

Thermal Stability of Grafted Fibers

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Synopsis

This paper presents the experimental results on the study of thermal stability of grafted fibers, i.e., polypropylene-, polyester-, and rayon-grafted fibers. These fibers were obtained by radiation grafting processes using hydrophylic monomers such as 1-vinyl 2-pyrrolidone, acrylic acid, *N*-methylol acrylamide, and acrylonitrile. The thermal stability of the fibers was studied using a Shimadzu Thermal Analyzer DT-30. It was found that the thermal stability of the fibers, which can be indicated by the value of the activation energy for thermal degradation, was not much improved by radiation grafting. The degree of improvement depends on the thermal stability of the monomers used for grafting. The thermal stability of a polypropylene fiber, either a grafted or an ungrafted one, was found to be inferior compared to the polyester of a rayon fiber, which may be due to the lack of C=O and C=C bonds in the polypropylene molecules. The thermal stability of a fiber grafted with acrylonitrile monomer was found to be better than that of an ungrafted one. However, no improvement was detected in the fibers grafted with 1-vinyl 2-pyrrolidone monomer, which may be due to the lower thermal stability of poly(1-vinyl-2-pyrrolidone), compared to the polypropylene or polyester fibers.

INTRODUCTION

Synthetic fibers such as polypropylene (PP) and poly(ethylene terephthalate) (PET) fibers have some drawbacks, i.e., low moisture regain, low dyeability at low temperature, and contain electric charge. Radiation grafting of hydrophylic monomers on the fibers has been proved to overcome the mentioned drawbacks. On the other hand, some natural fibers such as cotton and semisynthetic fibers such as rayon have also some drawbacks, i.e., low crease recovery and soil release. Radiation grafting has also been proved to overcome the mentioned drawbacks.

Studies on the use of radiation grafting for improvement of either synthetic or natural fibers have been carried out by a number of research workers.¹ However, some of its properties, such as the thermal stability, has not yet been extensively studied. Thermal stability of fibers is very important, especially if the fibers will be used in the tropical countries. For this reason, our group has extensively studied the thermal properties of grafted fibers, both natural and synthetic fibers. This paper presents the thermal behavior of the mentioned fibers, based on the experimental results of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The activation energy for thermal degradation, E_a , and the rate of isothermal degradation can be computed using the mentioned method.

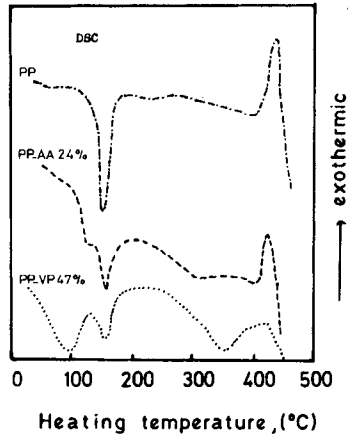


Fig. 1. Thermograms of polypropylene fibers. Influence of grafting on the endothermic peak of melting point.

THEORY

Thermogravimetric analysis (TGA) method is widely used to investigate the thermal decomposition of polymers, or to determine the decomposition kinetics such as activation energy and reaction order. These parameters can be used to indicate the thermal stability of polymers.

The rate of thermal decomposition of polymers is generally expressed by the equation

$$dC/dt = k(100 - C)^n = Ae^{-E_a/RT}(100 - C)^n \quad (1)$$

where dC/dt = rate of conversion, C = conversion (%), n = reaction order, E_a = activation energy, A = preexponential factor, and k = rate constant. If the

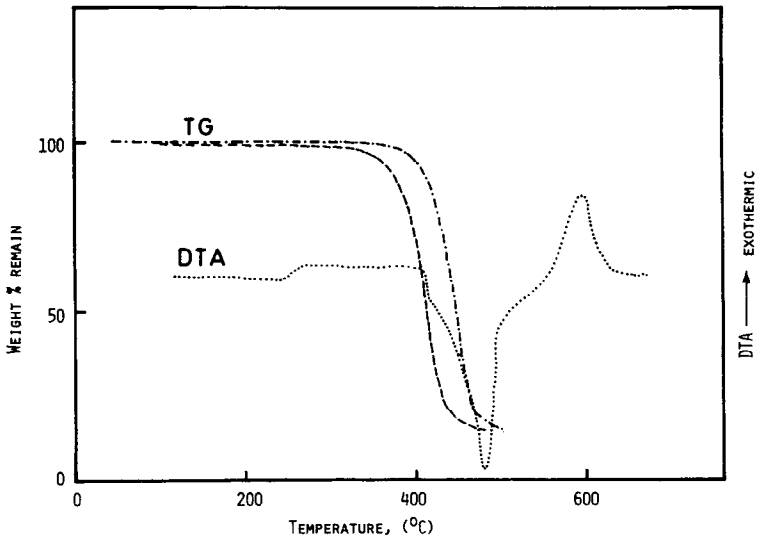


Fig. 2. Thermogram of PET fibers, unirradiated: (---) 5°C/min; (—) 30°C/min.

