



## Preparation and Properties of Novel Semi-Aromatic Co-Polyamide 6T/6

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Semi-aromatic co-polyamides 6T/6 was synthesized *via* solution polymerization using terephthalic acid, 6-diaminohexane and caprolactam as raw materials. The structure of the obtained samples was characterized by fourier transform infrared spectroscopy. The influence of solid-phase reaction on the melting point and melt index of copolymer and the effect of oligomer content and intrinsic viscosity on the mechanical properties were also discussed. The results show that the intrinsic viscosity can be adjusted by the solid-phase polymerization process, while the latter has no significant effect on the melting points. The intrinsic viscosity of the copolymer and the content of the monomer have a significant impact on the mechanical properties of materials.

**Keywords:** Semi-aromatic co-polyamide, Characterization, Solid-phase polymerization, Mechanical properties.

### INTRODUCTION

Semi-aromatic polyamides, as a novel polyamides resin, are combinations of aromatic and aliphatic functionalities by introducing aromatic rings into the molecular chain of the aliphatic polyamides. Semi-aromatic polyamides combine the high melting temperatures and heat resistance of wholly aromatic polyamides with the good melt processability of aliphatic polyamides such as polyamide 6 and 6,6. The symmetrical structure of semi-aromatic polyamides molecular chain having *p*-phenylene units shows straight and rigid conformation, which leads to strong intermolecular force and good crystallinity<sup>1-5</sup>. Polyamide 6T (PA6T) is a typical semi-aromatic polyamide, which exhibits not only good processing fluidity but also low water absorption, good heat resistance and mechanical properties. Polyamide 6T is a class of high heat-resistant resin between general aliphatic nylons and advanced engineering polymers such as polyether ether ketones (PEEK). Polyamide 6T with high heat resistance, wear resistance and strength can be extensively applied in industrial and other fields, such as peripheral components in automobile engine, circuit board surface mount technology, aerospace, machinery bearings frame, compressor valves and weapons industry<sup>6-10</sup>.

The melting point of pure polyamide 6T is 370 °C, higher than its thermal decomposition temperature (350 °C), resulting melt processing impractical. Therefore, it is necessary to find an alternative modification method to decrease the melting

points of polyamide 6T to appropriate melt processing temperature range and to keep excellent material properties. Seda Cakir<sup>10</sup> incorporated a nylon salt of 1,5-diamino-2-methylpentane and isophthalic acid into polyamide-6 in different weight percentages and obtained polyamide-6/semi-aromatic nylon copolyamides with low melting temperature. In this study, semi-aromatic copolyamides PA6T/6 were synthesized by solution copolymerization using  $\epsilon$ -caprolactam and polyamide salt of terephthalic acid and hexamethylene diamine as raw materials. The copolymerization process was systematically studied. The influence of solid-phase polymerization on the copolyamides melting point and melt index was studied and effects of oligomer or monomer content and intrinsic viscosity on the mechanical properties were discussed.

### EXPERIMENTAL

$\epsilon$ -Caprolactam, was manufactured by Yueyang Baling Petrochemical Co., Ltd. (Hunan, China); Commercial grade terephthalic acid and hexamethylene diamine were kindly provided by Junma Co., Ltd. (Zhangjiagang, China); sodium monophosphate, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), was of analytical grade. All the chemical reagents were used without further purification.

**Polyamide 6T salt preparation:** An appropriate amount of terephthalic acid and hexamethylene diamine were dissolved in 90 °C deionized water and formed a transparent solution. The pH value of the solution was adjusted using hexamethylene

diamine and stirring was continued for 2 h. After the obtained transparent solution was cooled to below 10 °C, the white precipitate appeared. The precipitate was filtered, washed 3 times by deionized water and dried at 80 °C in an oven under vacuum.

