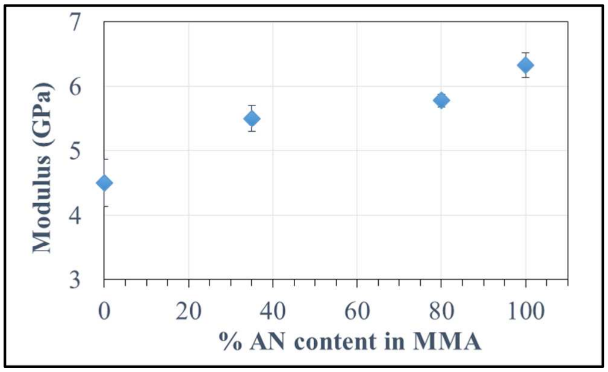


Figure 6: E-Modulus Vs the Acrylonitrile (Wt-%) Content of the Copolymer

Figure 6 shows the trend of the E-moduli as a function of AN content obtained from nano-indentation tests. The E-modulus also plays an important role in the scratch process, especially during the indentation stage. An increase in the modulus decreases the radius of the contact zone of the indenter tip on the testing surface and hence reduces the scratch depth.[4,5] It can be seen that as the amount of AN in the copolymer is increased, the E-modulus also increases from 4.5 GPa (neat PMMA) to 5.8 GPa (with ~82 wt% AN content). This is in agreement with the predictive molecular modelling study as discussed earlier (cf. Figure 3). Scratch tests performed with these copolymers showed that scratch resistance improves with increasing AN content in the copolymers and these results will be published elsewhere.

### (ii) Stress-Relaxation

The stress relaxation modulus, G(t) is a measure of the stress generated in the material in response to strain. Thus, a polymer with stiffer moieties is expected, generally to exhibit a higher G(t) and lower drop in relaxation modulus (ΔG(t)) than a polymer with no or a smaller amount of stiff moieties. Thus, a polymer with larger terminal G(t) (stress relaxation modulus at the beginning of the experiment) is expected to have better scratch resistance under normal scratching conditions due to its structural rigidity.

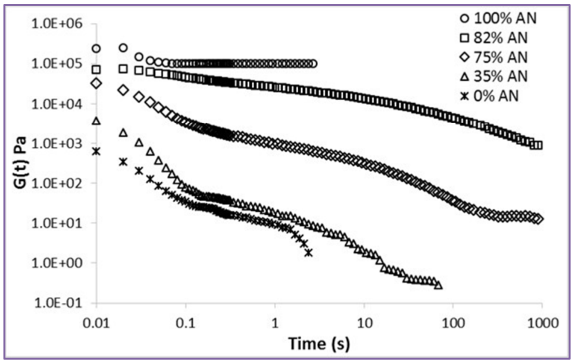


Figure 7: Stress Relaxation Modulus of PAN, PMMA and their Copolymers as a Function of Time

Figure 7 shows the terminal G(t) and the drop in G(t) for the homo- and co-polymers as a function of time. It can be seen that the PAN homopolymer has the largest terminal G(t) and also an insignificant drop in stress relaxation modulus with time due to its structural rigidity. On the other hand, neat PMMA has the smallest terminal G(t) and a significant drop in G(t) with time. This indicates it's primarily viscoplastic behaviour and hence it is expected to be the least scratch resistant of all the samples studied. The copolymers, on the other hand, have intermediate values for terminal G(t) which increased with increasing AN content in the copolymer. The ΔG(t) values follow the same trend.

Thus, rheological stress relaxation experiment correlated well with hardness and the E-moduli of the p(AN-co-MMA) copolymers as obtained from the nano-indentation test as well as with the predictions from molecular modelling studies.

## 4. Conclusion

The present study demonstrates that the Synthia molecular modelling (Bicerano model), can usefully predict the properties, such as E-modulus and shear yield stress, of p(AN-co-MMA) as a function of AN content. Furthermore, these predictions were validated experimentally for p(AN-co-MMA) copolymers using nano-indentation and rheological stress relaxation studies. Nano-indentation studies revealed >20% increase in E-modulus and >30% increase in surface hardness with high AN content in the copolymers with respect to neat PMMA. Rheological stress relaxation studies also indicated improved stress relaxation modulus at higher AN content, suggesting increased structural rigidity of copolymers as compared to neat PMMA. As E-modulus, surface hardness and shear yield stress can be considered as critical properties for predicting the scratch resistance of a polymer, the observed trends suggest that higher AN content should improve the scratch performance of p(AN-co-MMA) copolymers. Thus, this systematic study presents a useful approach to improve the scratch resistance of polymeric materials which are intended for use as coatings and/or molded articles on or in electronic displays, automotive, decorative home-appliances as well as building and construction.

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