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Research Article

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Mechanical Properties of Styrene Acrylonitrile and Chlorinated Polyethylene Blends: Effect of Chlorine Content

Al Mamun[1*] and Mohammad A K Khan[2]

[1]*Department of Chemistry, University of Montreal, Montreal, Quebec, Canada H3C3J7*

[2]*Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada L8S 4M1*

[*]*Corresponding Author, E-mail: amamun@fsu.edu, Phone: +18504106526, Fax:+18504106526*

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Abstract: The mechanical properties of binary blends of styrene acrylonitrile (SAN) and chlorinated polyethylene (CPE) were investigated. Blend compositions ranging from pure SAN to CPE, in 10% increments, in solution, and used to investigate mechanical properties as a function of compositions, chlorine (Cl) content in CPE and temperatures. In general, the mechanical properties of the SAN/CPE blends were found to be between the values of the corresponding pure components. Comparison of the yield stress and modulus of the blends with Cl content in CPE showed that these properties are in decreasing order: SAN/CPE(25%), SAN/CPE(36%), SAN/CPE(42%) and SAN/CPE(48%). For any blend composition, Young's modulus decreases with temperature and levels off at and above ~100^{o}C.

Keywords: Mechanical Properties; SAN/CPE Blend; CopPolymer; Chlorine Effect; Temperature Effect

1. INTRODUCTION

Polymer blends are increasingly employed in the design of novel polymeric materials to improve mechanical properties, such as high modulus with toughness, effective diffusion barriers with good mechanical properties, improved biodegradability and recycling characteristics, low investment costs in new materials design [1]. Some polymers are brittle, while others are very strong, and one can design new materials by combining them both using either copolymerization, or blending, or making composite materials. Among them blending of the two polymers with different properties is sometime much easier to get a new material having the desired properties of both.

Poly (styrene-acrylonitrile) (SAN) is a copolymer consists of styrene and acrylonitrile (AN), a widely used engineering thermoplastic owing to its desirable properties like chemical resistance and easy processing characteristics. It is used in place of polystyrene due to its greater thermal resistance, optical transparence, and brittleness [2,3]. Larger acrylonitrile content improves mechanical properties and chemical resistance, also adds a yellow tint to the normally transparent plastic[4]. By blending a rubber component like chlorinated polyethylene (CPE) with the rigid SAN, the impact strength of the brittle

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SAN can be improved. CPE is a thermoplastic polymer, composed of high molecular weight polyethylene which has been chlorinated – a process that yields a flexible rubber-like material. It has good chemical and UV resistance, flexibility and high tear strength. CPE can be blended as impact modifier for brittle SAN to improve mechanical properties. Many studies have been reported to improve the compatibility that results the final mechanical properties of SAN by blending with other polymers including nylon [5], poly(phenylacrylate) [6], polyvinyl chloride (PVC) [7,8], poly carbonate [3,9], poly(caprolactone) [10-12], polypropylene [13]. Compatibility is a technical term defining the property profile of the blend in view of a certain application and, it is a function of the interaction of polymer molecules in the blend and can be detected using various methods including mechanical and interfacial measurements. If the combination of properties is advantageous and corresponds to the expectation, the compatibility of the polymers in question is good, and they are incompatible when properties are not acceptable. The compatibility of polymer pairs is often modified by physical (compatibilizers, block copolymers) or chemical (e.g. reactive processing) means. In compatible blends, the mechanical properties show a linear relationship between blend compositions. In general, a negative deviation from the linear relationship is considered an indication of poor compatibility between blend components, whereas a positive deviation is considered an indication of improved compatibility[14]. The phase morphology and rheology in blends of polycarbonate/styrene-acrylonitrile copolymer (SAN) was studied by Jung *et al.*[3]. They confirmed the acrylonitrile (AN) content of the SAN polymer influences the phase morphology and rheology, with varying AN content due to the variation of viscosity of SAN. Ultrafine fibers of styrene–acrylonitrile copolymer/isotactic polypropylene (iPP) blends were studied, where SAN acted as a polymeric nucleating agent in iPP fibers. The morphological distribution of SAN in iPP fibers depend on the SAN content [15]. Poly (vinyl chloride) (PVC)/α-methylstyrene-acrylonitrile-butadiene-styrene copolymer/chlorinated polyethylene (CPE) ternary blends were studied by Zhang *et al.* [16]. With the addition of CPE, no significant influence in both the glass transition temperature and heat distortion temperature was found. Thermogravimetric analysis also do not showed negative role in the thermal stability. With regard to mechanical properties, high toughness was observed combined with the decrease in tensile strength. The combination of acrylonitrile butadiene styrene and CPE improves the toughness, and the value of notched impact strength can be enhanced to the same level of super-tough nylon. Most of the studies are conducted by blending the polymers in melt.