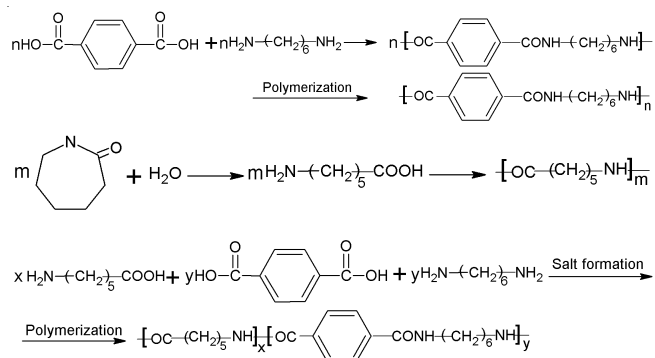
**PA6T/6 copolyamides preparation:** New semi-aromatic copolyamides PA6T/6 were prepared by solution copolymerization. Polyamide 6T salt and deionized water were added into an autoclave and formed the aqueous solution of concentration of 60 wt %, then different amounts of  $\epsilon$ -caprolactam and a small amount of sodium monophosphate as catalyst were added to the solution. Charge and discharge of carbon dioxide were carried out five times to replace the air in the autoclave at room temperature. Subsequently the autoclave was heated to 200 °C and kept 3 h, then raised the temperature to 280 °C. The pressure during all the reaction is maintained at less than 4 MPa. After 2 h, the pressure of the autoclave was gradually decreased to 0.05 MPa pressure in 2 h by deflating. The autoclave was filled with carbon dioxide to raise the pressure to 0.15 MPa. The prepolymer of PA6T/6 was obtained after extrusion and pelletizing. The prepolymer of PA6T/6 was added into a solid-state polymerization kettle. The kettle was evacuated to 10 Pa and the reaction temperature was increased to 170 °C. After 5 h, the kettle was cooled to room temperature and the PA6T/6 was obtained.

**Characterization:** The intrinsic viscosities of the polyamides were determined in an Ubbelohde viscometer at 25  $\pm$  0.1 °C, with them being dissolved in 96 % concentrated sulfuric acid and the sample concentration was 0.01 g/mL. Fourier transform infrared spectroscopy spectra of KBr powder-pressed pellets were recorded on a NICOLET NEXUS870 spectrometer to analyse the composition of samples and changes in molecular structure. DSC was carried out in a nitrogen stream using a NETSCH DSC200 F3 calorimeter. The samples were heated to 310 °C at a rate of 20 °C/min and allowed to stay for 5 min to remove all memory of previous thermal history and then cooled to 50 °C at a rate of 10 °C/min and then heated to 310 °C at a rate of 10 °C/min. Mechanical properties were investigated by a universal testing machine according to ASTM D638, ASTM D790 and ASTM D4508-06. Monomer or oligomer content were measured according to GB/T 6509-2005; Melt index was measured according to GB/T 3682-2000.

## RESULTS AND DISCUSSION

Equimolar ratio monomers are good for the synthesis of high molecular weight polycondensation. Using polyamide 6T salt as raw materials can accurately regulate the copolymerization. The molar ratio of terephthalic acid and hexamethylene diamine is 1:1 in the preparation of polyamide 6T salt. During the heating in the salt-forming process, there will inevitably be a small amount of hexamethylene diamine volatiles. Therefore a slight excess of hexamethylene diamine is added and the pH value of the solution needs to be slightly larger than 7. The polymerization process is showed by the following reaction formula.

Polyamide 6T salt and  $\epsilon$ -caprolactam have different reactivity rate, so the copolymerization reaction is not in accordance with a completely random manner, often by the



way of the block copolymerization<sup>2</sup>. Compared to polyamide 6T salt, the polymerization reactivity rate of caprolactam is much higher and the resulting product is a block copolymer of the two monomers.

**FTIR analysis:** FTIR may reveal structural changes of samples in the overall synthesis process. The characteristic FTIR absorption bands of samples are given in Fig. 1. In Fig. 1(1-2), the strong absorption peaks at 2938 and 1550  $\text{cm}^{-1}$  are attributed to the stretching and bending vibration of -N-H- in the typical polyamide. Fig. 1(3-4) show the infrared absorption spectrum of PA6T/6 and the prepared PA6T/6 salt in an equimolar ratio of terephthalic acid with hexamethylene diamine. The peaks at 1641 and 1571  $\text{cm}^{-1}$  are assigned to -C=O vibration absorption in PA6T/6 salt, which shifts towards lower wavenumber, compared to -C=O vibration absorption at 1686  $\text{cm}^{-1}$  in terephthalic acid. In Fig. 1(4), the FTIR absorption band of PA6T/6 is similar to PA6. The absorption peak at 3310  $\text{cm}^{-1}$  is corresponding to the vibration of -N-H-, the peaks at 2938 and 2860  $\text{cm}^{-1}$  are attributed to the vibration absorption of -CH<sub>2</sub>- in polyamide molecular chains. And the strong peaks at 1638 and 1546  $\text{cm}^{-1}$  are assigned to amide group. The peaks at 1500  $\text{cm}^{-1}$  in Fig. 1(3) and (4) are related to the vibration absorption of benzene, which is different from polyamide-6. The above analysis shows that amide groups and benzene structure exist in the obtained copolyamide *via* organic monomers ring-opening, salt formation and copolymerization process.