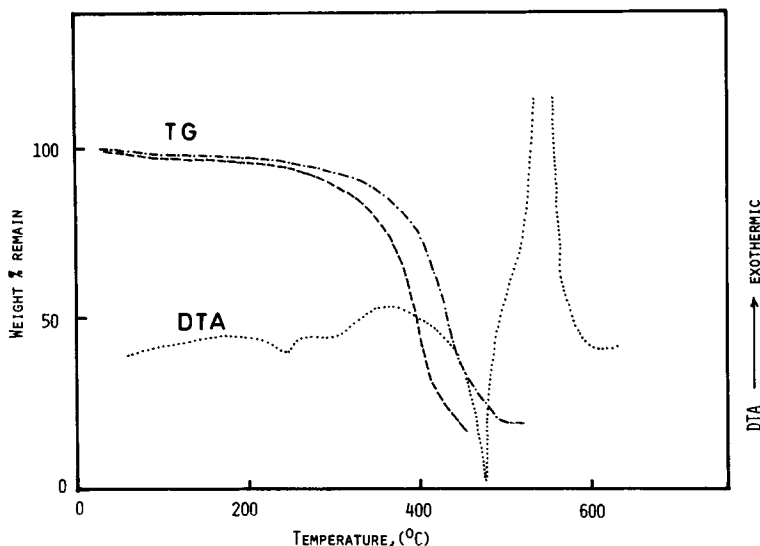


Fig. 3. Thermogram of PET-AA (21.5%) fibers: (---) 5°C/min; (—) 30°C/min.

heating rate is defined as $\beta = dT/dt$, eq. (1) can be rewritten as

$$dC/dt = A\beta^{-1}(100 - C)^n e^{-E_a/RT} \quad (2)$$

It is difficult to calculate the activation energy E_a using this differential equation, without any information about the order of the reaction. Several methods, based on the displacement of the thermogravimetric curve due to the increase of heating rate, have been used to calculate the activation energy for thermal degradation. By comparing two thermogravimetric curves with different heating rates β_1 and

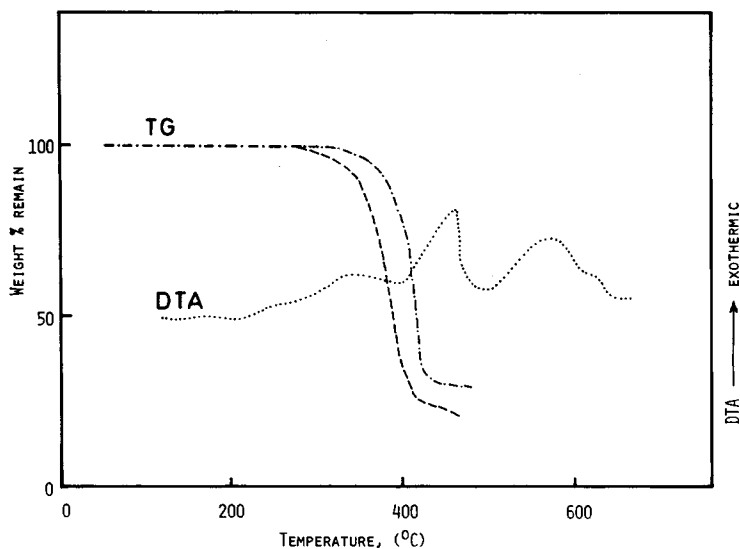


Fig. 4. Thermograms of PET-AN (15.5%) fibers: (---) 5°C/min; (—) 30°C/min.

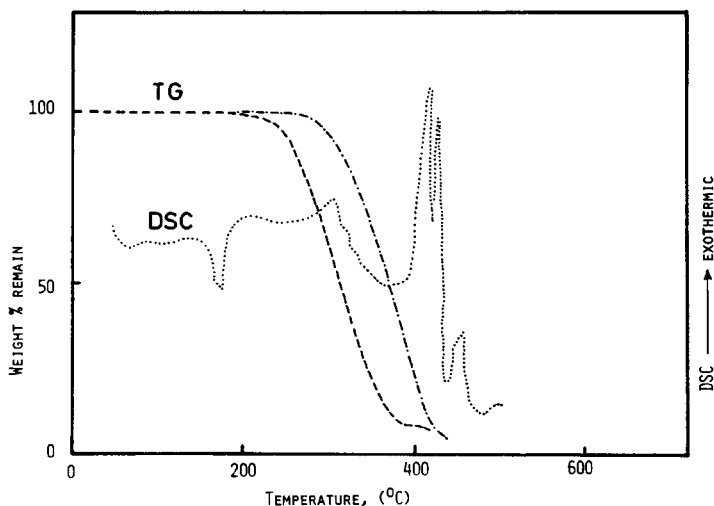


Fig. 5. Thermogram of PP fibers, unirradiated: (---) 5°C/min; (-.-) 30°C/min.

