

Poly(methyl Methacrylate)–Cellulose Nitrate Copolymers. II. Physical and Mechanical Properties

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Synopsis

Poly(methyl methacrylate)–cellulose nitrate copolymers were prepared by bulk polymerization using benzoyl peroxide as initiator. Cellulose nitrates of two different nitrogen contents (11.4 and 12.2%) were used. The prepared copolymers were γ -irradiated for specified periods of up to 11.83 Mrad. Their physical and mechanical properties were measured before and after irradiation. The title copolymers showed lower modulus, tensile strength, and elongation at break than poly(methyl methacrylate) itself, but they showed better hardness and abrasion. Irradiation of up to 6.57 Mrad improved the modulus of the copolymers. Hardness and abrasion were improved by increasing cellulose nitrate content. The prepared copolymers that contained cellulose nitrate of 11.4% nitrogen showed secondary transition points. The increase of cellulose nitrate concentration shifted both first and second transition points to relatively higher values.

INTRODUCTION

The graft copolymerization of cellulosic materials with vinyl monomers^{1,2} in the presence of ceric ions,^{3,4} persulfates,⁵ and by irradiation^{6,7} has been discussed much. No effort has been made so far to modify cellulose nitrate (CN) despite its versatile applications in the field of plastics, surface coatings, and leathers. More recently, CN was grafted in solution by methyl methacrylate (MMA) monomer using benzoyl peroxide⁸ and ceric ammonium nitrate⁹ as initiators to produce cellulose nitrate lacquer and lacquer emulsions. In our previous work,¹⁰ poly(methyl methacrylate)–cellulose nitrate (PMMA–CN) copolymers were prepared in the form of sheets $250 \times 250 \times 6$ mm and rods of different sizes by bulk polymerization using benzoyl peroxide as initiator, in the same way as PMMA but at lower temperatures. It was found that PMMA–CN copolymers did not dissolve in any conventional solvent either before or after irradiation and that the percent homopolymer amounts to zero.

The aim of the present work is to measure the physical and mechanical properties of the prepared PMMA–CN copolymers, to evaluate them, and maybe to throw a searchlight on their ultimate structure and the field in which they may be used.

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EXPERIMENTAL

Materials

(1) MMA monomer was freed from inhibitor by washing with aqueous sodium hydroxide solution (10%), dried over anhydrous calcium chloride, and distilled under reduced pressure.

(2) CN of 11.4 and 12.2% nitrogen content (N) (supplied by Abu-Zaabal Company for Speciality Chemicals, Egypt) were purified by washing with water and dried to constant weight.

(3) BDH benzoyl peroxide was used.

Techniques

Preparation of PMMA and PMMA-CN Copolymers

CN was impregnated in MMA monomer for 24 hr at room temperature with continuous shaking. The blends were copolymerized by bulk polymerization using benzoyl peroxide as initiator.¹⁰

Irradiation

Irradiation of the prepared PMMA and PMMA-CN copolymers was carried out in air. The samples were irradiated at 25°C for specified periods at a dose rate of 73 rad/sec by using a ⁶⁰Co source located at the Regional Centre for Radioactive Isotopes, Cairo.

Stress-Strain Tests

Swick-tensile testing machine 1487 was used for measuring the tension and compression tests.

Tension Tests

The samples were tested according to ASTM D-638 at room temperature with a crosshead speed of 50 mm/min. The mean value of seven measurements per group was taken.

Calculations

(1) Modulus (σ_M) = F_M/A , where F_M is the maximum force at maximum load and A is the cross-sectional area of the specimen.

(2) Tensile strength (σ_R) = F_R/A , where F_R is the force at break.

(3) Elongation at break (Σ_M) = $(V_m \times X_m)/(V_p \times L_o) \times 100$, where V_m is the crosshead speed of the machine, X_m is the maximum strain, V_p is the speed of recording paper, and L_o is the original length of the specimen.

Compression Test

The samples were tested according to ASTM D-695, but the capacity of the machine cannot stand up to the rigidity of the samples at room temperature, thus the samples were measured at 60°C. The test was done with a crosshead speed of the machine of 5 mm/min. The mean values of seven measurements was taken.

The compressive strength is calculated as follows:

$$\sigma_{el} = F_{el}/A$$

where σ_{el} is the compressive strength, F_{el} is the compressive force at elastic, and A is the cross-sectional area of the specimen.

