Design and Development of Poly (acrylonitrile-co-methyl methacrylate) Copolymer to Improve Viscoelastic and Surface Properties Critical to Scratch Resistance (ID: RA-ART-10-2015-022264)

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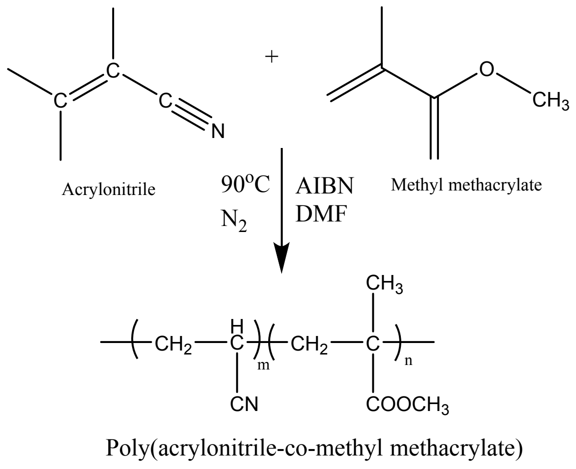
Supplementary information

Poly(acrylonitrile-co-methyl methacrylate), p(AN-co-MMA) copolymers were synthesized in DMF solution using AIBN as initiator and continuous nitrogen purging (Scheme-1). The reaction was carried out at 90ºC for 5 hours. Subsequently, the reaction was stopped and the reaction mixture was allowed to cool down to room temperature. A yellow polymer solution was obtained which was precipitated in a large excess of water-methanol, filtered, washed with excess of water to remove unreacted products and dried to a constant weight at 60ºC *in vacuo*.



Scheme 1: Reaction scheme for the synthesis of p(AN-co-MMA) copolymer

Characterization

The following analytical techniques were used to characterize the homopolymers and copolymers

Nuclear Magnetic Resonance (NMR) was used for composition analysis of the polymers. The ^{1}HNMR spectra were run in a 600 MHz Agilent instrument using a 5 mm OneNMR® probe in

DMSO media. The polymer samples were dissolved in deuterated DMSO with the help of a horizontal shaker. For acquiring the ^1H NMR spectra, 16 scans were averaged with 5s relaxation delay.

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the acrylonitrile and methyl methacrylate groups in the polymers. The spectra were recorded using FTIR system Spectrum GX, Perkin Elmer at 230°C in the range from 400 cm^{-1} to 4000 cm^{-1} with the resolution of 4 cm^{-1}.

Thermal Characterization: The Differential Scanning Calorimetry (DSC) analysis was carried with a Q1000 from TA Instrument in the temperature range 30 to 300^{o}C at a ramp of 7^{o}C/min under a nitrogen atmosphere. Thermo-Gravimetric analysis (TGA) was carried out on Q5000 from TA Instruments in the temperature range of RT – 800^{o}C at a ramp of 5^{o}C /min under air atmosphere.

Gel Permeation Chromatography (GPC) was used to investigate the molecular weight, molecular weight distribution and polydispersity index of the samples as well as to ensure that only a single peak was observed, indicating that the polymers are indeed copolymers.. The conditions were: Mobile Phase:- DMF + 10 mM Li Br; Diluent:- DMF + 10 mM Li Br; Concentration:- 1 mg/ mL; Flow rate:- 1 mL/min; Runtime:- 30 min; Injection Volume:- 100µL; Column used:- PLgel 5 µm MIXED-D, 300 x 7.5 mm; Detector:- RI; GPC Calibration standards**:-** Monodispersed PMMA standards.

Scanning electron microscopy (SEM): The surface morphology of the polymers was investigated by scanning electron microscopy (Zeiss, EVO18) at an accelerated voltage of 15 kV.