β_2 , it can be deduced that

$$(dC/dT)_1 \cdot (dC/dT)_2^{-1} = (\beta_2)(\beta_1)^{-1} e^{-E_a(1/T_1 - 1/T_2)/R} \quad (3)$$

where T_1 and T_2 are the temperatures at the same conversions for heating rates β_1 and β_2 , respectively.

For a number of experiments and in a limit region of conversion, it was found that $(dC/dT)_1 = (dC/dT)_2$. Hence by the assumption that (dC/dT) is the same for every heating rate, eq. (3) can be simplified as follows:

$$(\beta_1)(\beta_2)^{-1} = e^{-E_a(1/T_1 - 1/T_2)/R} \quad (4)$$

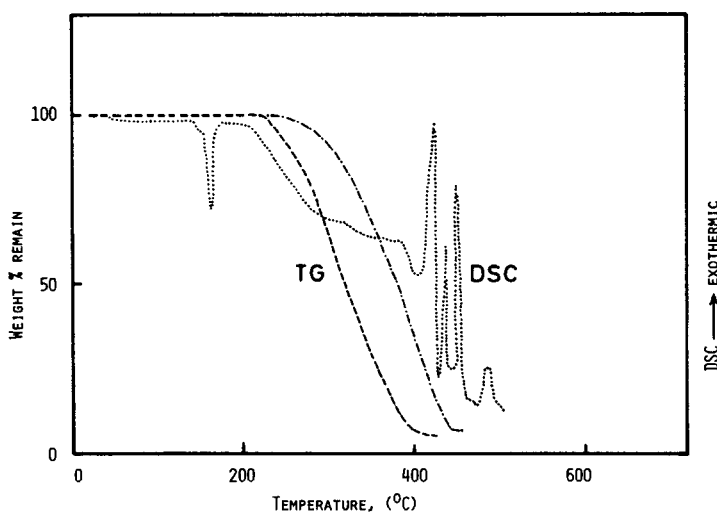


Fig. 6. Thermogram of PP fibers, irradiated, 2 Mrad: (---) 5°C/min; (-.-) 30°C/min.

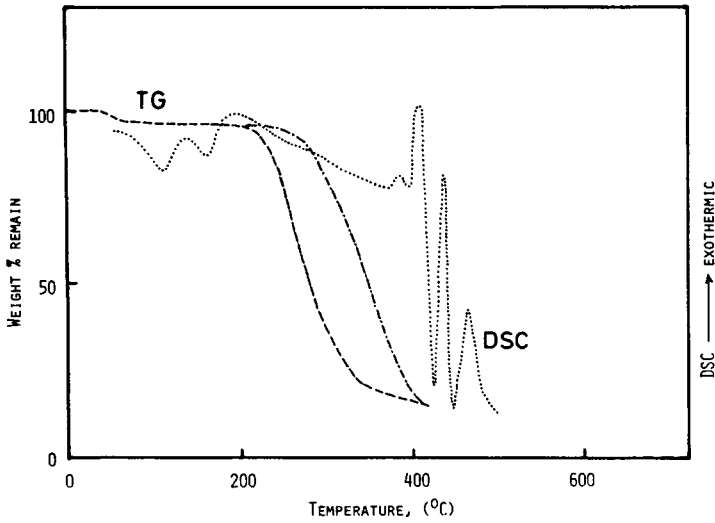


Fig. 7. Thermogram of PP-VP (32%) fibers: (---) 5°C/min; (-·-) 30°C/min.

or

$$E_a = R(T_1 T_2)(T_1 - T_2)^{-1} \ln(\beta_1/\beta_2) \tag{5}$$

Equation (5) is known as Osawa equation,^{2,3} that is, the equation based on the assumption that the displacement of thermogravimetric curve is parallel.