Measurements of Abrasion

The testing machine APG 1, TGL 0-53516, was used to measure abrasion. The machine consists of a driving motor, a spindle holder which puts the sample (a disk of 16-mm diam and 6-mm thickness) into contact with the rotating drum covered by a standard sand paper, and a rotating drum with a force of 1 kg. The samples covers a distance of 40 m around the drum. During the test, the drum revolves around its own axis through a gear connected to its holder. The abrasion is calculated as percent loss in weight:

$$\text{Percent loss in weight} = \frac{W_o - W_l}{W_o} \times 100$$

where W_o is the original weight of the specimen, and W_l is the final weight of the tested specimen.

Determination of Hardness

Zwick-hardness tester 3102 was used to measure hardness. The indenter of the tester is a truncated cone. The resistance represented for the indenter is transmitted to a calibrated spring and indicated in Shore hardness numbers on a scale. The specimens were tested at seven different points. These points were a minimum distance of 5 mm apart from each other and a minimum of 13 mm apart from the edges of the specimen. The samples were compressed with a load of 5 kPa at temperature $20 \pm 2^\circ\text{C}$. The reading was taken 30 sec after the contact surface of the tester had touched the specimen.

Impact Resistance

Zwick-impact testing machine 5102 was used for measuring the impact strength. The tests were done according to ASTM D-256, but unnotched samples were used. They were tested at room temperature and the mean value of ten measurements per group was taken.

Determination of the Coefficient of Thermal Expansion

Netzsch (GmbH) dilatometer 402-T was used for measuring the coefficient of thermal expansion. It has a temperature range of -160 to $+420^{\circ}\text{C}$. The tests were done according to ASTM D-696. The rate of increasing temperature was $2^{\circ}\text{C}/\text{min}$. The coefficient of thermal expansion is calculated as follows:

$$\alpha = \frac{\Delta L}{L_o(T_m - T_o)}$$

where α is the coefficient of thermal expansion per $^{\circ}\text{C}$, $\Delta L = L_m - L_o$, L_o is the original length of the specimen, L_m is the length of the specimen at T_m , T_o is the starting temperature, and T_m is the measured temperature.

RESULTS AND DISCUSSION

Cellulose nitrate was dissolved in MMA monomer in different concentrations, then they were copolymerized in bulk using benzoyl peroxide as initiator.¹⁰ CNs of two different nitrogen contents (11.4 and 12.2%, i.e., in the range that is generally used in plastics and surface coatings) were used. The PMMA-CN copolymers were prepared in the form of sheets $250 \times 250 \times 6$ mm and rods of different sizes. The prepared PMMA-CN copolymers were irradiated for specific periods of up to 11.83 Mrad.

It is interesting to find out the effects of CN concentration, nitrogen content of CN, and irradiation on the physical and mechanical properties of such type of copolymers, which may throw a searchlight on ultimate structure and the field in which they may be used.

Tension Tests

A tension-stress-strain curve was determined for each specimen where modulus, tensile strength, and elongation at break were measured.

Modulus of Elasticity

The effect of irradiation on modulus of PMMA and PMMA-CN copolymers were determined. Figure 1 illustrates the relation between modulus and irradiation dose at different concentrations of CN of 11.4 and 12.2% nitrogen content (N). It is clear that the modulus of PMMA decreases sharply, crossing the PMMA-CN curves with irradiation dose. This means that degradation takes place in PMMA even at low irradiation doses and it increases at higher doses. Also, the introduction of CN into PMMA matrices decreases its modulus. This decrease is aggravated with the increase of CN concentration and N; for example, the modulus of PMMA and PMMA-CN copolymers of 2% CN of 11.4 and 12.2% N are 714, 595, and 465 kg/cm^2 , respectively. Irradiation of these copolymers increases their modulus and it reaches maximum at 6.57 Mrad for CN of 11.4% N and at 8.25 Mrad for CN of 12.2% N.