Additional results and discussion:

NMR: The weight ratio of AN to MMA in the copolymer was calculated from the ^1H NMR spectra of the copolymer samples A, B,C and composition of homopolymer was confirmed for samples D (PMMA) and E (PAN). Figure 1 shows the ^1H NMR spectra of all the samples. The peak assignments, associated with PMMA and PAN, indicated in Figure 7, are labelled in the ^1H NMR spectra of all samples. It can be observed that the signal intensity associated with $–CH_3$ group in ester linkage of PMMA labelled as (a) increases in the following order: Sample E< Sample A<

Sample B< Sample C< Sample D, where Sample E shows does not show a peak related to this group. Vice-Versa, the signal intensity of –CH in PAN, labelled as (d), decreases in the following order: Sample E> Sample A> Sample B> Sample C> Sample D. These results are summarized in Table 2 which shows the final composition as calculated from the ^{1}H NMR spectra of all 5 samples.

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 co-polymers by ^{1}H NMR

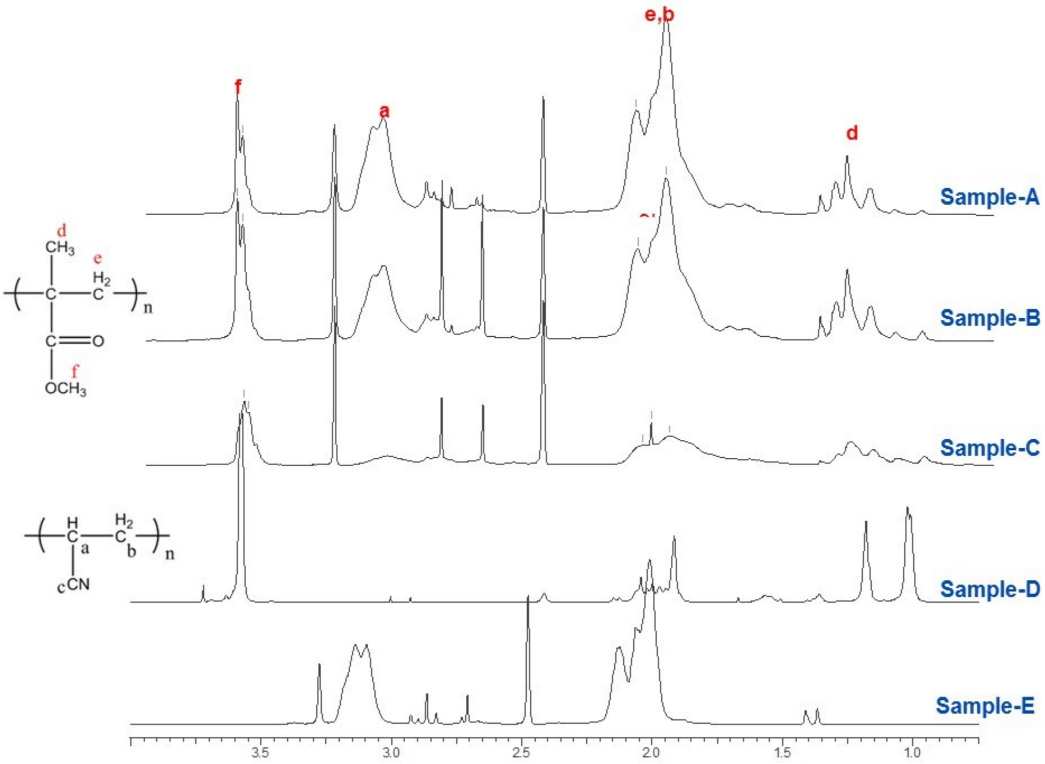
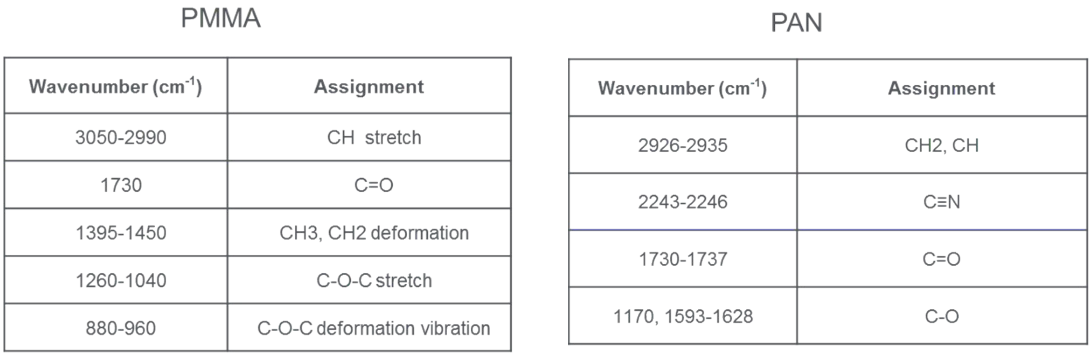