According to Reich,^{2,3} the activation energy E_a can be calculated using the following equation:

$$E_a \approx 4.6(1/T_1 - 1/T_2)^{-1} \log(\beta_2/\beta_1)(T_1/T_2)^2 \tag{6}$$

where E_a is defined in cal/mol and T in °K. It is found that, according to some experimental results, the activation energy calculated based on the equation of

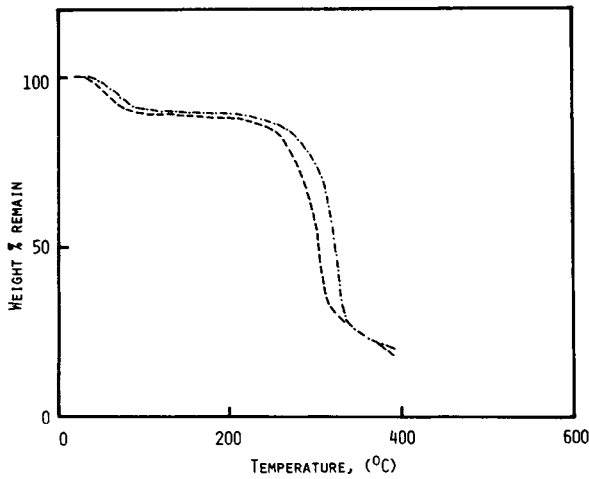


Fig. 8. Thermogram of Rayon fibers, unirradiated: (---) 5°C/min; (-·-) 30°C/min.

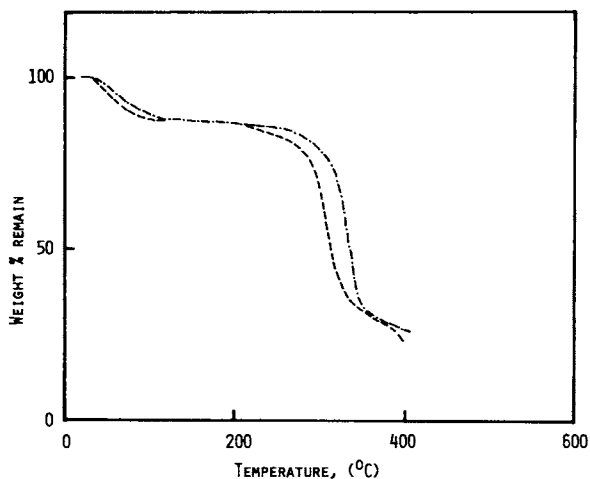


Fig. 9. Thermogram of Rayon-NMA fibers: (---) 5°C/min; (—) 30°C/min.

Osawa or Reich, do not differ much. The preexponential factor A and the reaction order n can be computed using eq. (1).

Another method for calculating E_a is by measuring the displacement of an exotherm peak by increasing the heating rate.⁴ A general equation was deduced for such a method:

$$\log \beta = 0.457E_a(1/T_m)/R \quad (7)$$

where β is the heating rate, 0.457 is a factor obtained from mathematical deduction, R is the universal gas constant, E_a is the activation energy, and T_m is the peak temperature ($^{\circ}\text{K}$). By plotting \log against $1/T_m$, a straight line is obtained whose slope is proportional to E_a .

EXPERIMENTAL

Poly(ethylene terephthalate) fibers were obtained from Indonesian Toray Synthetic. The samples were in the form of staple fibers, purified by washing

TABLE I
Bond Strength and Length⁷

Bond	Length (Å)	Dissociation energy (kcal/mol)
C—H	1.07	98
C—C	1.54	81
C—N	1.47	68
C—O	1.42	87
C=O	1.21	174
H—O	0.96	110
C≡N	1.16	200
C=C	1.33	145
C—Cl	1.76	79
C—Br	1.94	66
C—S	1.81	84
O—O	—	34

TABLE II
Kinetic Parameters of Thermal Degradation of Irradiated and Grafted Fibers

No.	Fiber	E_a (kcal/mol)		Reaction order (n)
		Reich	Osawa	
1	PET (0 Mrad)	49.03 ± 1.62	48.98 ± 1.57	1.30
2	PET (2 Mrad)	49.68 ± 1.25	49.60 ± 1.12	1.50
3	PET (4 Mrad)	42.97 ± 2.13	43.25 ± 2.05	0.90
4	PET (6 Mrad)	51.49 ± 2.45	51.25 ± 2.36	1.60
5	PET-AA (21.5%)	42.34 ± 3.45	42.56 ± 3.34	2.27
6	PET-ANa (23%)	49.66 ± 4.15	49.50 ± 3.34	4.17
7	PET-AN (15%)	52.87 ± 7.82	52.50 ± 7.42	0.16
8	PET-VP (21%)	40.75 ± 3.95	41.06 ± 3.80	1.41
9	PP (0 Mrad)	20.05 ± 2.74	21.22 ± 2.67	1.04
10	PP (2 Mrad)	21.17 ± 1.28	22.32 ± 1.29	1.42
11	PP (4 Mrad)	17.85 ± 1.09	19.16 ± 1.05	0.99
12	PP (6 Mrad)	18.69 ± 0.49	19.95 ± 0.50	1.27
13	PP-AA (21%)	25.10 ± 5.66	26.07 ± 5.45	3.11
14	PP-ANa (21%)	23.51 ± 2.35	24.21 ± 2.34	5.32
15	PP-AN (29%)	25.43 ± 1.94	26.21 ± 1.78	2.54
16	PP-VP (32%)	16.56 ± 1.50	17.86 ± 1.47	1.28
17	Rayon (0 Mrad)	55.65 ± 4.74	54.78 ± 4.51	0.92
18	Rayon (2 Mrad)	50.62 ± 5.58	50.33 ± 5.45	0.65
19	Rayon (4 Mrad)	49.68 ± 5.72	49.24 ± 5.77	0.99
20	Rayon-NMA	57.19 ± 13.54	56.16 ± 12.85	1.71

