CARBONIZATION OF WASTE PVC TO DEVELOP POROUS MATERIAL WITHOUT FURTHER ACTIVATION

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1. Introduction

Poly vinyl chloride (PVC) is widely used in many fields because of its low price and excellent mechanical properties. Its production amount exceeded 26 million tons/year in the world [1], in which it Japan account for 1/10. The combustion to recover the energy is the most conventional for common solid wastes. However, the combustion of waste PVC produces many detrimental contaminants such as hydrochloric acid, chlorine gas and especially dioxin, causing heavy pollution problems. Pyrolysis is an alternative to prepare chlorine free tar/pitch from waste PVC by recovering HCl. Although some papers about heat-treatment of PVC were published [2-7], most researchers paid much attention to the mechanism and kinetics of PVC pyrolysis. The carbonization of pure PVC and preparation of carbon fibers from the obtained pitch appears very attractive [2, 3]. Recently, the present authors also developed activated carbon fibers from commercial PVC resin, which showed a comparable De-SOx property with commercial ACF [8]. However, it is difficult to prepare carbon fiber and even ACF from waste PVC because of there is such additive as $CaCO_3$. Activated carbon may be another choice to be developed from waste PVC. Of course, it is very important to remove chloride from the waste PVC when its utilization is planned. The two-stage heat-treatment of waste PVC can be a procedure to remove chlorization and control its carbonization to prepare the precursor of porous carbon. In general activation process, activating agent is necessary to develop porous structure from carbon materials.

In this study, two kinds of waste PVCs were heat-treated and pyrolyzed in two stages (280°C for 2h and 410°C for 2h, respectively) under nitrogen to prepare waste PVC based pitch. Efficient removal of chlorine from waste PVC achieved by two-stage heat-treatment (280°C for 2h and 410°C for 2h, respectively) provided chlorine-free isotropic pitch containing additive. The obtained pitch was stabilized and direct carbonized to prepare porous carbon without activation to develop porous structure from waste PVCs. The properties of the resultant porous carbon were analyzed by the aid of N_2 adsorption, temperature programmed desorption (TPD), X-ray diffraction and moisture adsorption.

2. Experimental

2.1 Heat-treatment of waste PVC

Two kinds of waste PVCs (pipe and pellet), provided by Kureha Kankyo Company, was heat-treated in two-stage process under nitrogen where the treatment conditions of the first and second stages were 280°C for 2h and 410°C for 2h, respectively. Pyrolysis of waste PVC was also followed by using TG/DSC (heating rate: 5°C/min; atmosphere: N_2). Morphologies and composition of waste PVCs were shown in Fig. 1 and Table 1.

2.2 Preparation and carbonization of waste PVC pitch

10g PVC was placed into glass-reactor and heat-treated in two-stage processes under nitrogen blow of 200ml/min (treatment conditions of the first and second stages were 280°C for 2h and 410°C for 2h, respectively. Heating rate was 5°C/min.) to prepare PVC based pitch. The resultant pitch (softening point: 250°C) was stabilized up to 340°C (1°C/min) in air, carbonized up to 500~900°C (5°C/min) in Ar.

2.3 Analysis method

Thermal decomposition process of PVC was followed with TG/DSC. Residual chlorine content of waste PVC based pitch was measured using the cylinder combustion-ion chromatography (CMICG). The surface area of the obtained products was measured using BET method. The chemical state of calcium in pitch and carbonized product was examined through X-ray diffraction (XRD). The decomposition of $CaCO_3$ was checked through temperature programmed desorption (TPD), in which sample weight is 0.1g (heating rate: 10oC/min; carrier: He with a flow of 20ml/min). Moisture adsorption of carbonized product was carried out at 20°C in a sealed vessel containing H_2O.