Figure 1: ^{1}H NMR characterization of polymers of varying composition

FTIR: FTIR data was used to confirm the compositions given in Table 1. Figure 2 contains the FTIR spectra of samples: A to E. The FTIR peak assignments have been tabulated in Table 2(a) and Table 2(b) for PMMA and PAN respectively. Figure 5 shows IR peaks at ~2243-2246 cm^{-1} and 1730 cm^{-1} corresponding to -C≡N(nitrile stretching) and -C=O(carbonyl peak) respectively. Other peaks at various wavenumbers (cm^{-1}), mentioned in Table 2(a) and 2(b), are marked in Figure 2. Qualitatively, the decreasing acrylonitrile content in the samples was in the following order: Sample E > Sample A > Sample B > Sample C > Sample D. Sample E was a PAN homopolymer; Samples A, Sample B, and Sample C were p(AN-co-MMA) copolymers; and Sample D was a PMMA homopolymer.



PMMA

Wavenumber (cm^{-1})	Assignment
3050-2990	CH stretch
1730	C=O
1395-1450	CH3, CH2 deformation
1260-1040	C-O-C stretch
880-960	C-O-C deformation vibration

PAN

Wavenumber (cm^{-1})	Assignment
2926-2935	CH2, CH
2243-2246	C≡N
1730-1737	C=O
1170, 1593-1628	C-O

(a) (b)