Notes: PP = polypropylene; PET = poly(ethylene terephthalate) (polyester); PP-AA = polypropylene-acrylic acid; PP-VP = polypropylene-vinyl pyrrolidone; PP-AN = polypropylene-acrylonitrile; PET-AA = poly(ethylene terephthalate)-acrylic acid; PET-VP = poly(ethylene terephthalate)-vinyl pyrrolidone; PET-AN = poly(ethylene terephthalate)-acrylonitrile; Rayon-NMA = rayon-*N*-methylol acrylamide.

in a detergent solution and dried before used. Polypropylene employed in these experiments were in the fibrous form, supplied by Phillip Company. These fibers were purified by washing in a detergent solution, and dried before used.

Irradiation of the fibers were carried out in a Panoramic GAMMA Co-60 irradiator, of 70,000 Ci. Doses of irradiation were 2, 4, and 6 Mrads, in open air. These experiments were carried out to investigate the effect of irradiation on the thermal stability of the fibers.

Grafted fibers were prepared using trapped radicals grafting technique, for polypropylene, poly(ethylene terephthalate), and rayon fibers.^{1,6} The irradiation dose needed for this grafting technique did not exceed 2 Mrad, and the irradiation was carried out in a vacuum tube.

Shimadzu Thermal Analyzer DT-30 was used for the thermal analysis. These experiments were carried out in a stream of nitrogen. The E_a for thermal degradation of the samples were determined using the Reich and Osawa equation.

RESULTS AND DISCUSSION

Effect of Radiation Grafting on Crystallinity

The thermograms of either grafted and ungrafted polypropylene fibers can be seen in Figure 1. It is found that either radiation or radiation grafting of hydrophilic monomer on polypropylene fibers do not have any influence on the

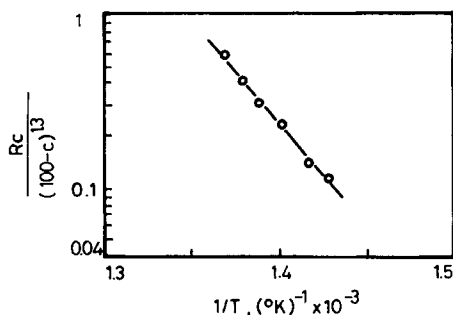


Fig. 10. Arrhenius plot of the 1.3rd reaction order of thermal degradation of PET fibers. 0 Mrad.

crystallinity of the fibers. It is seen that the endothermic peaks of melting point of polypropylene fibers, which is around 170°C, do not disappear by radiation or radiation grafting. These experimental results can be used to indicate that the crystalline regions of the fibers still exist even after radiation grafting process. It can be concluded that the grafting process only occurs in the amorphous regions and not in the crystalline region, which may be due to the difficulty of the diffusion of monomer into the crystalline region. And so, it can be expected that the storage life of trapped radicals in the crystalline region is longer than in the amorphous regions. For this reason, some ideas arise stating that grafting reaction only takes place in the boundary of the crystalline regions and not in the amorphous regions.

The endothermic peaks at temperature below the crystalline melting point (Figs. 1 and 4) may be due to the evaporation of water absorbed by the grafted fibers, which shows the hydrophilicity of the grafted fibers. It was found that the hydrophilicity of PP-VP 47% is higher than the PP-AA 24% fibers.