3. Results

3.1. TG/DSC curves of waste PVC pyrolysis

Fig. 2 showed TG/DSC curves of waste PVCs. Three main pyrolysic exothermic peaks were observed. The first peak at 200-320°C was attributed to the removal of HCl, where weight losses were about 52% for pipe and 56% for pellet, respectively. PVC is transformed into polyene chains with conjunated double bonds, producing some artomatic benzene structures [3, 6]. The second peak at 320-400°C (weight loss: about 4%) was owing to the decomposition and the condensation of the polyenes into three dimensional network and plasticising agent such as DOP. The third peak at 400-470°C was ascribed to aromatization of small molecular size and further transformation into pitch. Weight decrease over 500°C was attributed to carbonization of PVC pitch and decomposition of additive such as $CaCO_3$.

Although there are three peaks in DSC of PVC pyrolysis, the first two peaks often overlap, which will lead the second peak to be hidden in the regular pyrolysis. Moreover, a heating rate of 5°C/min conducted the second stage reaction during heating. Thus, in the following experimental, two stages isothermal processes (280°C and 410°C, respectively), were examined to prepare waste PVC based pitch.

3.2. Preparation and carbonization of waste PVC based pitch

Table 2 showed some properties of the obtained pitches prepared through the two-stage heat-treatment (280°C for 2h and 410°C for 2h, respectively.). Waste PVCs showed higher yield than commercial PVC. Pitch yields of pipe and pellet are 25% and 32%, respectively. Two kinds

of waste PVC pitches showed a similar softening point of 250-255°C (Table 1). It should be noted that pellet pitch contain higher ash than pipe pitch, indicating pellet contains more amount of additive.

After pipe pitch was oxidatively stabilized at 340°C in air, its carbonized product at 700°C showed high yield and middle surface area, 59% and 195m^{2}/g, respectively. However, direct carbonization gave a very low surface area and slightly higher yield. In the meanwhile, after pellet pitch was oxidatively stabilized at 340°C in air, its carbonized products at different temperature varying from 600 to 900°C showed similar yield and surface area, 58% and 220m^{2}/g, respectively. Low temperature carbonization gave a high yield and very low surface area, 65% and 30m^{2}/g, respectively. Direct carbonization also provided low surface area.

3.3. Isotherm of adsorption-desorption of carbonized product

Fig. 3 showed the isotherm curves of carbonized products derived from waste PVCs. Carbonized products obviously showed the hysteresis loop, indicating their mesoporous structures. Washing appeared to increase the area of hysteresis loop and mesoporous structures.

3.4. XRD pattern of carbonized product

Figs. 4 and 5 showed XRD pattern of pitch derived waste PVC (pellet) and its carbonized forms varied from 500 to 900°C. Fig. 4 demonstrates that the main additive in waste PVC is $CaCO_3$ and it remains after pyrolysis of waste PVC and carbonization at low temperature at 500°C. At higher carbonization temperature than that, carbonized products showed similar XRD patterns, indicating that $CaCO_3$ additive is decomposed at higher carbonization temperature than 600°C into CaO and remains no change at higher temperature.

3.5. TPD profile of carbonized product

Fig. 6 showed TPD profiles of pitches of waste PVCs carbonized at 500°C in Ar after stabilization. CO and CO_2 were released from 550 to 800°C because of the decomposition of $CaCO_3$ additive in waste PVCs.

3.6. Moisture adsorption of carbonized product

Fig. 7 showed moisture adsorption isotherm of carbonized products derived from waste PVCs at room temperature of 20°C. Carbonized products at 700°C without washing using acid showed very highly hygroscopic. In the contrast, carbonized products washed by acid, showed very poor hygroscopic adsorption.

4. Discussion

Two-stage heat-treatment method is effective to remove chloride from waste PVCs to prepare isotropic pitch with high softening point of ca. 250°C. The as-prepared pitch contains some additive such as $CaCO_3$ which retard the spinnablity. However, it is very interesting that special porous structures with middle surface area of 300m^{2}/g can be developed through a simple carbonization from waste PVCs.