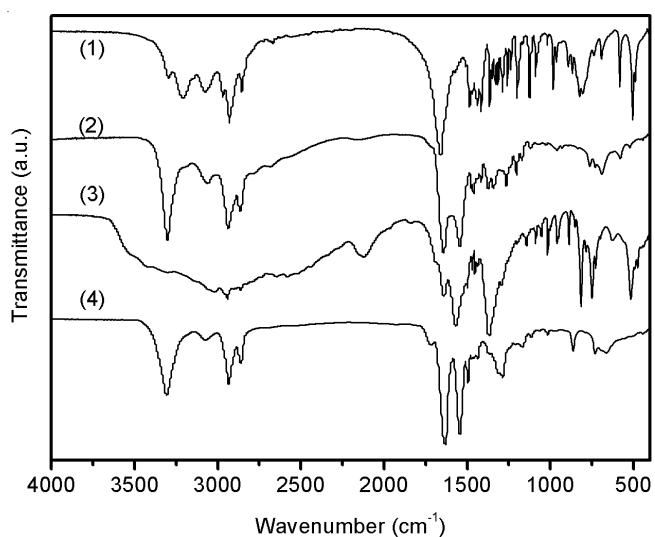


Fig. 1. FTIR spectra of the samples (1) caprolactam (2) PA6 (3) PA6T salt (4) PA6T/6

**Effect of solid-state polymerization on the melting behaviour:** The semi-aromatic copolymer PA6T/6 was prepared using  $\epsilon$ -caprolactam and polyamide 6T salt with high elongation polyamide recipe. The melting behaviour was tested by DSC. The typical second heating DSC curve is shown in Fig. 2.

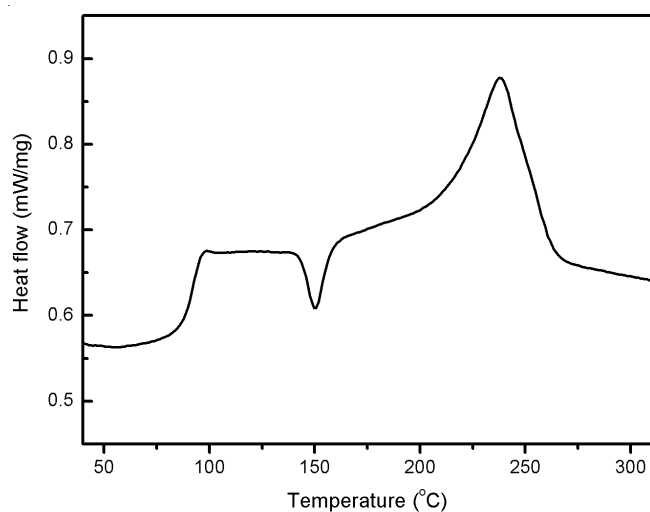


Fig. 2. DSC curve of PA6T/6

It can be seen that the glass transition temperature appears at 95 °C, which is higher than that of pure polyamide-6. This indicates polyamide 6T and polyamide-6 have good compatibility in the amorphous regions. The introduction of polyamide 6T with high glass transition temperature and the rigid segment leads to the reduction of the ability of the average activity of the amorphous region segments and helps to improve the thermal deformation temperature of materials. A crystallization exothermic peak appears in the vicinity of 150 °C and a wide melting peak appears at 238 °C, no multiple melting peaks, which indicates that a similar crystalline region is formed in the copolymerization system of polyamide 6T and polyamide-6.

The relation between intrinsic viscosity and the melting points was studied by solid-phase polymerization of PA6T/6 prepolymer, as shown in Fig. 3. With the improvement in the level of the solid-phase polymerization, the melting point of