Effect of Grafting on the Thermal Stability

Figures 2 and 4 show the thermograms of PP and PP-VP fibers. It can be seen that, at the rate of temperature increase of about 30°C/min, either PP and PP-VP fibers begin to degrade at temperature of about 40°C. It is clear that,

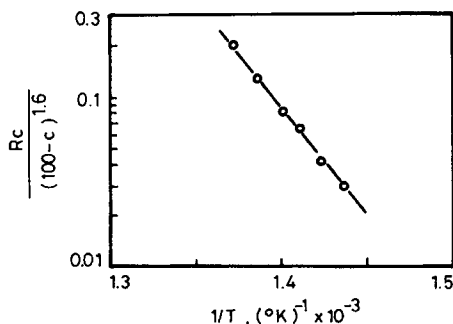


Fig. 11. Arrhenius plot of the 1.6th reaction order of thermal degradation of PET fibers, irradiated with a dose of 6 Mrad.

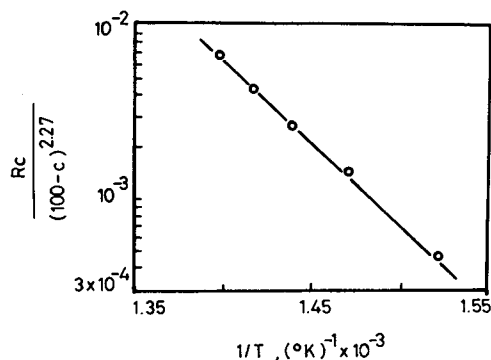


Fig. 12. Arrhenius plot of the 2.27th reaction order of thermal degradation of PET-AA fibers.

using these thermograms, it is difficult to make a conclusion concerning the effect of grafting on the thermal stability.

Figures 5-9 show the thermograms of PET, Rayon, and grafted fibers. It is clear that PET, PET-AA, and PET-AN begin to degrade at a temperature of about 400°C and finish at a temperature of about 450°C. It can be concluded that PET fibers are more thermostable compared to PP fibers, but the effect of grafting on the thermal stability is not clear. For this reason it is necessary to find another method of detection. Determination of the activation energy of thermal degradation may be the best method for studying the effect of radiation grafting on the thermal stability of fibers.

The thermal stability of any polymeric material is largely determined by the strength of the covalent bond between the atoms inside the polymer molecules. The value of any bond strength has been calculated and tabulated in Table I.

Based on the data in Table I, it can be calculated that the average complete dissociation energy of PET fibers is about 103.8 kcal/mol, about 91.6 kcal/mol for PP fibers, about 102 kcal/mol for poly-AA, about 92.6 kcal/mol for poly-VP, and about 106 kcal/mol for poly-AN. The lower dissociation energy of PP fibers compared to PET fibers is largely due to the lack of C=C and C=O bonds in the PP molecule. However, although poly-VP also contains the C=O bond, the average dissociation energy is found to be comparable to PP fibers, because poly-VP contains the C-N bond, which is very weak.

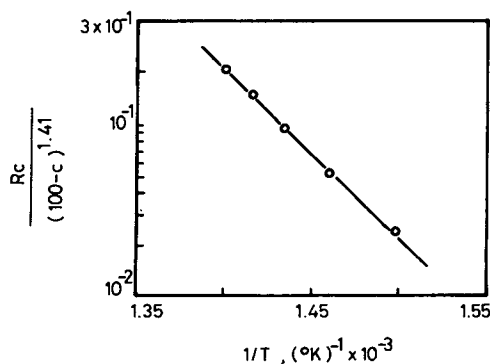


Fig. 13. Arrhenius plot of the 1.41st reaction order of thermal degradation of PET-VP fibers.

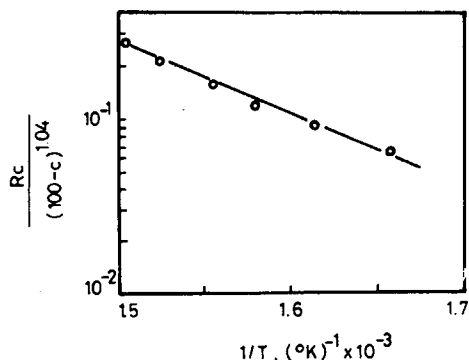


Fig. 14. Arrhenius plot of the 1.04th reaction order of thermal degradation of PP fibers. 0 Mrad.

Using the mentioned calculation, it can be predicted that grafting AA monomer onto PET fibers cannot improve the thermal stability of the fibers, because the average dissociation energy of PET fibers is higher compared to poly-AA. By the same reason it can be predicted that radiation grafting of AA monomer onto PP fibers will improve the fibers thermal stability. It can be predicted that radiation grafting of VP monomer onto PET and PP fibers cannot improve the thermal stability of the fibers. On the other hand, radiation grafting of AN monomer onto either AA or PET fibers can be expected to get the improvement of its thermal stability, due to the higher dissociation energy of poly-AN compared to PP and PET fibers.