Additive, especially $CaCO_3$, is certainly responsible for the development of porous structures. $CaCO_3$ in waste PVCs remains unchanged during its pyrolysis and residues in the resultant pitch. Low temperature carbonization of the pitch at 500°C could not change the chemical state of calcium. High carbonization temperature over 600°C leads to the decomposition of $CaCO_3$ into

oxide to develop porous structures in the carbonized product. So, the surface area of the carbonized product at 500°C is very low. In the contrast, middle surface area can be obtained at carbonization temperature of 600°C and no changes in both surface area and carbonization yield produce at high temperature of 700~900°C.

Development of porous structures is ascribed to the activation agent of CO_2 which is releases owing to the decomposition of $CaCO_3$ distributed in the resultant pitch at high temperature. The released CO_2 activates carbon wall to develop porous structures. CO_2 activation is usually employed to prepare activated carbons. in general, the method need high activation temperature than 850°C. The released CO_2 can activate carbon material at low temperature to give out CO gas, indicating much more active than general CO_2.

The carbonized products displayed similar isotherms of adsorption-desorption. The curves display a large hysteresis loop, indicating the development of mesoporous structures (2~50nm, 0.25<P/Po<0.90). Of course, the self-activation provides some micropores (0.7~2nm, 0.05<P/Po<0.25). After washing using acid to remove the residuary oxide, the area of hysteresis loop trends to be enlarged, indicating the increase of mesopores and formation of supermicropores (<0.7nm, P/Po<0.05). With the removal of oxide, surface area trends to increase. The surface area of pellet based carbonized product shows a increase of 100m^2/g since it contains more amount of ash or oxide. The removal is responsible for the changes as shown in Fig. 8. Theoretically, $CaCl_2$ plays a part in the process since it may produce during the pyrolysis of waste PVC owing to HCl release, which can react with $CaCO_3$. However, it was not checked out in this experimental.

Stabilization of the resultant pitch is necessary to develop porous structures in carbonized products. Pitch and $CaCO_3$ have different densities, 1.2 and 2.7g/ml, respectively. The stabilization retards the precipitation of $CaCO_3$ and keeps its uniform distribution in the carbonized products. Thus, direct carbonization results in a very low surface area. In the contrast, the carbonization after stabilization provides a middle surface area with mesopores.

It should be noted that the carbonized products without washing show highly hydroscopic properties, up to 200% for pellet one and 110% for pipe one, respectively. Carbonized products with HCl-washing display normal moisture adsorption properties, only 12% for pellet one and 9% for pipe one, respectively. The contributions for the highly hydroscopic property are the following: one is from porous carbon itself, namely one kind of physical adsorption, it seems to not be a main cause. The other is from CaO distributed in porous carbon, one kind of chemical adsorption, which appears to be responsible for the adsorption. Certainly, distribution of CaO in porous carbon is also important, and activated carbon provides a good support to the distribution of CaO. Thus, the combination results in the excellent moisture effect.

5. Conclusion

Isotropic pitch (SP: about 250°C) containing $CaCO_3$ additive can be prepared from waste PVCs (pipe and pellet) according to two-stage process in which chlorine was efficiently removed from waste PVCs to recover aq. HCl. It was found to be difficult to spin the resultant pitch because of the presence of fine oxide such as $CaCO_3$ in such pitch. In our past report, ACF was

successfully prepared from commercial PVC resin through similar method. In the following paper, we will report that PVC extraction from waste PVC by solvent to remove the infusible contaminants and prepare CF and ACF from the extracted PVC.

In the present study, pyrolysis and carbonization of two kinds of waste PVCs (pipe and pellet) were examined to understand the carbonization process of waste PVC and develop mesoporous structures in carbonized products derived waste PVCs. $CaCO_3$ in waste PVC based pitch decomposes during carbonization at higher temperature than 600°C and the decomposition is responsible for the porous structures and high moisture adsorption.