The miscibility and morphology of the SAN/CPE blends prepared by solvent cast method was previously analyzed[17]. Here we are reporting the details mechanical properties of these SAN/CPE blends. To the best of our knowledge this is the first attempt to study the effect of Cl content of CPE on mechanical properties of SAN/CPE blends. The mechanical properties are essentially governed by the mixing of molecular network in solution which strongly depends on the compositions, Cl content in CPE and temperatures. The mechanical properties of SAN/CPE were studied by performing a series of tensile tests for different compositions in blends. Then, by comparing tensile tests at different temperatures, we studied the temperature effect on the contributions of the CPE in blends.

2. EXPERIMENTAL

2.1 Materials

Poly(styrene-acrylonitrile) with 25% of acrylonitrile (AN) and chlorinated polyethylene (CPE) with four different Cl content of (25, 36, 42 and 48%) were purchased from Aldrich Chemicals and used without purification. In order to prepare thin films for mechanical analysis, both polymers were dissolved in tetrahydrofuran (THF), stirring for 24 hrs at room temperature, dried in vacuum for 1 week. The compositions of the blends are ranged from pure SAN to pure CPE, and at 10% (weight to weight)

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intervals for each and every Cl content in SAN/CPE blends. Blend compositions indicated in this report are always weight compositions. The blend of SAN/CPE, containing 25% of Cl in CPE is henceforth labeled as SAN/CPE(25%).

2.2 Mechanical Properties

Mechanical properties were tested by Instron 4201 Universal Tester (Instron Corp., Canton, MA) equipped with computer control, data acquisition, and data analysis system. Tensile tests were conducted at crosshead speed of 5mm/min with data acquisition rate of 10 pts/s. A minimum of five specimens per sample were tested and the data were averaged to calculate yield stress, yield strain, and modulus. Young's modulus (referred to as modulus in this report) was obtained from the slope of a least square linear fit of the steepest linear region of the load-displacement data.

3. RESULTS AND DISCUSSION

3.1 Load-Displacement Profiles of Pure Polymers

The load-displacement profiles of the neat polymers in this work are shown in figure 1. Every curve represents independent tensile tests. Pure SAN shows very high ultimate load, which is also it's yield load, immediately followed by it's break load with very short displacement (Figure 1a). This indicates the rigidity of SAN, resistance to deformation and brittleness. Also, there isn't much area under the load-displacement curve which means SAN is strong, but not very tough. Further, the steep slope of the plot indicates the requirement of force to deform this rigid plastic. A similar properties of high resistance to deformation and brittleness is reported by Han *et al.*[18]. On the other hand, pure CPE has lower ultimate load but very high displacement compare to SAN. Among CPE's with four different Cl content, CPE(25%) shows the lowest ultimate load, which was slightly higher than its yield load. The load at break and displacement increases with Cl content in CPE. For example, CPE(36%) showed higher ultimate load than that of CPE(25%) and has slightly higher break load than its yield load. CPE(42%) showed a similar profile as CPE(48%) that includes a yield load much lower than the ultimate load (Figure 1b).