Table 2: FTIR wavenumber assignments for (a) PMMA (b) PAN

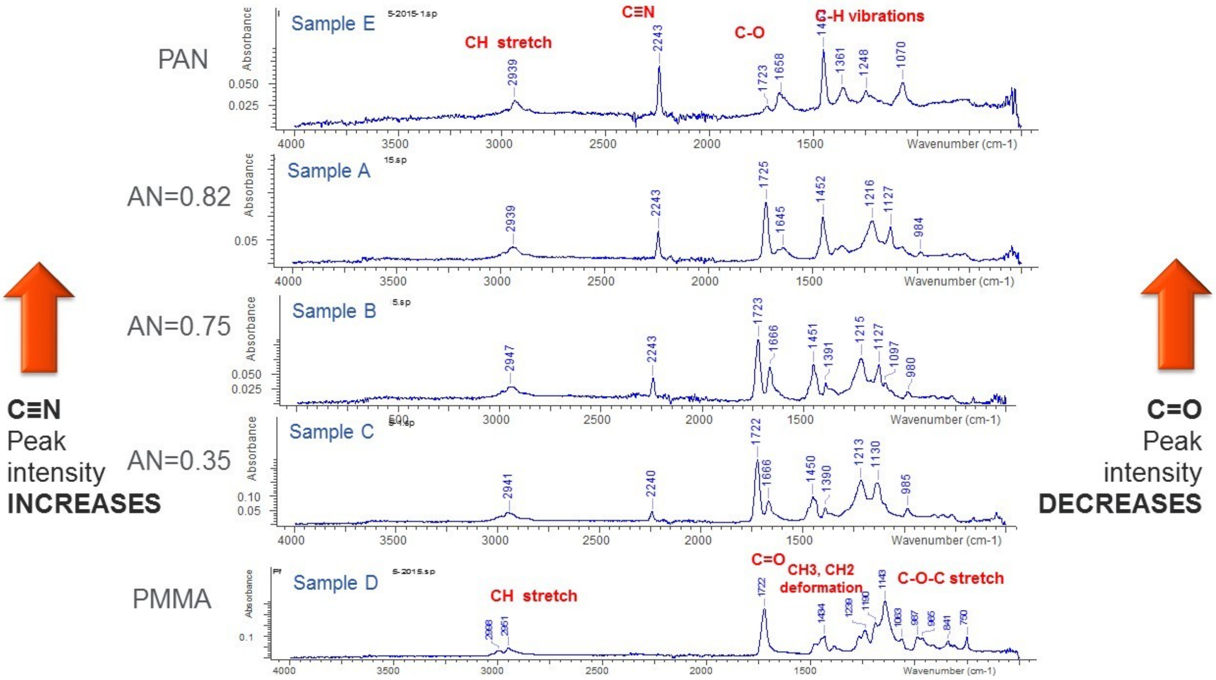


Figure 2: FTIR Spectra of synthesized copolymers and homopolymers

Thermal Characterization

DSC study: The overlaid DSC exotherms of the p(AN-co-MMA) copolymers and hompolymers-PAN and PMMA, are shown in Figure 3. It can be observed that the DSC profiles of PAN and p(AN-co-MMA) possess an exothermal character due to structural changes mainly cyclization through nitrile groups, whereas PMMA exhibits endothermal behavior. PAN (Sample E) shows a narrow thermal transition peak at ~278 ºC. PMMA (Sample D) does not show any exothermal character due to its amorphous nature. Figure 3 indicates a gradual shift of the thermal transition peak to a higher temperature as the MMA content increases in the copolymer in the following order: T(Sample A) < T(Sample B) < T(Sample C) where T represents the peak of the thermal transition. This can be attributed to influence of MMA content on the cyclization phenomenon associated with PAN. The gradual change of the temperature of the exotherm with composition is a corroboration that the materials (Samples A, B and C) are indeed copolymers. The T_g's for PMMA and PAN could not be clearly identified from the DSC.