Acknowledgements

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References

[1] Homepage (http://www.vec.gr.jp).
[2] Otani S. Carbon 1965;3:31-8.
[3] Otani S. Tanso 1965;42:30-5.
[4] Ohrbach KH, Radhoff G, Kettrup A. Thermochimica Acta 1985;85:403-6.
[5] Marcilla A, Beltran M. Polymer degradation and stability 1996;53:251-60.
[6] Miranda R, Yang J, Roy C, Vasile C. Polymer degradation and stability 1999;64:127-44.
[7] Kim S. Waste management 2001;21:609-16.
[8] WM Qiao, SH Yoon, Korai Y, Mochida I, Sakurai T. Carbon 2004 (in press).

Table 1 Some properties of waste PVC, pitch and carbonized product

	Yield	S.P.	Cl	Elemental analysis, %				Ash
	%	^{o}C	%	C	H	N	Others	%
Pipe				37.89	4.77	0.00	57.34	1.36
Pipe pitch	25	250	0.77					
Pipe pitch-700oC				75.38	1.40	0.25	22.97	9.41
Pipe pitch-700oC-HCl				87.90	1.61	0.07	10.42	1.56
Pellet				37.62	4.67	0.02	57.71	8.99
Pellet pitch	31	255	0.36					
Pellet pitch-700oC				54.84	1.30	0.05	43.81	35.44
Pellet pitch-700oC-HCl				85.08	1.43	0.03	13.46	5.30

S.P.: softening point; Weight-gain after stabilization: 10% for pipe pitch and 8% for pellet.

Table 2 Carbonization of waste PVC based pitch after stabilization

Raw material	Carbonization temperature , ^{o}C	Washing (using HCl)	Carbonization yield* wt%	S_{BET} m^2/g	Pore Vol. ml/g	D** nm
Pipe	700	no	59.2	195	0.111	2.28
	700	yes	53.7	220	0.128	2.32
	900	no	58.2	200	0.117	2.34
	900***	no	65.2	15	0.007	
Pellet	500	no	65.0	30	0.046	
	600	no	58.2	21	0.131	2.37
	700	no	57.9	205	0.135	2.63
	700	yes	33.6	**302**	0.172	2.28
	800	no	57.8	225	0.148	2.63
	900	no	57.6	224	0.152	2.70
	900***	no	71.2	27	0.032	

*Base: stabilized form; D (average pore size)=4*Vol./S_{BET};; **Direct carbonization without stabilization.

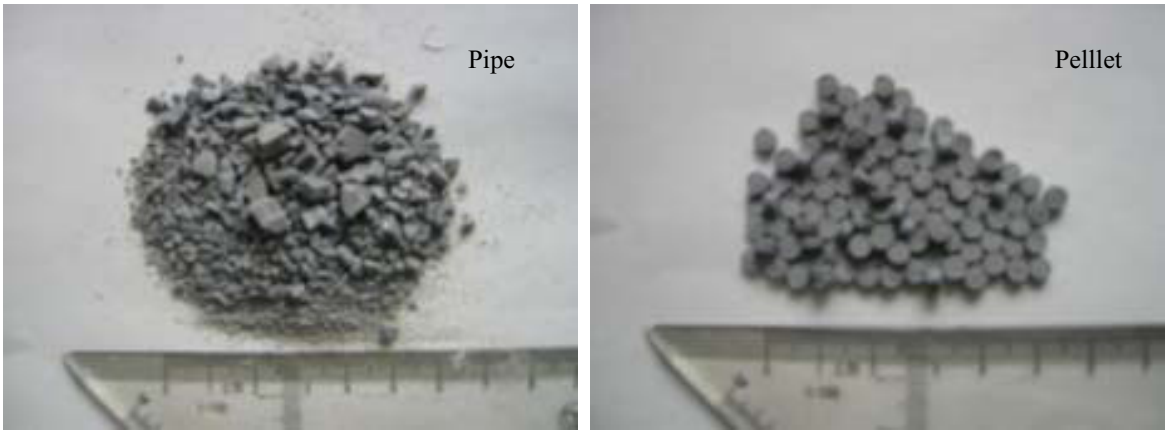

Fig. 1 Morphology of waste PVCs (pipe and pelllet).