In general, it can be concluded that during irradiation of PMMA-CN copolymers, two processes take place simultaneously crosslinking and degradation

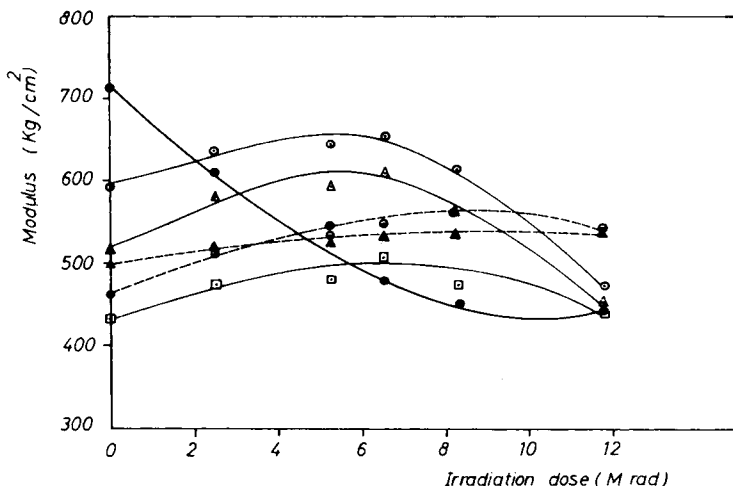


Fig. 1. Effect of irradiation dose on Modulus of PMMA-CN copolymers. (—) 11.4% N; (- - -) 12.2% N; (●) 0% CN; (■) 2% CN; (▲) 4% CN; (□) 6% CN; (⊙) 2% CN; (▲) 4% CN.

in PMMA branches and bridges. At 6.57 Mrad, crosslinking reaches maximum in the copolymers containing CN of 11.4% N and at 8.25 Mrad for those containing CN of 12.2% N.

Tensile Strength

Figure 2 shows the relation between irradiation dose and tensile strength of PMMA and PMMA-CN copolymers of different concentrations of CN of 11.4 and 12.2% N. It is apparent that the tensile strength of PMMA decreases sharply, crossing down all the copolymer curves, with irradiation dose indicating high degradation in the polymer chains as predicted.

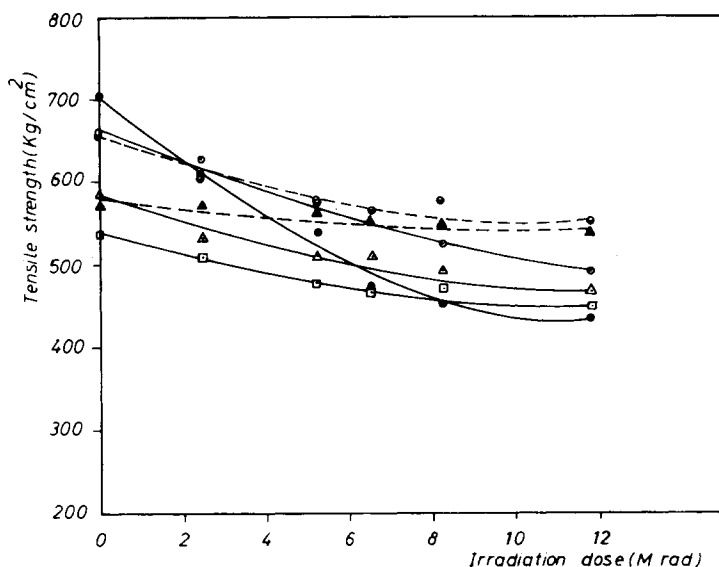


Fig. 2. Effect of irradiation on tensile strength of PMMA-CN copolymers. (—) 11.4% N; (- - -) 12.2% N; (●) 2% CN; (▲) 4% CN; (●) 0% CN; (⊙) 2% CN; (▲) 4% CN; (□) 6% CN.

On the other hand, the tensile strength of PMMA-CN copolymers decreases with CN concentration before irradiation. This may be due to the long chains of CN which join across the PMMA chains and separate them, thus reducing the physical forces which attract the PMMA chains. But swelling and solubility tests¹⁰ showed that all PMMA-CN copolymers do not dissolve in any conventional solvent, but swell. Thus, it can be concluded that CN solvates the physical forces that attract the PMMA chains and crosslinking occurs at the same time, but the degree of crosslinking does not offset the lost attractive forces, hence low tensile strength was observed.

On irradiation, a continuous slow decrease was observed. The difference in tensile strength of unirradiated and irradiated PMMA to 11.83 Mrad is 271 kg/cm², while the differences in PMMA-CN copolymers containing CN of 11.4% N are 170, 125, and 85 kg/cm² for 2, 4, and 6% CN, respectively, and 105 and 34 kg/cm² for 2 and 4% CN of 12.2% N. This leads to the conclusion that not only higher CN concentrations protect the prepared copolymers against irradiation, but also CN of higher N gives best results especially at higher irradiation doses.