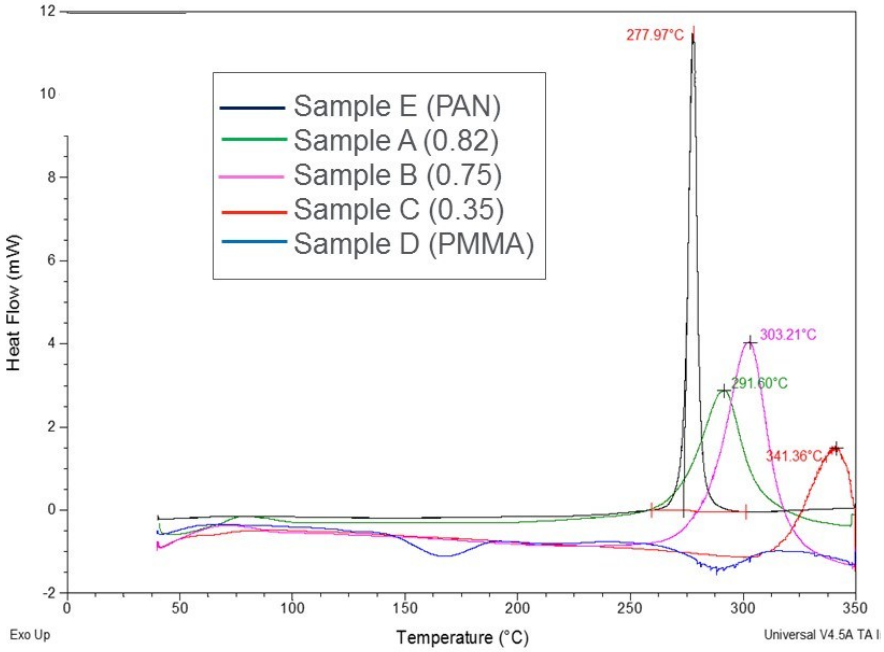


Figure 3: Overlaid DSC traces of the co- and homopolymers

TGA Study: Figure 4 shows the overlaid TG thermograms of the different co- and homopolymers. The TG curve of PMMA, recorded in air, shows a three stage degradation profile. Sample A(AN-0.82) shows improved thermal stability than PAN; this may be because the incorporation of MMA in PAN structure during copolymerization possibly alters the stabilization mechanism during cyclization of copolymer giving a better thermal stability. Sample B(AN-0.75) shows similar thermal stability as of PAN. Sample C(AN-0.35) shows lower thermal stability than PAN because of presence of lesser AN content as compared to Samples A & B.

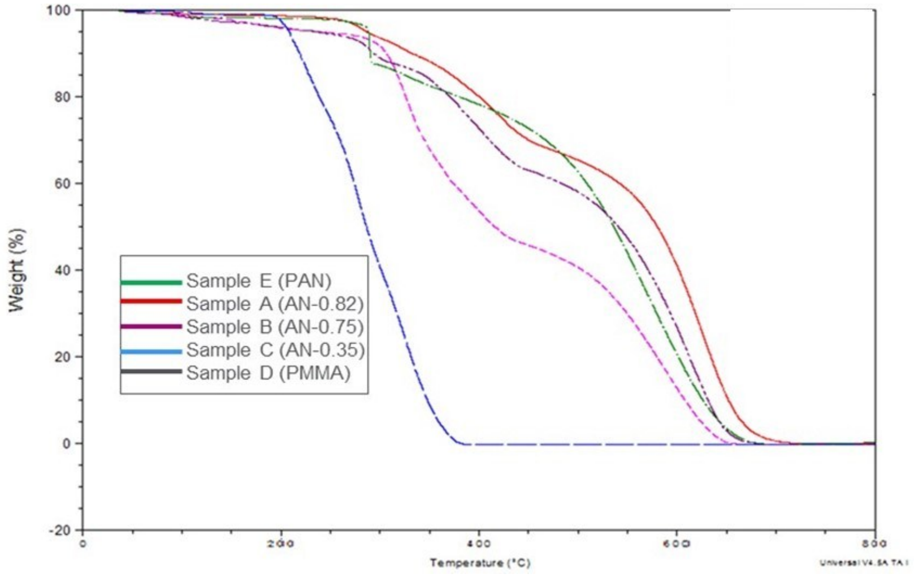


Figure 4: Overlaid TG thermograms of co-and homopolymers

GPC: GPC technique was used to investigate the molecular weight, molecular weight distribution and polydispersity index of the samples. Figure 5 shows the overlaid chromatograms of the copolymers and homopolymers. Table 3 shows the number-averaged molecular weight, weight-averaged molecular weight and polydispersity index for all compositions.

The GPC chromatogram shows a narrow distribution curve. The polydispersity index range was between 1.8-2.5 and weight-average molecular weight in the range of 35,000-40,000, as reported in Table 3. The lower molecular weights of copolymers and homopolymers under study are targeted for coating applications with these copolymers,

Table 3 GPC Molecular weights of homopolymers and co-polymers

Sample Code	**M_n**	**M_w**	**PDI**
A	19508	35176	1.8
B	18233	34277	1.9
C	20500	36975	1.8
D	18513	38767	2.1
E	20919	51878	2.5

