COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 28 ANNÉE 1982

The Carbonisation of Synthetic Polymer Mixtures - I
The Carbonisation of Polyacrylonitrile and Polyethylene Terephtalate Mixtures

By

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Communications de la Faculté des Sciences de l'Université d'Ankara

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(Received May 24, 1982; accepted May 28, 1982)

Summary

The following work concerns with the carbonisation polyacrylonitrile and polyethylene terephtalate mixtures of different compositions. Polyacrylonitrile originated carbons predominate in the corbonisation products of the mixtures containing more than 30 % of this polymer. The increasing proportions of polyacrylonitrile increases carbonisation yield. All carbonisation product give BET Type-I adsorption isotherms. Activation to 30 % burn-off increases the adsorption capacity while further activation decreases. At low polyacrylonitrile concentrations adsorption and activation characteristics are determined by polyethylene terephtalate.

INTRODUCTION

The industrial usage of active carbon has increased rapidly since 1854 when it was first used to adsorb pathogenic micro organisms[1]. In recent years, continuously rising petrol prices forced car manufacturers to take some measures to reduce the petrol consumption. Hence, emission control system was developed. The basic component of this system is active carbon containing canisters. Thus besides the other industries, the active carbon is also an important input of automative industries of this century[2].

For the poduction of active carbon, different naturally occuring raw materials are in usage[3]. For the last decade the thermosetting resins and thermoplasts were used largely for this purpose since, they preserve their highly ordered structure and homogeneity of the size and the shape of porous system, after being thermally degraded[4,5]. The research works in this field are concentrated on the thermal degradation of homopolymers and copolymers[6,7]. However, the carbonisation of the physical mixtures of different polymers are not considered. For instance, the amount of the wastes obtained from textile industries which are usually fibre blends; can offer a big potential of the raw material for the production of active carbon. Bearing this potential in mind, in the following article, the carbonisation properties of the blends of polyacrylonitrile and polyethylene terephtalate are investigated. The carbon dioxide activation of the carbons obtained and the adsorption properties of the carbonised and activated products are also investigated.

EXPERIMENTAL

a– Materials: Polyacrylonitrile (PAcN), was prepared in the laboratory from vinylcyanide (BP: 77°C) obtained from B.D.H. and purified by freeze and thaw method. 0.8 g of diazoaminobenzene (as catalyst) was dissolved in 80 g (100 ml) of vinylcyanide. This solution was divided into 25 ml portions and transferred in suitable test tubes and then were sealed-off. They were then immersed into hot water bath (100°C) for 2-3 hours. Polymers were taken out by breaking the tubes. To remove unpolymerised vinylcyanide, the polymer was let to stand overnight in a vacuum dessicator at room temperature and 200 mm Hg pressure.

Polyethylene terephtalate (PETP), the other polymer selected, was obtained from ICI Plastic Division.

Binary mixtures of these polymers were prepared so that the weight per cent of one them was increasing while the other decreasing. These mixtures were milled in a ball mill to reduce the particle size to 20 mesh and to reach possible highest homogenisation.

b– Method: The mixtures were carbonised in a tube furnace in nitrogen atmosphere (500 $cm^3. min^{-1}$) at 900°C. The heating rate was $5°C.min^{-1}$. Before the carbonisation started the furnace was purged for two hours. The same nitrogen flow was kept on throughout the experiment.

5 g of mixture, in a quartz float, was situated in the homogeneous heating zone of the furnace and the temperature was taken up to 900°C at which the samples were stayed for four hours. Then the power was

turned off and the system was let to cool to the ambient temperature. The carbons thus obtained were preserved in a dessicator over silicagel under nitrogen atmosphere.

Activation of the carbons were performed in a modified Stanton TR-I recording thermobalance using 200 $cm^3 . min^{-1}$ carbon dioxide flow as activator[8]. By definition activation is the per cent weight loss of the sample under investigation in experimental terms and it is called as degree of activation, burn-off or gasification. The activation temperature was the same as that of carbonisation and the degree of activation selected was 10, 30 and 50 % for each sample. The densities taken were 0.808 $g. cm^{-3}$ at -196°C and 1.56 $g. cm^{-3}$ at -79°C for nitrogen and carbon dioxide respectively to convert the data obtained from adsorption measurements when it is necessary[9]. The time required for the adsorption equilibrium was normally 20 to 30 minutes for most of the samples. However, the equilibrium time for the nitrogen adsorption of the unactivated samples was very long (more than 24 hours in some cases), hence only a few nitrogen adsorptions of those could be measured.

RESULTS

The yield of the carbonisation products and their ultimate analyses are presented in Table-I. Figure-1, on the other hand shows the plots of percent values of carbon, hydrogen and nitrogen against the original compositions of the mixture.

Since all the adsorption isotherms, either for carbon dioxide or nitrogen, were Type-I in BET[10] classification, only typical ones for 50 % PAcN – 50% PETP mixture carbons are included. Figure-3 and 4, show the adsorption isotherms of carbon dioxide and nitrogen of the sample obtained afore' mentioned mixture.