Elongation at Break

The obtained results of elongation at break of PMMA and PMMA-CN copolymers at different irradiation doses are displayed graphically in Figure 3. The curves of the figure show that the elongation of PMMA decreases sharply with the irradiation dose, but the decrease in the elongation at break of PMMA-CN copolymers occurs with slow rate.

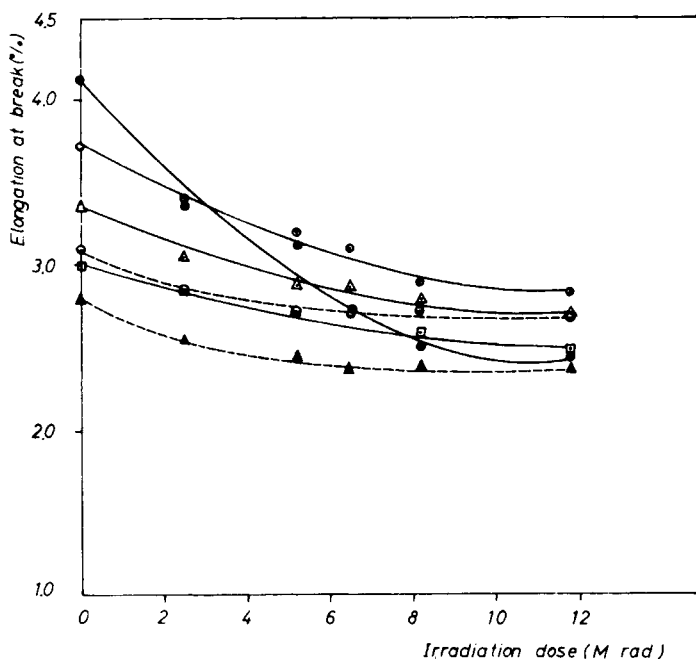


Fig. 3. Effect of irradiation on elongation at break of PMMA-CN copolymers. (—) 11.4% N; (---) 12.2% N; (●) 2% CN; (▲) 4% CN; (●) 0% CN; (○) 2% CN; (▲) 4% CN; (◻) 6% CN.

Compressive Strength

The compressive strength test is the test of the ability of rigid plastics to stand uniaxial force. Figure 4 illustrates the relation between compressive strength and CN concentration in PMMA-CN copolymers. It is obvious that the compressive strength of PMMA decreases sharply (by 775 kg/cm²) when MMA monomer is copolymerized with 2% CN of 11.4% N. The increase of CN concentration was found to have, more or less, no effect on the compressive strength. But when 2% CN of 12.2% N was copolymerized with MMA monomer, the difference in the compressive strength between PMMA and PMMA-CN copolymers amounts to 279 kg/cm².

A comparison of the compressive strength of the copolymers shows that the small difference in nitrogen content (0.8%) of the two CNs used in this investigation has a great effect on the compressive strength of their copolymers.

Abrasion

In the abrasion process, high temperatures may be produced in localized areas, where the asperities of one surface contact the other material and produce large localized stresses and strains. At these hot points, chemical reactions that speed up the rate of abrasion or wear, such as oxidation, can occur.¹¹ Figure 5 shows the relation between abrasion (as percent loss in weight of sample) and CN concentration in PMMA-CN copolymers. It is clear that CN improves the abrasion of PMMA-CN copolymers. Also, it can be observed that CN of 11.4% N gives better results in this respect. This may be due to the fact that copolymers containing CN of 11.4% N show secondary transition temperatures (Fig. 8); thus when the temperature of friction reaches the region of this secondary transition temperature, the mobility of the chains may dissipate some of the heat. Copolymers containing CN of 12.2% N do not show secondary transition temperatures.

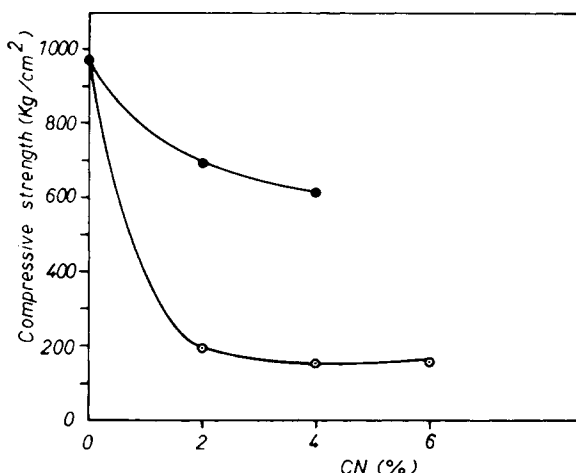


Fig. 4. Effect of CN on compressive strength of PMMA-CN copolymers. (●) 12.2% N; (○) 11.4% N.