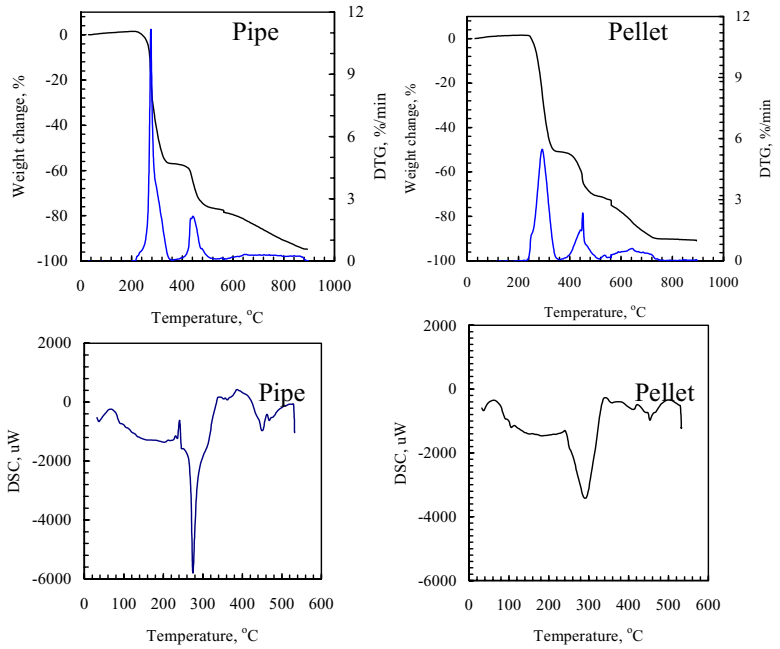

Fig. 2 TG-DTG-DSC curves of waste PVCs

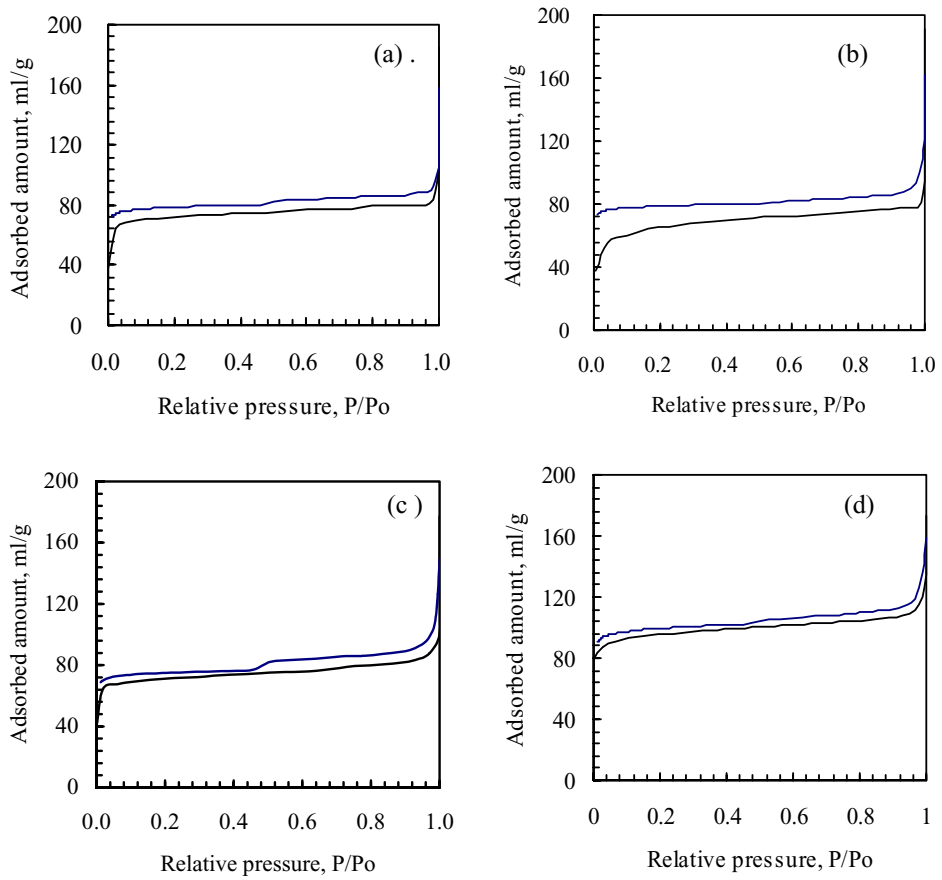

Fig. 3 Adsorption-desorption isotherms of carbonized products.