The adsorbed amount of the adsorbates "C values", at adsorption temperatures and saturation vapour pressures were used for the comparison of adsorption behaviour of the carbons prepared. Figure-5 and 6 illustrate the variation of (C) values with original compositions of the polymer mixtures at different degrees of activations and unactivated carbons, for carbon dioxide and nitrogen respectively. The saturation vapour pressures used for carbon dioxide was 1.86 atm at -79°C[11] and

Table - I: The yield of 900°C carbonisation products of different PAcN-PETP mixtures and the results of the ultimate analysis of the carbons produced

Composition of original polymer mixtures.		The yield of carbonisation	The results of ultimate analysis of the carbon produced.			
PAcN, %	PETP, %	%	C, %	H, %	N, %	O* %
100	0	51.0	85.5	1.52	12.5	—
90	10	51.5	84.0	1.50	13.5	1.00
80	20	49.5	82.0	1.50	14.0	2.50
70	30	47.5	80.5	1.50	14.5	3.50
60	40	44.0	79.3	1.51	14.5	4.69
50	50	40.0	78.5	1.55	14.5	5.45
40	60	36.0	78.5	1.52	14.0	5.98
30	70	32.0	79.0	1.51	12.5	6.99
20	80	27.5	80.5	1.50	10.5	7.50
10	90	24.0	83.0	1.53	7.5	7.97
0	100	20.5	86.0	1.51	Trace	12.49

*: by difference. Pure PAcN excepted.

1.00 atm for nitrogen at -196°C[12]. (C) values of carbon dioxide and of nitrogen are also tabulated in Table-II.

In Figure-2, the gasification rates (as mass of gasified carbon per second per unit mass of sample, $g.g^{-1}.\ sec^{-1}$) of the carbons in carbon dioxide are plotted against the composition of the original polymer mixtures.

The Dubinin equation is used to characterise the pore structure of the carbons. The developed form of this equation is as follows[13]:

$$\log V = \log V_o - \frac{B\ T^2}{\beta} \log^2(P_o / P)$$

where; V: amount adsorbed at equilibrium pressure P, V_o: micropore capacity, P_o: saturation vapour pressure at T°K, B: constant, β: affinity coefficient of adsorbate relative to nitrogen.

Table – II : The variations of (C) values with original polymer mixtures at different burn-offs and the deviations from Dubinin plots.

Composition		(C) values for CO_2, $mg.g^{-1}$				(C) values for N_2, $mg.g^{-1}$				Type of deviations			
PAcN %	PETP %	B.O 0 %	B.O 10 %	B.O 30 %	B.O 50 %	B.O 0 %	B.O 10 %	B.O 30 %	B.O 50 %	B.O 0 %	B.O 10 %	B.O 30 %	B.O 50 %
100	0	7.0	75.0	51.0	25.0	—	49.5	56.0	29.5	M/L	N	N	N
90	10	2.5	77.0	97.5	55.0	—	—	—	—	—	—	—	—
80	20	4.0	66.5	91.0	29.5	—	46.0	73.0	15.0	L	N	N	N
70	30	4.5	76.0	88.5	19.0	—	43.5	80.0	10.0	L	N	N	N
60	40	7.5	66.0	90.5	24.0	—	—	—	—	—	—	—	—
50	50	10.6	69.0	101.0	65.0	—	43.0	82.0	57.0	M	L/N	N	N
40	60	10.0	82.0	150.0	156.0	—	54.0	105.0	129.0	M	L/N	N	N
30	70	44.0	131.0	192.0	221.0	—	81.0	143.0	171.0	L	L	N	N
20	80	90.0	174.0	265.0	293.0	—	112.0	190.0	224.0	L	L	N	N
10	90	155.0	221.0	349.0	412.0	—	128.0	251.0	333.0	M	M	L	N
0	100	255.0	302.0	515.0	710.0	—	195.0	315.0	529.0	M	M	M/L	N

According to Dubinin[14], Plotting log V values against $\log^2(P_o/P)$ produces a line. The slope of it which is equal to (BT^2/β), is a measure of microporosity of the sample under investigation and the intercept equals to log V_o. Some of the Dubinin plots are given in Figures- 7,8,9 and 10.

In some cases, deviations from the Dubinin plots are observed and they are classified by Marsh[15,10]. This classification states that two main types of deviations are observed; one of them is concave relative to abscissa, called Type-M, while the other convex to the same axis called Type-N deviations. It is also stated that these deviations arise from the structural changes of the pore system. The types of deviations from the Dubinin plots for the carbons prepared are depicted in Tablo-II.

DISCUSSION

As can be seen from Table-I and Figure-1, the carbonisation yield of pure PAcN which is around 51 %, decreases by increasing amount of PETP in the original polymer mixture. The carbonisation yield of PETP is only 20 % . Reduction of PAcN, starting from the mixture of 70 % PAcN – 30 % PETP, results almost a linear decrease of the yield of carbonisation product. Thus increasing the ratio of PETP in the original mixture reduces the yield of carbonisation.

It is quite natural that the yields of carbonisation of the binary polymer mixtures are closely related to the carbonisation characteristics of individual components. Considerable differences exist in the carbonisation behaviours of PAcN and PETP.

The carbonisation yield of PAcN is approximately 2.5 fold of that PETP (see Table-I) which is found to be in good agreement with the literature[17]. During the carbonisation of PAcN neither polymer itself nor intermediate products of thermal degradation melt or pass through a plastic state. At the early stages of the carbonisation, it is assumed that the linear chain structure of the polymer is converted into condensed ring systems[17], due to the intra-or interchain cyclisation which in turn retains carbon atoms in the structure and increase the carbonisation yield[18,91]. In return, PETP melts at 247°C, turns into liquid and from the early stages of carbonisation it disintegrates largely by chain scission. Meanwhile the removal of side chain substituents is also observed[20]. Under these circumstances the possibility of the retaining carbon atoms in the structure is remote. The overall result of this phenomena is the decrease of the carbonisation yield. If the main concern of the carbonisation of this mixture is high yield, the proportion of PAcN should be higher or at least equal to 70 %.