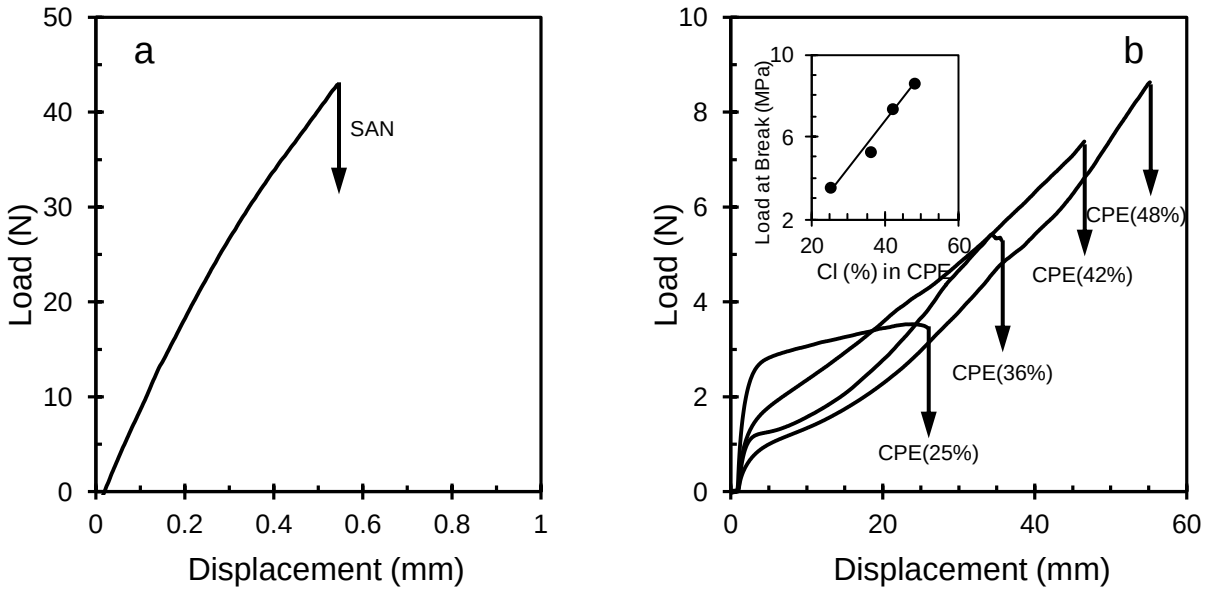

Figure 1. Load-displacement profiles for neat polymer of; (a) SAN, and (b) CPE with different Cl content. The inset image represents the load at break as a function of Cl content in CPE.

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3.2 Load-Displacement Profiles of Blends

Load–displacement profiles of binary blends of SAN/CPE(42%) as a function of compositions is shown in Figure 2. Addition of CPE resulted in decreasing of the break load while increasing the displacement. As the fraction of CPE increases in SAN/CPE(42%) blends all loads (yield, ultimate, and break) decreases while displacement increases. For all other blends of SAN/CPE with different Cl content of CPE shows similar trend (for simplicity data are not shown here). The results clearly show that mechanical properties of the SAN/CPE blends are between the values of the corresponding pure components in the compositions. Nishar Hameed et al found the similar trend, where the Poly(styrene-*co*-acylonitrile) was used to modify diglycedyl ether of bisphenol-A type epoxy resin. The blends exhibited considerable improvement in mechanical properties [19].

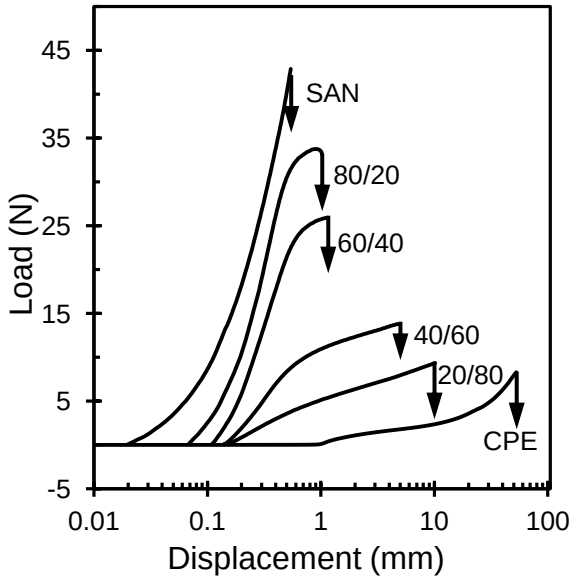

Figure 2. Load-displacement profile for SAN/CPE(42%) blends as a function of compositions.