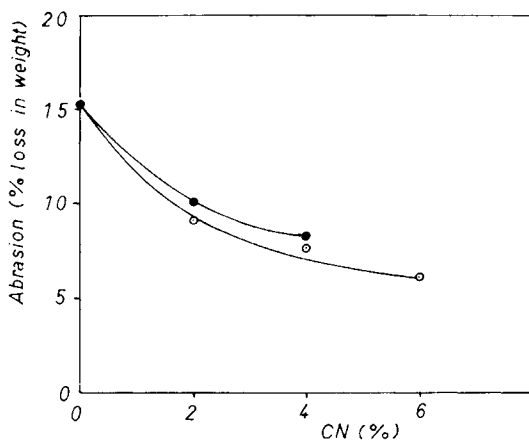


Fig. 5. Effect of CN on abrasion of PMMA-CN copolymers.

Hardness

In this investigation, Shore hardness was measured. The obtained results are represented graphically in Figure 6. In general, it can be seen that CN and nitrogen content increase the hardness of PMMA-CN copolymers. Also, irradiation of up to 6.57 Mrad has the same effect on the prepared copolymers.

Impact Strength

The impact test is a high-speed fraction test which measures the energy required to break a specimen. Unnotched specimens of PMMA and PMMA-CN copolymers were used to measure Charpy impact. Figure 7 shows the relation between Charpy impact and irradiation doses of up to 11.84 Mrad of PMMA and PMMA-CN copolymers containing CN of 11.4% and 12.2% N. It can be seen that the increase of CN reduces the impact resistance of the copolymers. Also, nitrogen content and irradiation dose have the same effect.

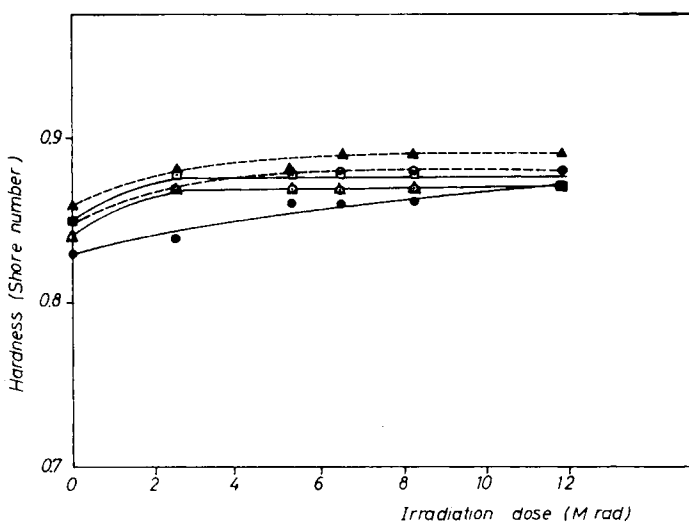


Fig. 6. Effect of irradiation on hardness of PMMA-CN copolymer. (—) 11.4% N; (- - -) 12.2% N; (●) 0% CN; (○) 2% CN; (▲) 4% CN; (◻) 6% CN; (◐) 2% CN; (▲) 4% CN.