As the nitrogen content of the carbons prepared from PAcN fluctuates in a considerably narrow interval[21,22,23], it was thought that it would be possible to use it, to trace the origines of the carbons obtained by the carbonisation of the PAcN-PETP mixtures. Actually, in the carbons produced from 90 to 30 % PAcN containing original mixtures, the nitrogen content stays unchanged and falls down quite rapidly when PAcN content of the original polymer mixture is less or equal to 30 % (see Table-I and Figure-1). The stability of nitrogen may lead to conclude that in this interval of PAcN the amount of carbon, originated from PAcN is higher than the carbon originated from PETP. As it was stated before, PAcN does not melt while PETP melts at 247°C. Thus at the early stages of carbonisation, liquid PETP surrounds the PAcN particles and prevents the removal of the volatiles resulting from the thermal disintegration of PAcN. Further heating resolidifies PETP to form a core raound PAcN particles that hinders exclusion of the thermal decomposition intermediates from PAcN. Under these conditions one can assume that the reactions of such carbons are conducted mainly by PETP carbon particles forming a core. The hydrogen values of the carbonisation products of the original polymer mixtures, are somewhat an experimental evidence for this assumption. Since the final products of thermal disintegration of PAcN are ammonia and hydrogen[24], it can be accepted that the only source of hydrogen left has to be PETP core. Having this core around PAcN particles should produce constant hydrogen values findings. In fact, if Table-I and Figure-1 are examined, it can be seen that hydrogen contents are constant and independent of the composition of original polymer mixtures.

The carbons obtained were activated with carbon dioxide at 900°C and the variations of the reaction rates that are expressed as loss of mass per second per unit mass of sample, with the original polymer mixture compositions are presented in Figure-2. The reaction rates (k), were found to be $5x10^{-5} g.g^{-1}. sec^{-1}$ for those samples containing 50 %

or more PAcN originally and they stay approximately constant. (k) values increases with decreasing proportion of PAcN. For instance, the (k) values estimated for the mixtures of 60 % PAcN – 40 % PETP and 20 % PAcN – 80 % PETP, are $7x10^{-5}$ and $12x10^{-5}$ $g.g^{-1}$. sec^{-1} respectively (see Figure-2). In addition to high and constant nitrogen content, the lower gasification rates at higher PAcN proportions in the original polymer mixtures, can be taken as another experimental evidence for the predominance of PAcN originated carbons in the sample under investigation.

Activation energies found by using Arrhenius equation were 38.24 and 28.68 kcal. mol^{-1} for PAcN and PETP carbons respectively. According to these results, it is very easy to understand faster gasification rate of PETP carbons compared to PAcN carbons. Thus higher the proportion of PAcN in an original polymer mixture is, slower the gasification rates are. Based on this observation it can be said that the original mixture having a high proportion of PAcN, contains more PAcN originated carbon. Moreover, the comparison of the activation energies indicates that the preferable retention of PAcN carbon is reflected to the relative reaction rate.

As it is already mentioned that increasing PETP ratio increases also the gasification rate. (k) values for the 95 % PETP – 5 % PAcN mixture and pure PETP are $13.2x10^{-5}$ and $9.1x10^{-5}$ $g.g^{-1}$. sec^{-1} respectively (see Figure-2). That is, the mixture reacts 1.5 fold faster than pure polymer. The attention has been focused to the gasification rate enhancement of the 5 % PAcN; since the search of the reason of this observation is out of the main concern of this work, it was not investigated here.

Since, all of the adsorption isotherm were Type-I in BET[9] classification, only typical ones, belonging to 50 % PAcN - 50 % PETP mixture carbons, are given (see Figure-3 and 4). Thus pore diameters of the samples prepared are no wider than a few adsorbate molecule diameter. In addition, no hysteresis loops were observed in none of the carbons prepared. This is the indication of the complete filling and emptying of the pores of all sizes, during the adsorption desorption cycle[25].

As it was expected, Figures-3 and 4 reveal that the activation increases of the adsorbed amount. "Sharp Knee" obviously seen in the carbon dioxide and nitrogen adsorption isotherms of unactivated and activated to 10 % burn-off carbons, becomes less conspicuous or disappears altogether by further activation (see Figures-3 and 4). This transformation signifies to some alteration on the pore system i.e, convertion from microporosity to the transitional porosity, due to the heat treatment and C-CO_2reaction[26]. The samples activated to 30 % burn-off adsorbs more than those activated to 50 % burn-off. This can be explained by assuming the formation of ordered crystalline centers[27] and of constricted entrance of the pores.

The variations of (C) values for carbon dioxide and for nitrogen with original compositions of the mixture at different burn-offs are presented in Figures-5 and 6. As it can be seen from these figures, (C) values are rapidly increasing in the samples containing less than 50 % PAcN in original polymer mixtures and highly activated carbons. The maximum (C) values are obtained at 30 % gasification for each individual mixture. Further activation (e.g. 50 %) reduces the (C) values (see Table-II). No big differences were observed on the (C) values of unactivated and activated carbons prepared from the polmer mixtures containing PAcN in the range of 90 % - 50 %. The predominancy of PAcN carbons in the samples just mentioned and the low capacity of adsorption of the PAcN carbons can be used to describe relatively low and approximately constant (C) values. The (C) values of the nitrogen are smaller than the (C) values of carbon dioxide. It was thought that this is due to the temperature dependency of diffusion rate of the nitrogen molecules into micropores rather than lower adsorption capacities of the samples prepared[28].

Decreased proportion of PAcN (less than 50 %) in the original carbonisation mixtures and higher degrees of activation increase the (C) values for both carbon dioxide and nitrogen. Since the amount of PETP carbon enveloping the PAcN carbon particles is higher in these samples, either activation or adsorption characteristics are determined by PETP carbon. If it is remembered that PETP carbonises by chain scission and elimination of the chain end groups and side chain substituents, it can be accepted that it produces highly porous carbon. In addition, during the activation process C – CO_2 reaction increases the numbers of adsorption sites. As a result of these two phenomena the adsorbed amount of the adsorbates increases considerably (see Table-II and Figures-5 and 6).