(a) pipe pitch- carbonized product at 700°C; (b) pipe pitch- carbonized product at 700°C and washed

(c) pellet pitch- carbonized product at 700°C; (d) pellet pitch- carbonized product at 700°C and washed

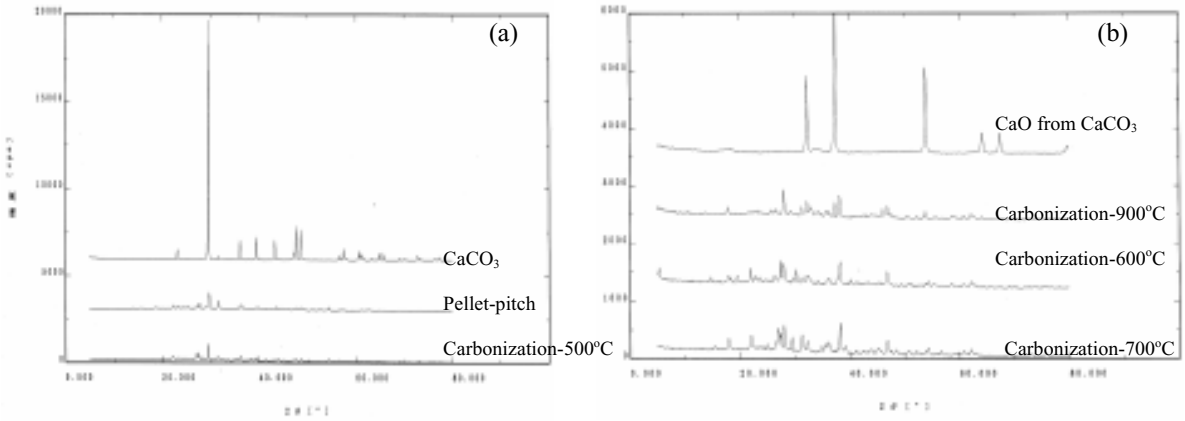

Fig. 4 XRD pattern of the resultant waste PVC pitch and its carbonized forms at 500~900°C.

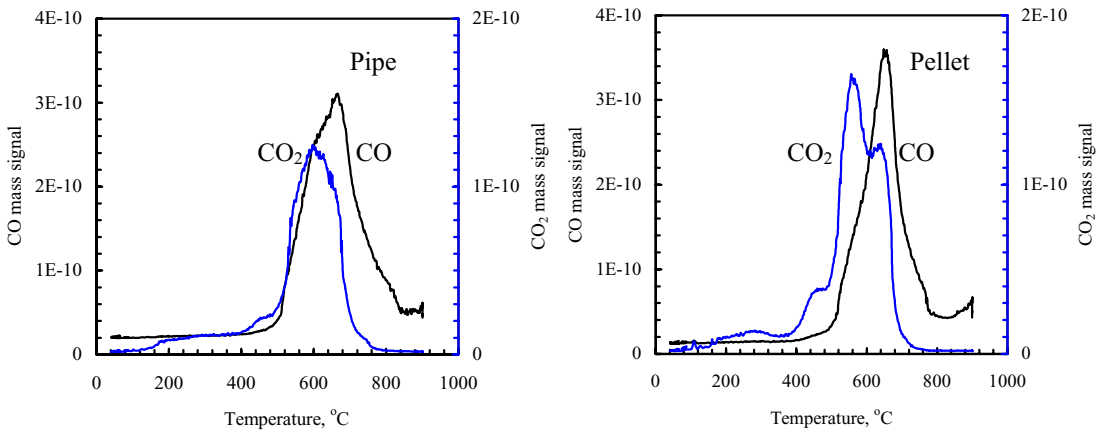

Fig. 5 TPD profiles of carbonized products at 500°C.