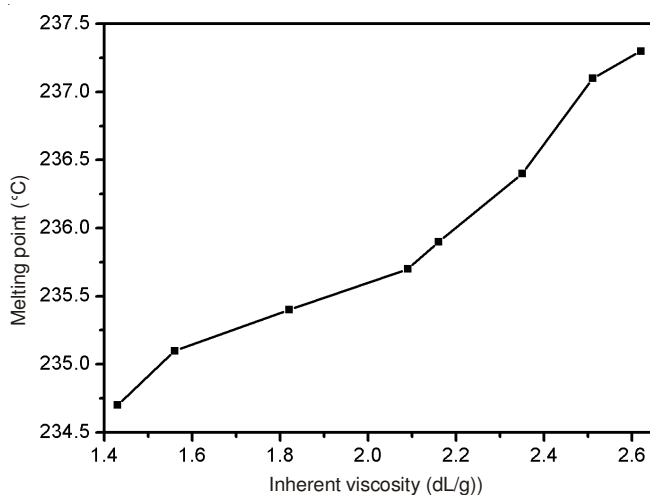


Fig. 3. Plots of the melting points against intrinsic viscosity

the copolymer increased with increasing intrinsic viscosity, but the increase magnitude of melting point is not large. The temperature variation is only 2.6 °C. The main reason of affecting the melting point of the copolymer is derived from the ratio of raw materials and the tacticity of polymer chain segments, while this has nothing to do with the molecular weight. Thus the effect is not obvious by the solid-phase polymerization to raise the melting point of the copolymer.

**Effect of solid-state polymerization on the melt index:** Fig. 4 shows plots of the melting index of PA6T/6 against intrinsic viscosity. During the solid-phase polymerization process, with improving the solid-phase polymerization temperature and longer time, a continuous increase in the intrinsic viscosity of the copolymer can be obtained. Simultaneously the melt index of PA6T/6 decreases. At higher reaction temperature, heating induction may increase the effective collision between the -COOH and -NH<sub>2</sub> ends groups. The end groups of PA6T/6 macromolecule diffuse to close to each other and interact. In addition, the increase of temperature and time in solid-state reaction is conducive to the diffusion of small molecule product and its escaping from the surface. Therefore the molecular weight of the copolymer is increased, the viscosity becomes large and the melt index is reduced<sup>11,12</sup>.

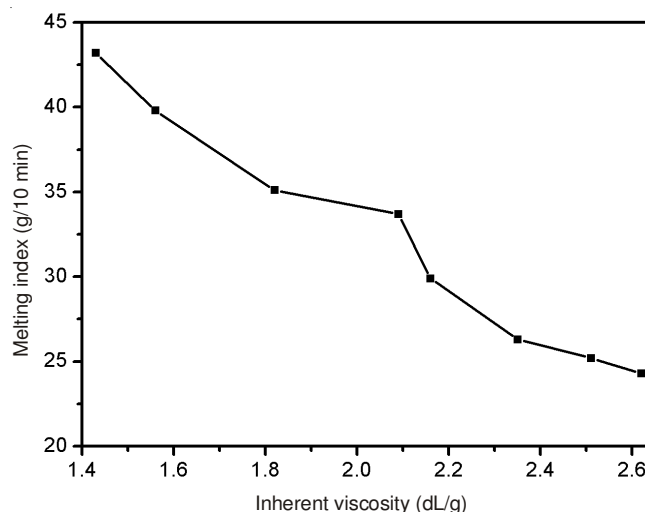


Fig. 4. Plots of the melting index against intrinsic viscosity

## Mechanical properties

**Effect of oligomer content on mechanical properties:** Fig. 5 shows the mechanical properties of PA6T/6 with different monomer content. As the monomer content increases, the tensile strength, the bending strength and bending modulus of PA6T/6 gradually fall, while the elongation at break and IZOD impact strength increase. The monomer or oligomer content in the copolymer can be regulated by high-temperature extraction using water as solvent. When monomer or oligomer content exceeds 1 %, the decrease of bending strength is greater than that of tensile strength, which is attributed to high unreacted monomer or oligomer content in the copolymer. Under certain loads, the higher monomer content may increase the activity of molecular chains in the amorphous region, thereby the deformation becomes easily. The copolymer exhibits lower