The ratio (S) of the adsorbed amount of nitrogen to carbon dioxide, i.e. the ratio of the (C) values of nitrogen to the (C) values of carbon dioxide, for different carbons obtained from different compositions of polymer mixtures, varies in the range of 0.6-1.2 (see Table-III). Although such proportioning does not have any quantitative significance due to the temperature dependency of nitrogen adsorption, some qualitative results can be obtained related to the enlargement of the pores.

Table - III: The ratio (S) of adsorbed nitrogen to carbon dioxide at saturation vapour pressure and adsorption temperature

Composition of original polymer mixtures		Burn - off		
PAcN %	PETP %	10 %	30 %	50 %
100	0	0.66	1.09	1.18
90	10	—	—	—
80	20	0.69	0.80	0.51
70	30	0.57	0.90	0.52
60	40	—	—	—
50	50	0.62	0.81	0.88
40	60	0.66	0.70	0.83
30	70	0.62	0.74	0.77
20	80	0.64	0.72	0.76
10	90	0.58	0.72	0.81
0	100	0.65	0.61	0.75

The lowest (S) values were found for the samples activated to 10 % burn-off. These low values accounted for non-equilibrium nitrogen saturation pressure adsorption that can be attributed to the low diffusion rates of nitrogen molecules[28]. In addition to the low diffusion rates of nitrogen at -196°C, the predominantly micropore structure of the samples may result low (S) values. The size of the micropores just mentioned are probably very similar to those of nitrogen molecule dimensions which can also be the reason of low nitrogen adsorption. As it can be seen from Table-III, further activation progressively increases (S) values irrespective of compositions of the original polymer mixtures. The process of activation widens such pores and enables nitrogen molecules to penetrate the entire accessible pore structure of these activated carbons rapidly at -196°C. Hence the amount of nitrogen adsorbed increases.

The (S) values of the samples that contain high proportion of PAcN carbons present high increments, the others on the other hand show lower and progressive rise (see Table-III). Based on this observation it can be said that, at a certain degree of gasification, the enlargement of the pores of the samples originally containing high proportion of PAcN (50 % or more), is higher than those containing low proportion or none of PAcN. The graduality of the deviations from the linearity of Dubinin plots can be taken as an experimental evidence for this conclusion.

It is a well established fact that the deviation from the linearity of the Dubinin plots arises from the alterations of pore structure of the samples under investigation. The concave deviation (M), relative to abscissa signifies fine micropore structure while convex deviation (N), indicates widened micropore structure[15].

Some of the typical Dubinin plots of the carbons produced are presented in Figures- 7, 8, 9 and 10. The variations of the shapes of these plots depends strictly on the structure and the degree of activation of the samples. Unactivated carbons give either linear (L) Dubinin plots or Type-M deviation (see Table-II). Activation alters (L) state or Type-M deviation and gives rise Type-N deviation. At 50 % gasification all of the deviations are Tpye-N. The deviations from (L) state of all of the high PAcN containing mixture carbons, are Type-N irrespective to degree of activation (see Table-II) which signifies widened micropore structure.

At low extent of activation (10 %) of the samples originally containing low proportions or none of PAcN give either (L) Dubinin plots or Type-M deviations. Further gasification and decreasing amounts of

PAcN convert gradually both (L) state and Type-M deviations to Type-N deviations which are again the indication of widened micropore structure. This pore widening can be explained by remembering that the amount of PETP carbon encrusting the PAcN particles is high in these samples. Thus as it was stated before, activation and adsorption characteristics are determined by PETP carbons. The thermal degradation characteristics of this polymer indicate the trend of formation of the micropore structure during carbonisation of it. While activating, the $C - CO_2$reaction causes the immediate gasification that widens micropores which results Type-N deviations.

In conclusion, it is possible to produce active carbons having high adsorption capacities by the carbonisation of PAcN - PETP binary mixtures. If the main concern is high carbonisation yield, the proportion of PAcN in the original carbonisation mixture, has to be more than 50 %. The highest adsorption capacity can be obtained by keeping the PAcN proportions low in the mixtures and the extent of activation around 30 %. However, low PAcN ratios decrease the carbonisation yields.

The enlargement of micropores is immediate of the high PAcN containing carbonisation mixtures. In return, it is gradual in low PAcN containing samples.

The reaction rate of the $C - CO_2$reaction was found to be high and approximately constant when the proportion of PAcN in the mixture is in the range of 90 to 30 %. This finding can be useful to produce oxidation resistant carbon artifacts. Reaction speeding action of PAcN was also noticed. Since the investigation of this observation was not the main concern of this work, it was suggested for further studies.