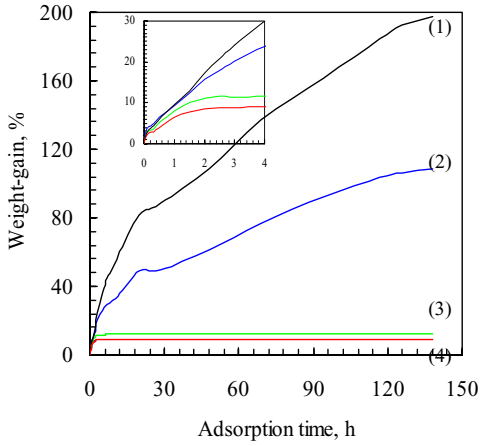

Fig. 6 Hydroscopic property of carbonized products and their washed forms at 20°C.

(1) Pellet pitch carbonized at 700°C; (2) Pipe pitch varbonized at 700°C

(3) Pellet pitch carbonized at 700°C-HCl; (4) Pipe pitch carbonized at 700°C-HCl

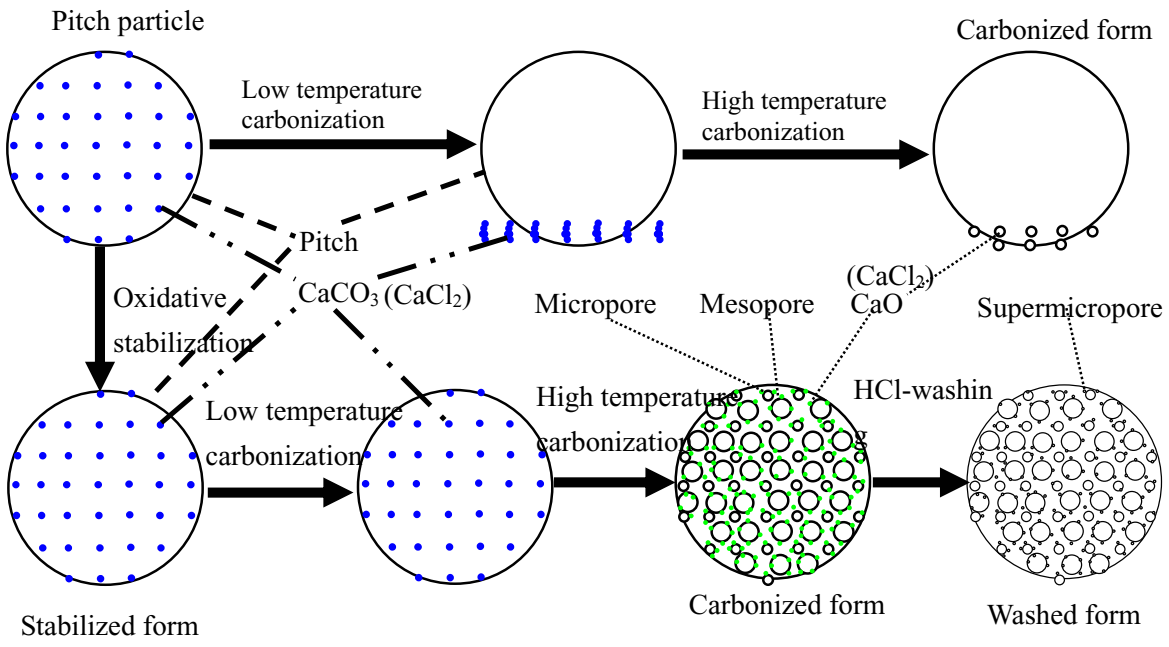

Fig. 7 Formation mechanism of porous structures in carbonized products derived from waste PVCs