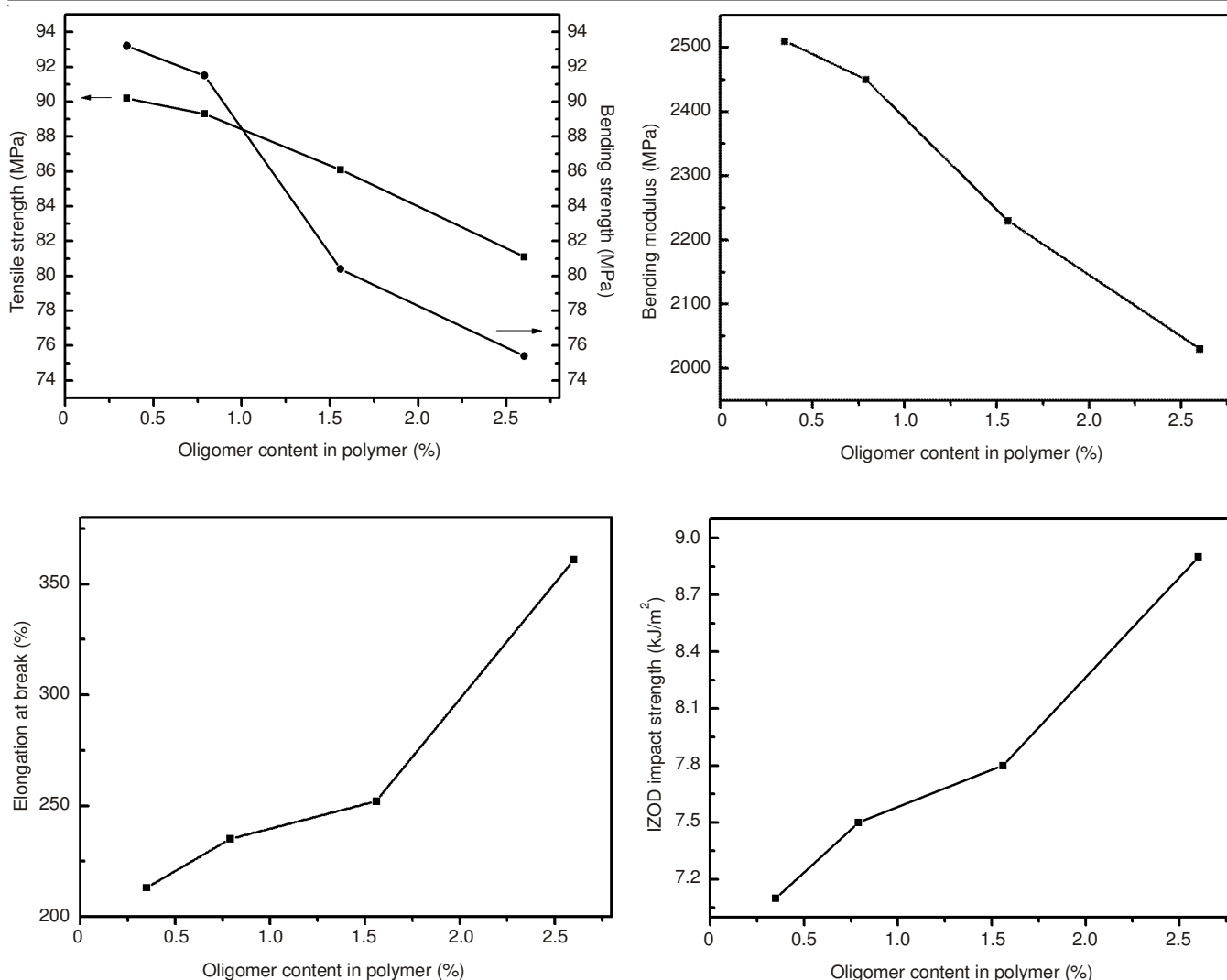


Fig. 5. Effects of oligomer content on mechanical properties

bending modulus, with gradually increasing of elongation at break. The increase of the content of the monomer or oligomer plays the role of toughening in the copolymer, resulting in the improvement of impact strength. Therefore, with the content of the monomer or oligomer being controlled in less than 1%, the copolymer shows good overall mechanical properties.

#### Effect of intrinsic viscosity on mechanical properties:

Effect of intrinsic viscosity on mechanical properties is shown in Fig. 6. The monomer content of PA6T/6 samples was 0.79%. With an increase in intrinsic viscosity, tensile strength, bending strength, bending modulus and IZOD impact strength of the copolymer gradually increase, while the elongation at break gradually decreases. The increase of intrinsic viscosity can reflect the change process of molecular weight from low to high. Carbonyl and amine groups in the copolymer may form hydrogen bonds with the increase of the molecular weight and the interaction between the molecular chains is enhanced. So tensile strength and bending strength increase and elongation at break decreases. Meanwhile, the activity of molecular chains in the amorphous region becomes lower. Molecular chains can not be easily deformed, resulting in large strain and the increase of the modulus and impact strength.