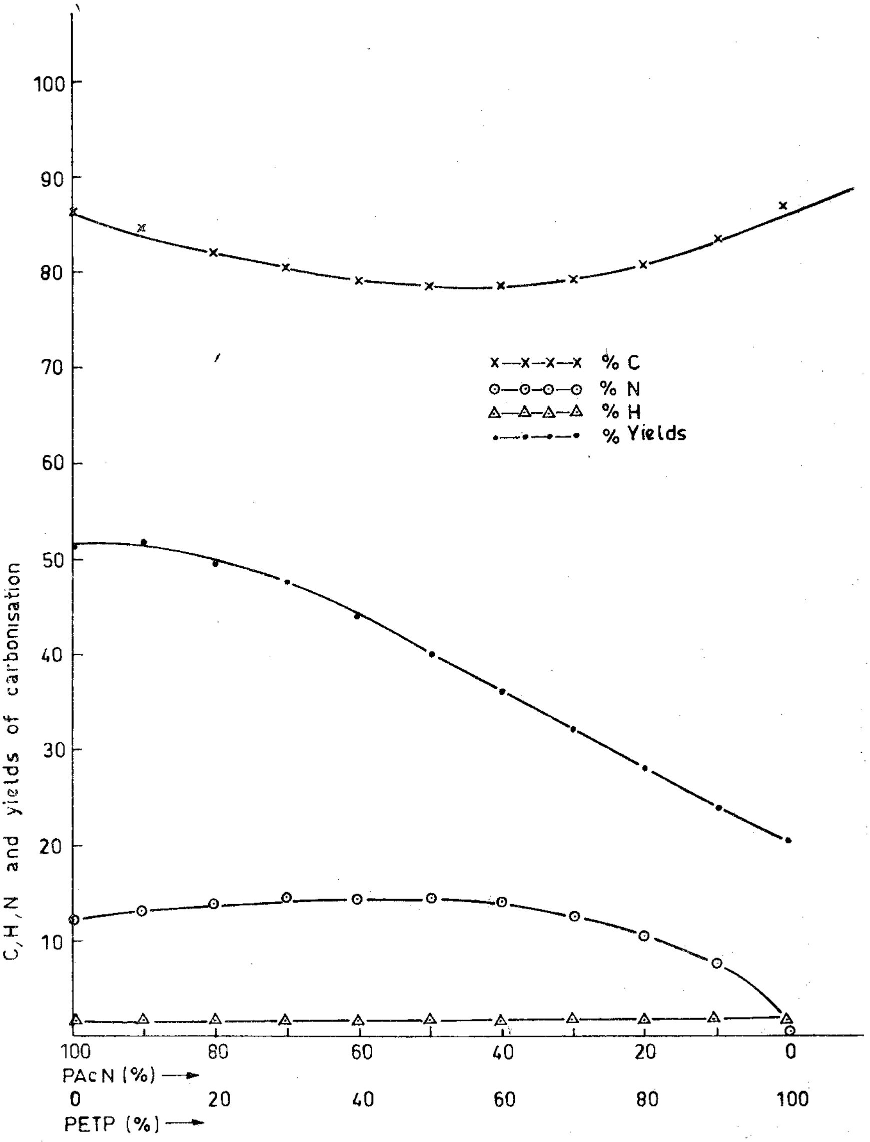

Figure - 1 : The variations of C,H,N and the yields of carbonisation with the composition of original polymer mixtures.

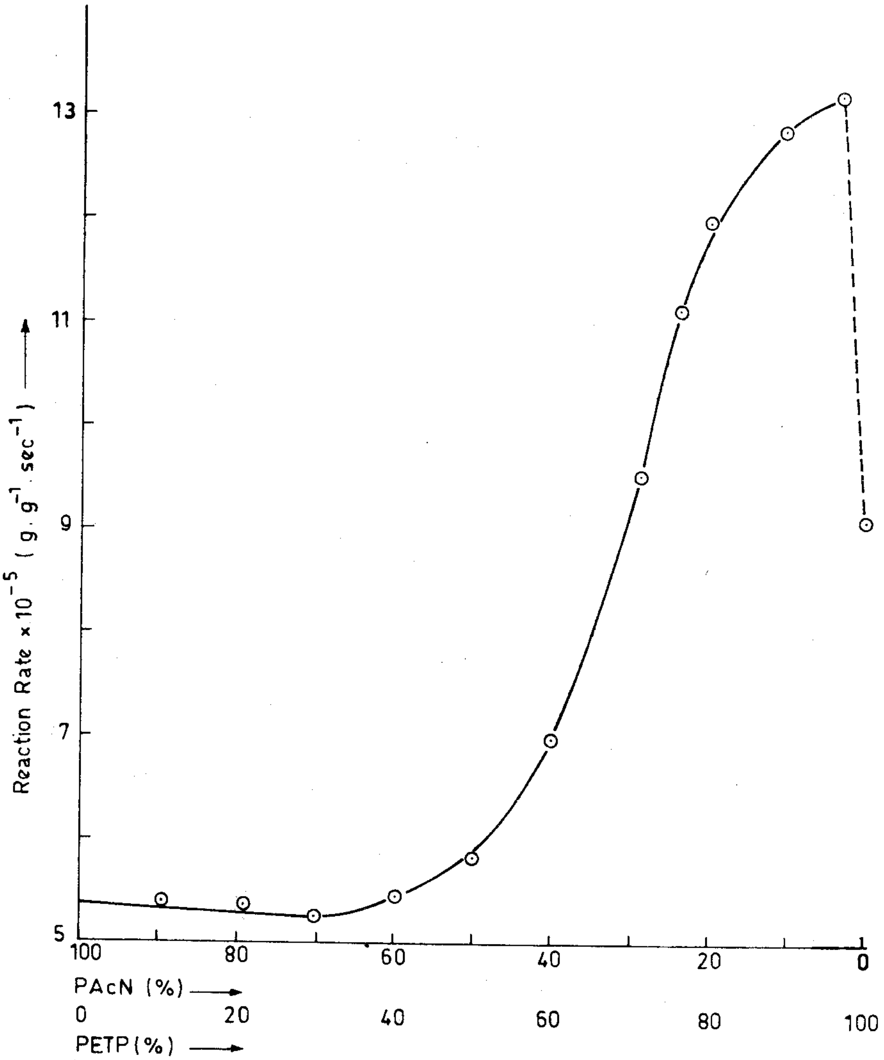

Figure - 2 : The variation of reaction rate with original polymer mixtures.