3.3 Effect of Cl Content in Blends

The Cl content in CPE has strong effect on mechanical properties of SAN/CPE blends due to the compatibility of the mixing of two compositions in the blends. The effect of increasing the fraction of CPE in SAN/CPE blends containing different Cl content on the CPE break load are shown in Figure 3. For all blend compositions with Cl content in CPE, the break load decrease with CPE compositions. The SAN/CPE blend containing 25% of Cl shows rapid decrease of breaking load with CPE which continue until 40/60 of the composition and remains constant above 60% CPE fraction. The SAN/CPE blend containing 25 and 36% of Cl shows exponential decrease of break load with CPE for all compositions, while blend containing 42 and 48% of Cl shows less exponential decrease of break load with increase in fraction of CPE in the blend. This is related to the compatibility of the copolymers where various degrees of compatibility are possible ranging from complete miscibility to phase separation [1,17] where a linear decrease is a signature of incompatible mixing of the two components. The relationship between %CPE and load at break of SAN/CPE blends for 42 and 48% of Cl content in CPE, small positive deviation from the linearity indicates relatively poor compatibility, where a large positive deviation from the linearity for 25 and 36% of Cl content in blend (exponential decrease) shows relatively better compatibility of mixing

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between the two components. This result clearly indicates that lower the Cl content of CPE in SAN/CPE blends higher the compatibility of mixing SAN and CPE.

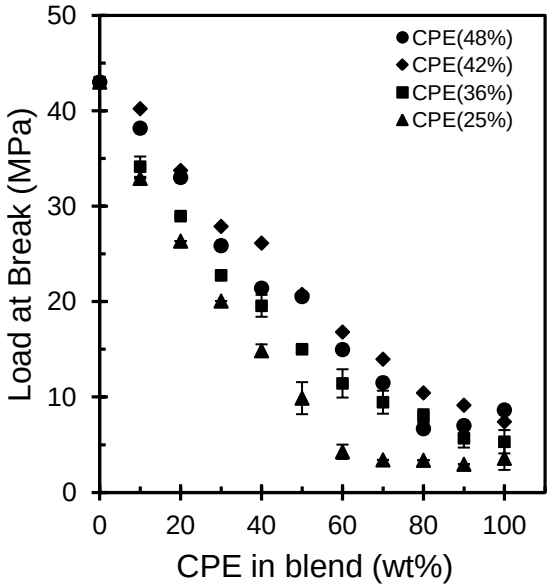

Figure 3. Effect of increasing fraction of CPE in SAN/CPE blends containing different Cl content on the CPE break load.

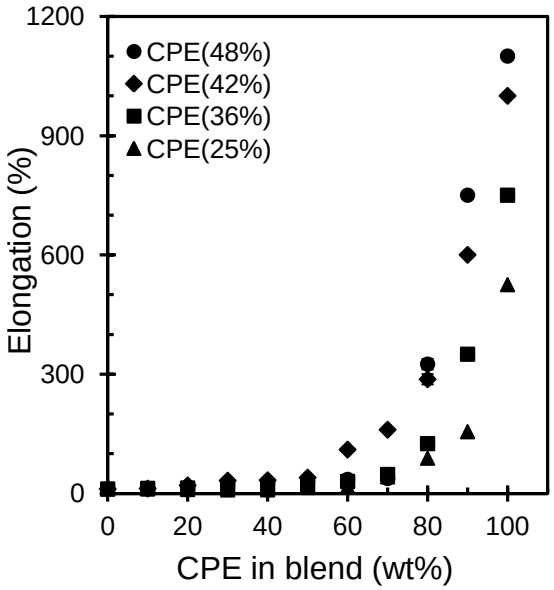

Figure 4. Composition of the SAN/CPE blend dependent ultimate elongation as a function of Cl content.

The elongation at break of the blends increases with CPE content, with the effect more pronounced as the Cl content in CPE increases (Figure 4). A brittle-tough transition in the impact strength is observed at a composition of about 50 wt % CPE (for all Cl% in CPE). Below 50 wt % CPE, a gradual increase in impact strength is observed with increasing CPE content, but the effect is small compared with the transition. The better mechanical properties of these blends are attributed to the superior mechanical properties of 25% of Cl and the better compatibility of SAN with CPE.