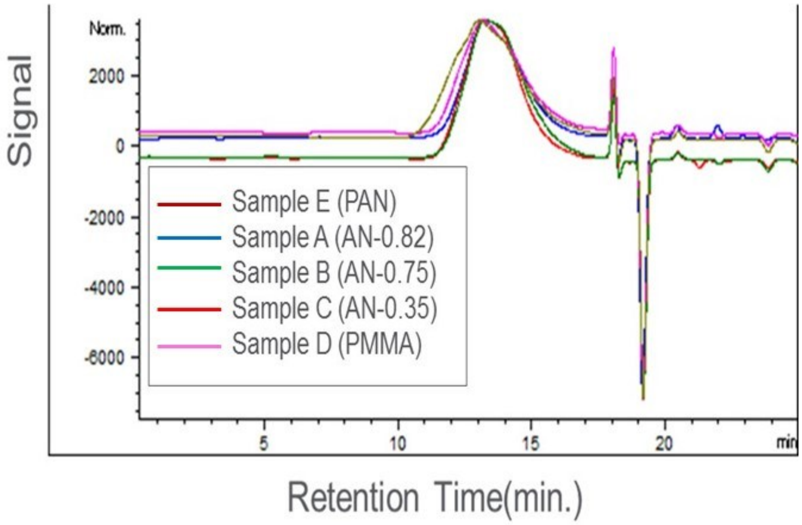
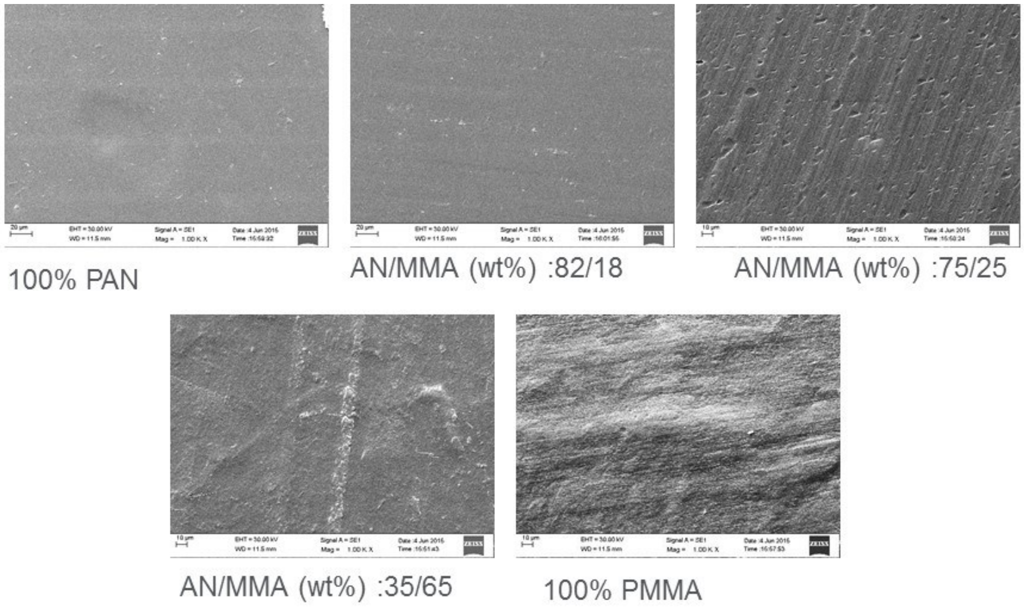


Figure 5: Overlaid GPC chromatograms of homo- and co-polymers

To ensure that we have made co-polymers, an extraction study was done. Accurately weighed co-polymer was extracted under vacuum with tetrahydrofuran (THF), which is a good solvent for PMMA and not for PAN. Extraction was repeated 3-4 times and final co-polymer material is dried and weighed with negligible loss of material, confirming the formation of co-polymer.

SEM Analysis:


100% PAN

AN/MMA (wt%) :82/18

AN/MMA (wt%) :75/25

AN/MMA (wt%) :35/65

100% PMMA

Figure 6: SEM micrographs of PAN, PMMA and p(AN-co-MMA) copolymers

SEM images in figure 6 shows no phase separation in any of copolymers and surface of pure PAN appeared to be smoother as compared to PMMA surface.