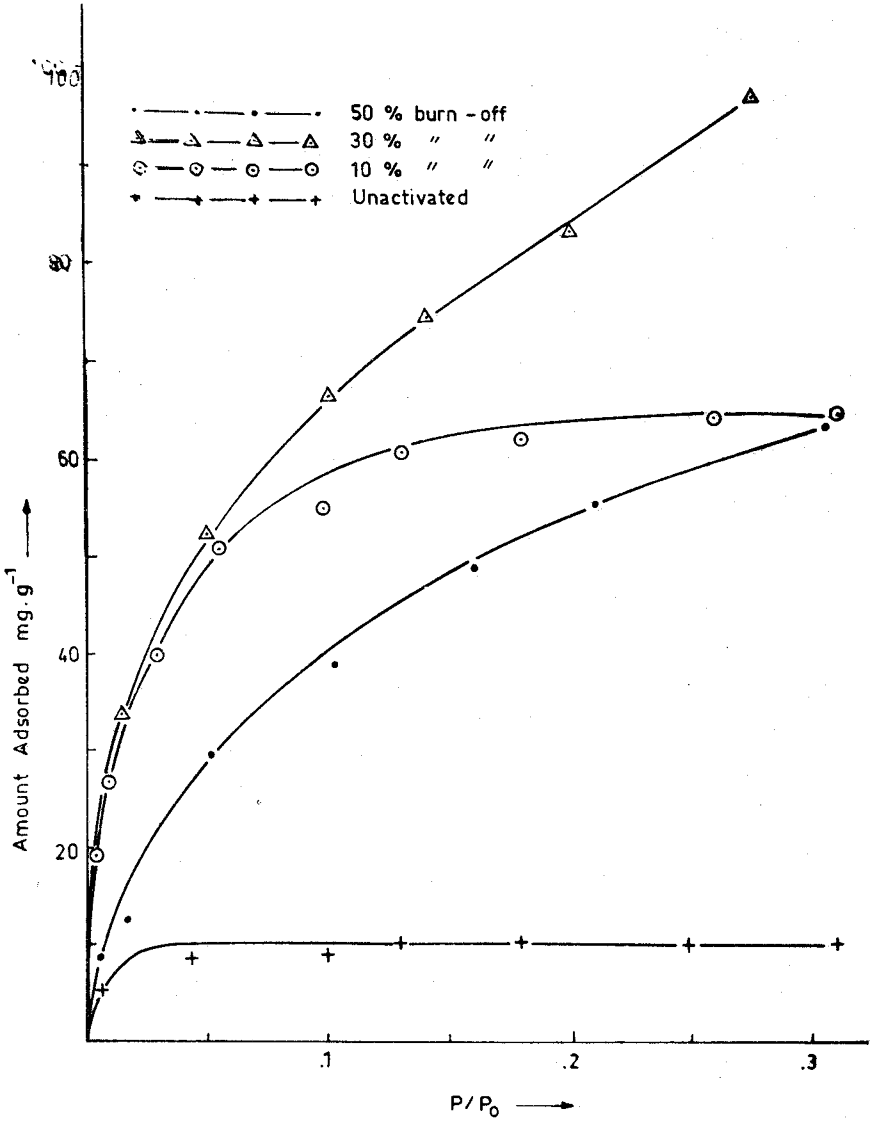

Figure - 3 : Carbon dioxide adsorption isotherms of the 50 % PAcN-50 % PETP mixture carbons at different activation degrees.

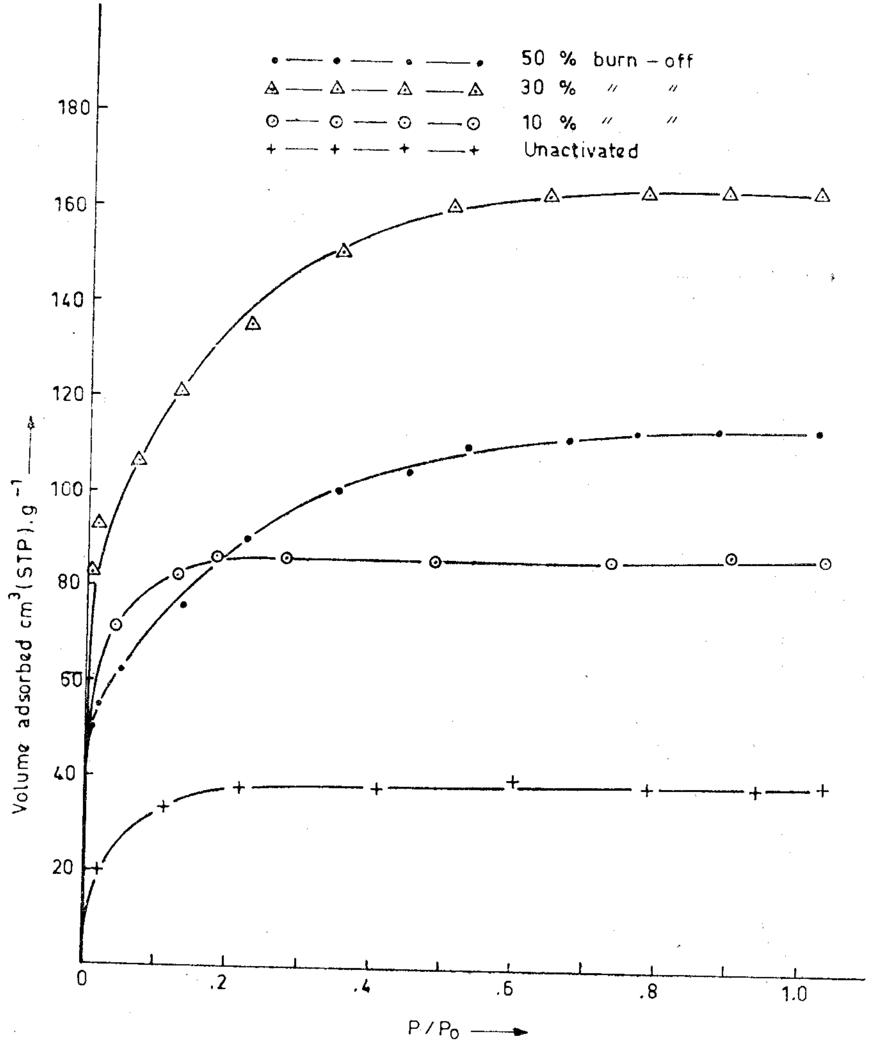

Figure - 4 : Nitrogen adsorption isotherms of the 50 % PAcN-50 % PETP mixture carbons at different activation degrees.