#### Conclusion

A series of semi-aromatic PA6T/6 can be synthesized *via* solution polymerization using pure terephthalic acid, 6-diaminohexane and  $\epsilon$ -caprolactam as raw materials. The intrinsic viscosity can be adjusted by the solid-phase polymerization which has no significant effect on the increase of melting point. The increase of temperature of solid-phase polymerization and longer time can improve the intrinsic viscosity of the copolymer and reduce its melt index. With the increase of the monomer content, tensile, bending strength and bending modulus fall, while the elongation at break and IZOD impact strength increase. The increase in intrinsic viscosity can lead to increasing tensile, bending strength, bending modulus and IZOD impact strength and decreasing elongation at break.

#### ACKNOWLEDGEMENTS

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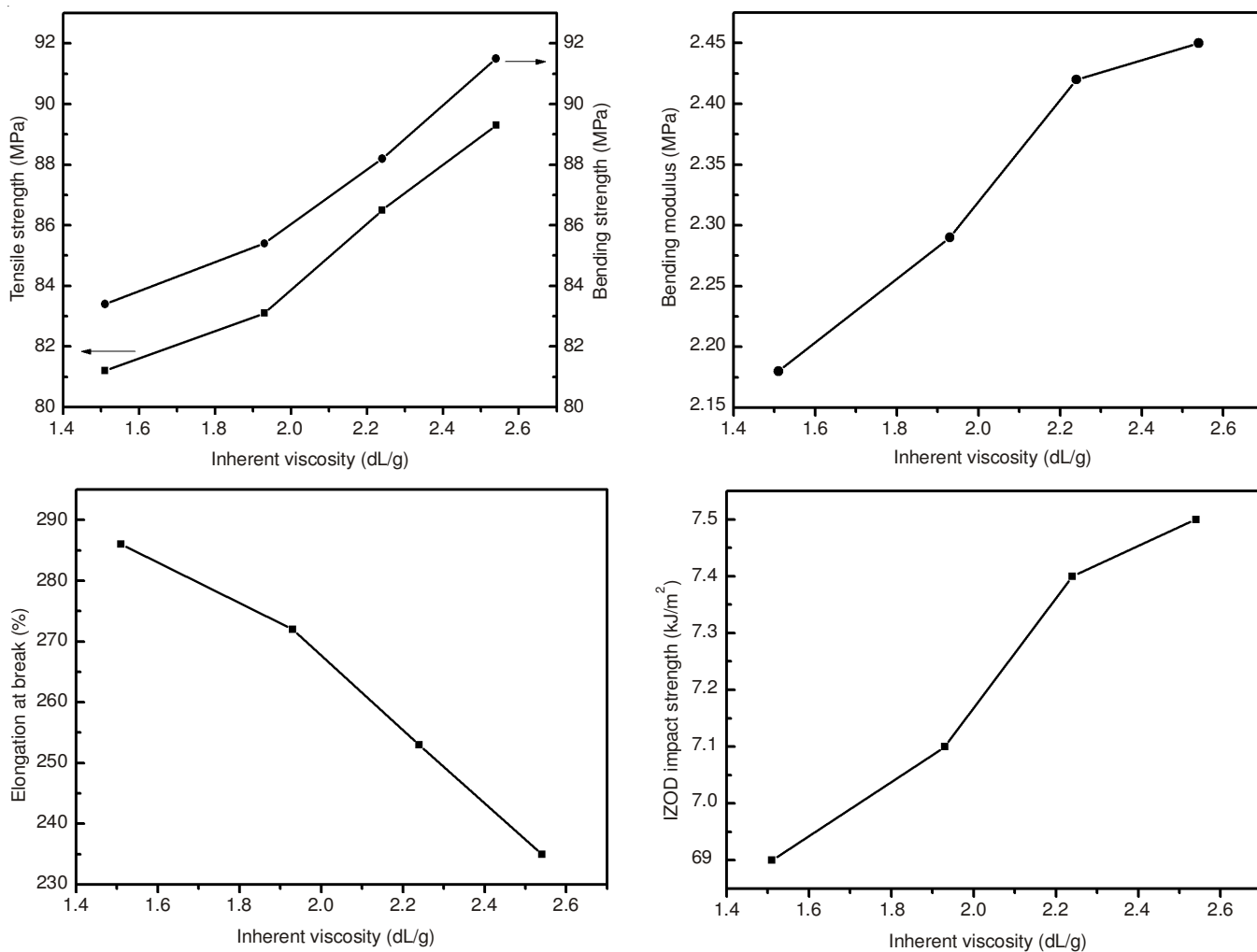


Fig. 6. Effects of intrinsic viscosity on mechanical properties

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