The average dissociation energy of the mentioned polymers were obtained by the assumption that the polymers were completely dissociated into atoms. However, in general, complete dissociation into individual atom never occurred. The degradation products of polymers are usually materials with small molecular weight. In this case, the average dissociation energy must be lower compared to the previous calculation. This idea is in agreement with the fact that the activation energy of thermal degradation of polymers are always lower compared to the expected dissociation energy.

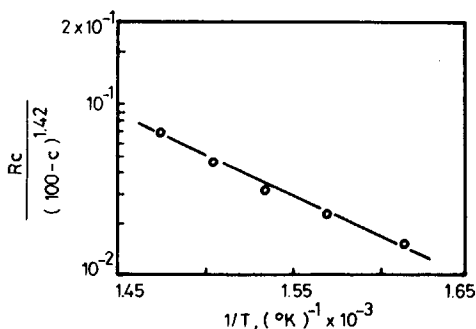


Fig. 15. Arrhenius plot of the 1.42nd reaction order of thermal degradation of PP fibers, irradiated with a dose of 2 Mrad.

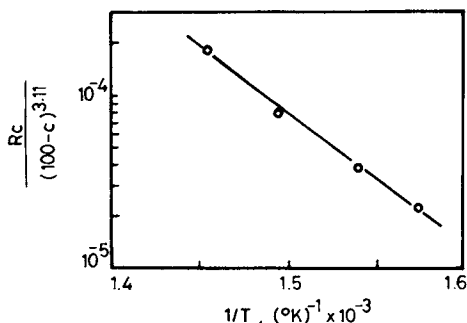


Fig. 16. Arrhenius plot of the 3.11th reaction order of thermal degradation of PP-AA fibers.

Studies on the effect of radiation grafting on the thermal stability of PP, PET, and Rayon fibers have been carried out using thermogravimetric method. Using this method, it can be determined the activation energy E_a , which can be used as an indicator for the thermal stability. Table II shows the activation energy of thermal degradation of various fibers obtained by the mentioned method. It can be seen that the activation energy of PP-AA is about 25.1 kcal/mol (Reich), which is higher compared to the activation energy of PP fibers. In the other words, it can be said that PP-AA fibers are less degradable compared to PP fibers, or radiation grafting of AA monomer onto PP fibers causes an increase in the fibers' thermal stability. By the same method it can be concluded that radiation grafting of AA monomer onto PET fibers will decrease the fibers thermal stability. It can be understood that these experimental results are in agreement with the mentioned theoretical prediction.

The activation energy of PP-VP and PET-VP fibers are found to be lower compared to the ungrafted one, as shown in Table II. In other words, it can be said that radiation grafting of VP monomer onto either PET or PP fibers will decrease the fibers' thermal stability. Again, these experimental results are in agreement with mentioned theoretical prediction based on the bond strength calculation.

Table II shows that the activation energy of PP-AN and PET-AN fibers are higher compared to the PP or PET fibers, which is in agreement with the theoretical prediction. According to this theory, the dissociation energy of poly-AN is higher than the dissociation energy of PP or PET fibers, due to the presence of $\text{C}\equiv\text{N}$ bond.

Effect of Radiation on the Thermal Stability

Table II shows the effect of radiation on the activation energy of thermal degradation of PET, PP, and Rayon fibers. It is found that the activation energy slightly decreases with the increase of irradiation dose and, after attaining a certain value, then increases again. The decrease of activation energy of thermal degradation by the increase of irradiation dose may be due to the formation of peroxide, which the bond energy is relatively low. On the other hand, the increase of activation energy may be due to the formation of double bond and crosslinking.

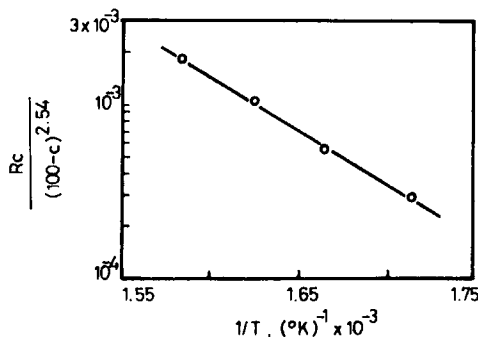


Fig. 17. Arrhenius plot of the 2.54th reaction order of thermal degradation of PP-AN fibers.

Reaction Order

The value of reaction order n can be determined by using eq. (1), after the value of the activation energy has been previously determined. The reaction order n of fibers thermal degradation, for the range of conversion between 30% and 70%, can be seen in Table II. It is seen that radiation, with dose up to 6 Mrads, will slightly influence the reaction order of the thermal degradation, which these values are close to 1. It means that radiation only slightly influences the mechanism of thermal degradation.