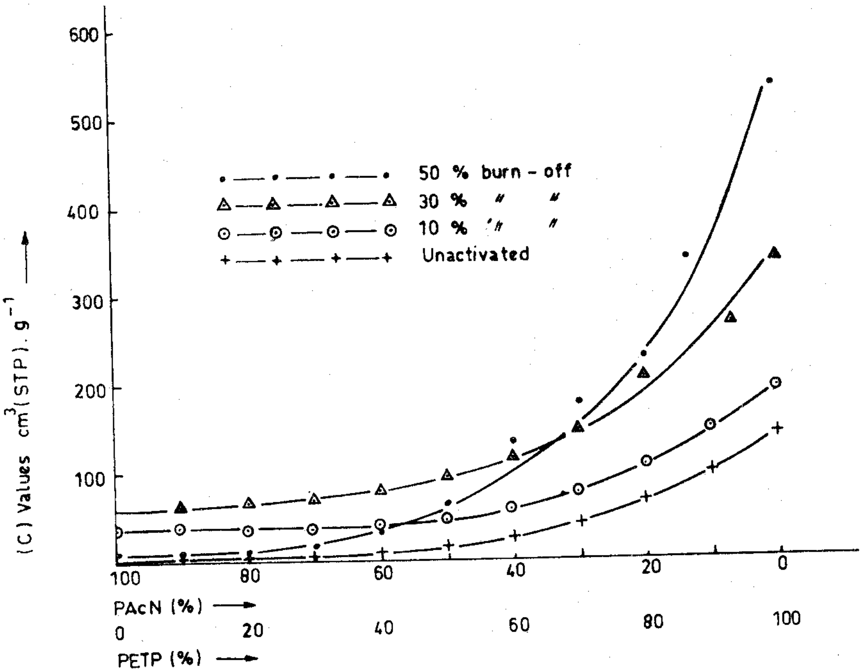

Figure - 5 : The variation of (C) values of carbon dioxide with the composition of original poylmer mixtures.

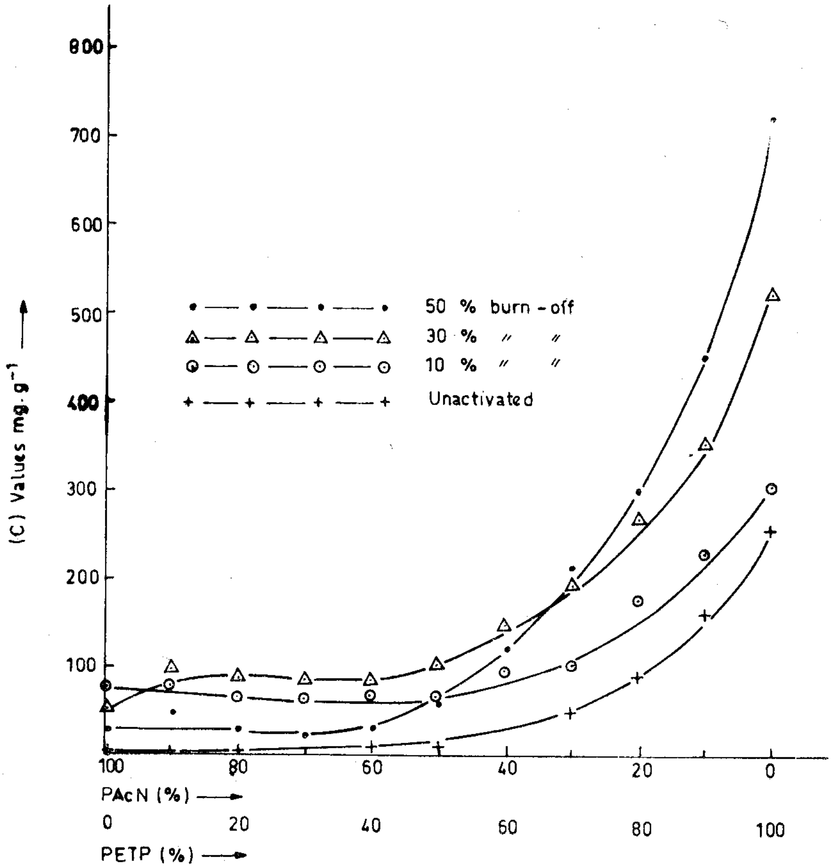

Figure - 6 : The variation of (C) values of nitrogen with the composition of original polymer mixtures.

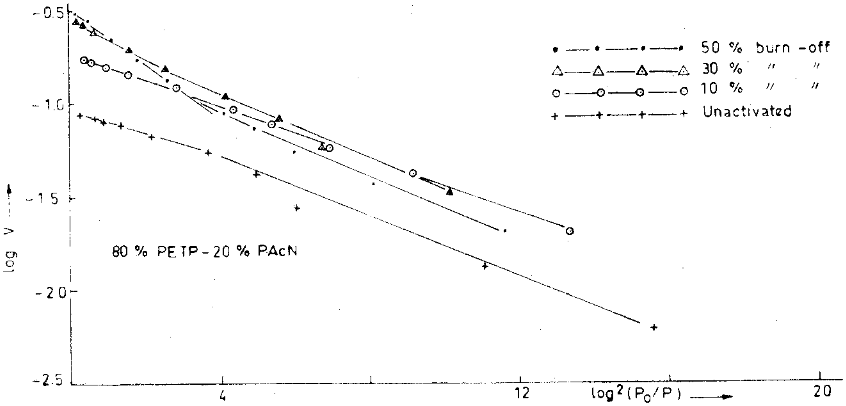

Figure - 7 : Dubinin plots of the 20 % PAcN - 80 % PETP mixture carbons at different activations.