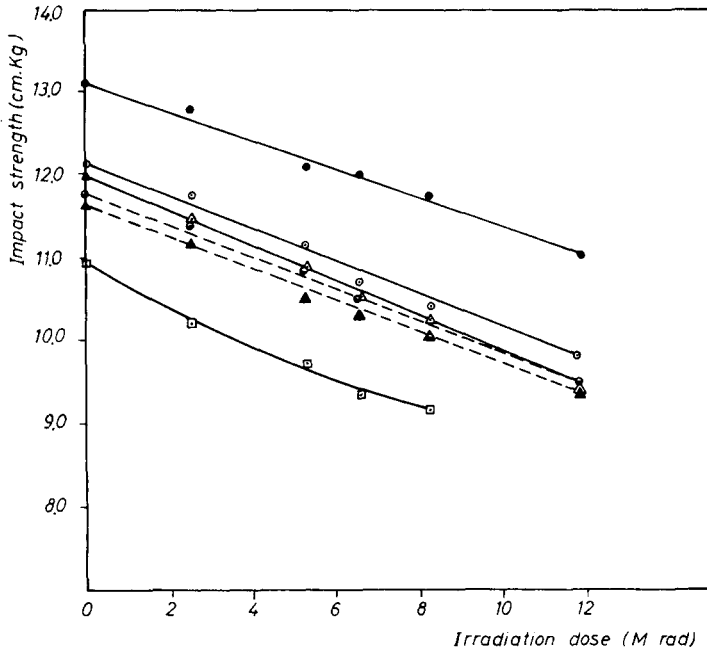


Fig. 7. Effect of irradiation on impact strength of PMMA-CN copolymers. (—) 11.4% N; (---) 12.2% N; (●) 2% CN; (▲) 4% CN; (●) 0% CN; (○) 2% CN; (△) 4% CN; (□) 6% CN.

Coefficient of Thermal Expansion

The change in length of a material with changing temperature is indicated by coefficient of thermal expansion. At transition points, the behavior of the coefficient will be changed.¹² Thermal expansion tests are useful for comparing

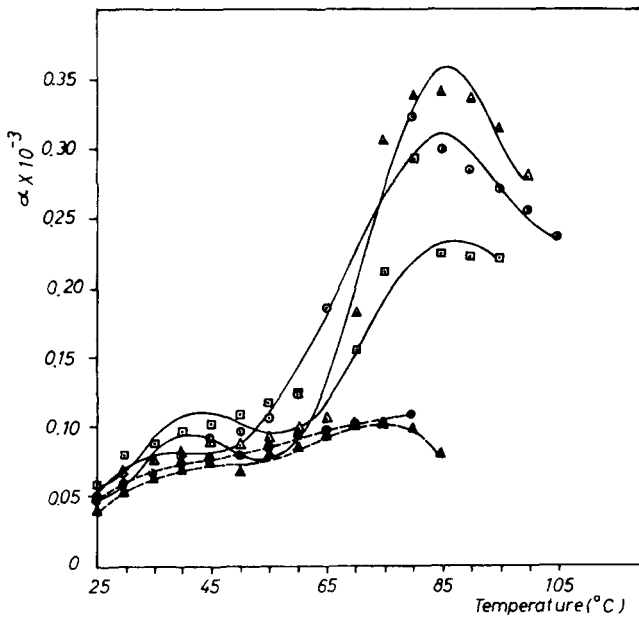


Fig. 8. Thermal expansion of PMMA-CN copolymers at different temperatures. (—) 11.4% N; (---) 12.2% N; (○) 2% CN; (▲) 4% CN; (□) 6% CN; (●) 2% CN; (△) 4% CN.

the relative behaviors of various materials under the test conditions.

The obtained results are illustrated graphically in Figure 8. The figure shows two transition points for each PMMA-CN copolymer containing CN of 11.4% N. The first transition point (at right) shifts to the right with the increase of CN concentration in the copolymer and were found to be 85, 86.3, and 87.8°C for 2, 4, and 6% CN, respectively. With respect to the second transition points (at left), as CN concentration increases they shift right also and the peaks become sharper; their values are 41 and 43.5°C for 4 and 6% CN, respectively; while the second transition point of the copolymer containing 2% CN could not be measured.

The copolymers containing CN of 12.2% N show regular behavior with rising temperature, and it is difficult to measure the transition temperature points of these copolymers.

It is well known that PMMA has one transition point, its value is 105°C. Thus, CN greatly affect the transition point of PMMA; also nitrogen content of the used CN plays an important role in this respect.

CONCLUSIONS

(1) PMMA-CN copolymers have lower modulus, tensile strength, and elongation at break than PMMA itself. Irradiation improves these properties in the copolymers but it has a bad effect on PMMA.

(2) PMMA-CN copolymers are harder than PMMA; their hardness increases with CN concentration, nitrogen content, and irradiation dose. Impact strength has the opposite effect.

(3) PMMA-CN copolymers have better abrasion resistance than PMMA. CN of 11.4% N gives better results in this respect.

(4) PMMA-CN copolymers containing CN of 11.4% N show secondary transition points. The values of the transition points increase with CN concentration. Copolymers containing CN of 12.2% N show no transition points.

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