On the other hand, it is found that radiation grafting markedly influences the reaction order of thermal degradation, which indicates the complexity of the thermal degradation reaction. If the rate of thermal decomposition can be denoted as R_c , then it can be computed that

$$\ln R_c / (100 - C)^n = -E_a / RT + \ln A \quad (8)$$

It is clear that the semilog plot of $R_c / (100 - C)^n$ vs. $1/T$ must be a straight line. The linearity of the semilog plot can be seen in Figures 10-17.

Isothermal Degradation

The rate of isothermal degradation can be computed using eq. (1), provided that all kinetics parameters needed for the computation are known. Table III shows the results of the computation for the rate of isothermal degradation at 50% conversion. It can be seen that radiation has a slightly influence on the rate of isothermal degradation, but radiation grafting has a significance. It is found that the rate of isothermal degradation of PET-AA and PET-VP fibers are higher than the PET fibers, which may be due to the higher thermal stability of the backbone chain (PET) compared to the graft chain (poly-AA and poly-VP). On the other hand, it is found that the rate of isothermal degradation of PP-AA and PP-AN fibers are lower compared to the PP fibers, which may be due to the lower stability of the backbone chain (PP) compared to the graft chain (poly-AA and poly-AN). These experimental results are in agreement with the theoretical prediction based on the computation of the bond energy. In general, it can be concluded that the improvement of the thermal stability of grafted fibers depends on the monomers used for the grafting. However, the stabilizing effect of grafting AN monomer onto PET fibers is difficult to be appreciated, because the disso-

TABLE III
Isothermal Degradation Rates of Fibers, at 50% Conversion

No.	Fiber	dC/dT (% conversion/min)		
		200°K	300°K	400°K
1	PET (0 Mrad)	1.15×10^{-37}	7.98×10^{-20}	6.66×10^{-11}
2	PET (2 Mrad)	3.20×10^{-38}	3.74×10^{-20}	4.04×10^{-11}
3	PET (4 Mrad)	2.43×10^{-33}	1.38×10^{-17}	1.04×10^{-9}
4	PET (6 Mrad)	2.83×10^{-39}	1.32×10^{-20}	2.89×10^{-11}
5	PET-AA (21%)	1.22×10^{-32}	3.89×10^{-17}	2.20×10^{-9}
6	PET-ANa (25%)	3.30×10^{-38}	3.55×10^{-20}	3.68×10^{-11}
7	PET-AN (15%)	1.93×10^{-39}	2.57×10^{-20}	9.40×10^{-11}
8	PET-VP (21%)	2.04×10^{-31}	1.85×10^{-16}	5.55×10^{-9}
9	PP (0 Mrad)	5.96×10^{-16}	3.20×10^{-8}	2.35×10^{-4}
10	PP (2 Mrad)	5.34×10^{-18}	7.22×10^{-9}	8.40×10^{-5}
11	PP (4 Mrad)	2.32×10^{-16}	2.22×10^{-7}	6.85×10^{-4}
12	PP (6 Mrad)	7.36×10^{-15}	1.34×10^{-7}	5.78×10^{-4}
13	PP-ANa (21%)	1.39×10^{-16}	9.15×10^{-8}	2.35×10^{-3}
14	PP-AA (21%)	1.68×10^{-19}	5.27×10^{-10}	2.95×10^{-5}
15	PP-AN (15%)	5.41×10^{-19}	1.91×10^{-9}	1.31×10^{-4}
16	PP-VP (32%)	4.72×10^{-13}	1.51×10^{-6}	2.71×10^{-2}
17	Rayon (0 Mrad)	5.39×10^{-39}	4.86×10^{-19}	4.62×10^{-9}
18	Rayon (2 Mrad)	6.65×10^{-37}	1.44×10^{-18}	2.12×10^{-9}
19	Rayon (4 Mrad)	1.30×10^{-36}	1.64×10^{-18}	1.82×10^{-9}
20	Rayon-NMA	1.82×10^{-46}	1.27×10^{-25}	3.29×10^{-15}

ciation energy of PET fibers and poly-AN are comparable, which are 103.8 kcal/mol and 106 kcal/mol.

CONCLUSION

Generally speaking, radiation grafting of hydrophylic monomers has a significant influence on the thermal stability of the fibers. The lower thermal stability of PP fibers compared to PET or Rayon fibers may be due to the lack of C=O and C=C bonds in the PP molecules. Even the PP fibers have been grafted with hydrophylic monomer until the degree of grafting reaches a value of 29% (PP-AN), the thermal stability is still lower compared to PET and Rayon fibers. In general, it can be concluded that the thermal stability of grafted fibers depends on the thermal stability of monomers used for the grafting reaction.

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