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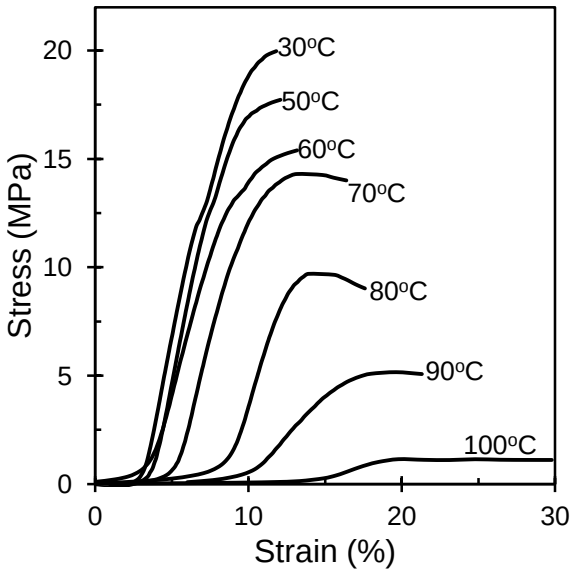

Figure 5. Stress-strain curve for 50SAN/50CPE(48%) blend as a function of temperature.

Figure 5 shows the stress-strain curve for a representative blend of 50SAN/50CPE(48%) as a function of temperature. In general, increasing the temperature resulted in the decreases of the stress and the increase of the yield strain. For example, almost four times lower stress can be read at 90°C, compare to the stress at 30°C. The Young modulus slowly decreases with temperature below 70°C, then rapidly decreases and labels off at 100°C (Figure 6). The rapid decrease of modulus may be related to the rubbery behavior of CPE at this temperature range with higher viscosity, and close to melting point of CPE.

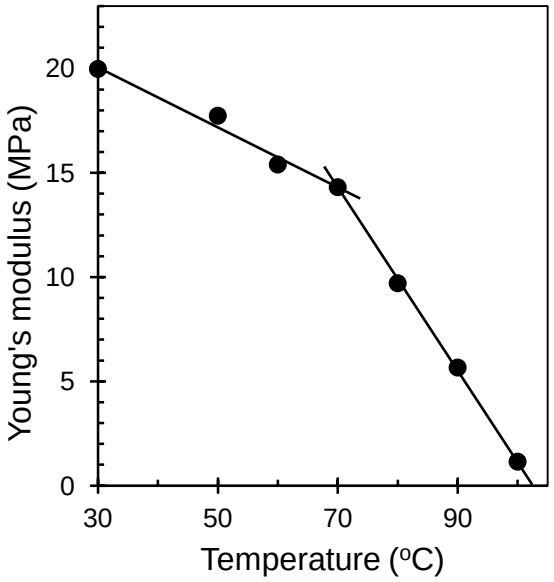

Figure 6. Temperature dependence Young's modulus for SAN/CPE(48%) blend.

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4. CONCLUSIONS

CPE can be blended as impact modifier for brittle SAN to improve mechanical properties. The mechanical properties of SAN/CPE blends were found to be between the values of the corresponding pure components. With increasing content of CPE, the elongation at break increases and the load at break decreases. The higher Cl content in CPE reduced the load at break linearly according to addition law of while lower Cl content decreases nonlinearly indicating an improvement of the mixing compatibility of the blends. The yield strain depends on the blend composition nonlinearly which indicates high impact of CPE on the compatibility of the blends. Comparison of the yield stress and modulus of the blends with Cl content in CPE showed these properties decreasing in the order of: SAN/CPE(25%)< SAN/CPE(36%)< SAN/CPE(42%) <SAN/CPE(48%). For a typical blend composition, the young's modulus decreases with temperature and level off at ~100^{o}C. The Cl content of CPE has strong effect in the mechanical properties of SAN/CPE blends where the blending is inexpensive and efficient avenue to balance mechanical and processing properties for specific industrial applications. Details of morphology and thermal stability of these blends will be another topic of the forthcoming article.

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The authors declare no conflict of interest

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