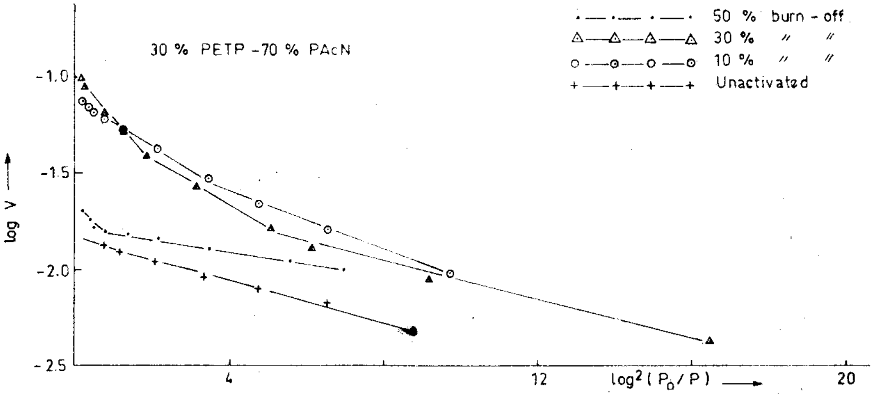

Figure - 8 : Dubinin plots of the 70 % PAcN - 30 % EPTP mixture carbons at different activations.

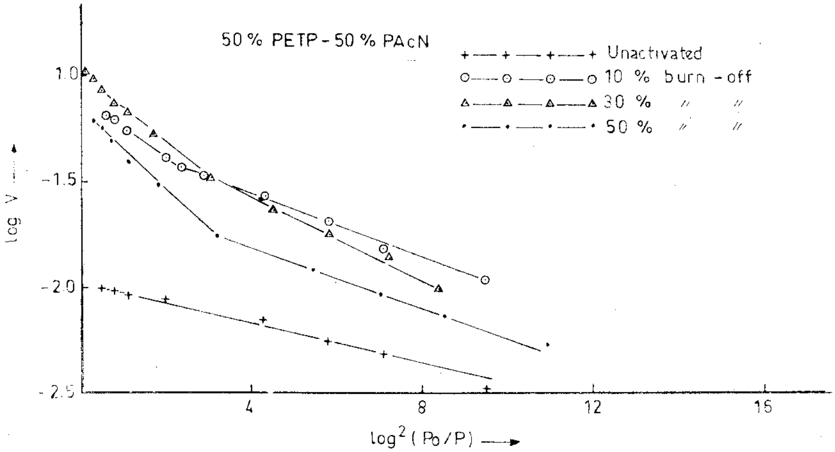

Figure - 9 : Dubinin plots of the 50 % PAcN - 50 % PETP mixture carbons at different activations.

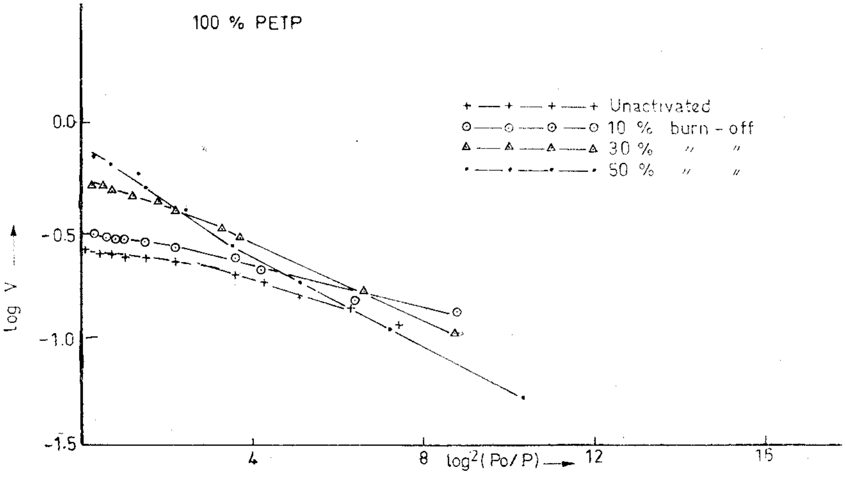

Figure - 10: Dubinin plots of the PETP carbons at different activations

Özet

Bu çalışmada poliakrilonitril ve polietilen tereftalatın farklı oranlardaki karışımlarının karbonizasyonu incelenmiştir. % 30 dan daha fazla poliakrilonitril içeren karışımlarda, adı geçen polimerden doğan karbonun daha fazla olduğu saptanmıştır. Ayrıca, karışımdaki poliakrilonitril oranının artması ile karbonizasyon veriminin arttığı da saptanmıştır. Karbonizasyon ürünlerinin tümü birinci tip BET adsorpsiyon izotermleri vermişlerdir. % 30 oranında aktivasyonla ve artan polietilen tereftalat oranları ile adsorpsiyon kapasitesinin arttığı, daha ileri aktivasyon ve azalan polietilen tereftalat oranı ile azaldığı gözlenmiştir. Düşük poliakrilonitril oranlarında adsorpsiyon ve aktivasyon karakteristiklerinin daha çok polietilen tereftalat karbonunca tayin edildiği de saptanmıştır.

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