Synthesis and Characterization of Alkali-Modified Styrene-Maleic Anhydride Copolymer for Dispersion of TiO$_2$

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ABSTRACT: A copolymer of styrene and maleic anhydride was synthesized by free radical polymerization at 80°C using N,N-dimethylformamide (DMF) as solvent and benzoylperoxide as initiator. The monomer feed ratio of styrene to maleic anhydride was varied in the range of 1 : 1 : to 3 : 1. The polymer yield was found to decrease with increase in styrene in the feed. The molecular weight of copolymers which were formed by taking styrene to maleic anhydride ratio of 1 : 1, 2 : 1, and 3 : 1, as determined by Ostwald Viscometery were about 1862, 2015, and 2276 respectively. The acid values of abovementioned three copolymers were found to be 480, 357, and 295, respectively. The typical viscosity values of 20% solids in ammonical solution of copolymers formed by taking feed ratios of Sty : MAn as 1 : 1 and 2 : 1 were 26 and 136 cp, respectively. For the feed ratio 3 : 1, a gel was formed. The synthesized copolymers were hydrolyzed by alkalis, namely, NaOH, KOH, and NH$_4$OH. The dispersing ability of hydrolyzed styrene-maleic anhydride (SMA) copolymers for dispersion of titanium dioxide was studied. The modified SMA copolymers were found to be effective dispersants for TiO$_2$. Among the three alkalis studied, the Sodium salts of SMA were found to give better dispersion. The copolymer having a 1 : 1 feed ratio showed the best dispersing ability for TiO$_2$ particles among the three ratios studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3194–3205, 2007

Key words: styrene-maleic anhydride (SMA) copolymers; dispersing ability; hydrolysis

INTRODUCTION

Many industries, such as paint, textile, paper agriculture, etc., involve the process of dispersing solid particles in liquid. This is because the process of dispersion has attracted a wide range of interests in both theoretical studies and practical applications.[1–4] In order to acquire a stable dispersion, a dispersant is usually added to help suspend solid particles in liquid. The main function of the dispersant is to provide the particles with electrostatic charges or with steric hindrance to produce a barrier so as to prevent coagulation.[5]

Due to the ability to provide a high density of charges and an efficient steric hindrance, polymers are widely used as dispersants in industry. In order to disperse particles efficiently, the polymers have to interact with and become adsorbed upon the surface of the particles effectively. Thus, the dispersion ability of a polymer is strongly affected by its chemical structure. The chemical structure, i.e., the hydrophobicity and the functional groups of the polymers have to be adjusted so that it effectively disperse particles having different surface properties.[6–7]

Polycarboxylates, such as the sodium salts of polyacrylic acid[8–13], have been widely used as dispersants for inorganic pigments with a polar surface[14,15] such as TiO$_2$, CaCO$_3$ etc. Styrene maleic anhydride is an important functional copolymer, as anhydride groups on backbone chain can react with other reagents such as alcohols, amines, water, etc. to produce their derivatives. Utilizing their characteristic functional nature, various modified styrene-maleic anhydride copolymers have been developed for a variety of possible applications such as pigment dispersants, protective colloids, and thickeners for paint formulations, as well as in adhesives.

Copolymer of styrene-maleic anhydride has been modified by reaction with amines, the resultant maleimide becomes soluble in aqueous acids after quanternization and can be used as a dispersing agent both for polar and nonpolar particles in aqueous solution. The modified styrene-maleic anhydride (SMA) resins can also be used as a softening agents for chromium containing compounds, during retanning process in the leather industry.[16]

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The SMA resins can be modified by various alkalis through reactive anhydride group present on the polymer which can react with alkalis and act as a pigment dispersant.[17] Although some investigators have studied various kinds of modified SMA, the systematic studies of alkali-modified SMA resins to act as a dispersing agent for inorganic pigments such as titanium dioxide (TiO_2) in aqueous solution have not been reported.

In this manuscript, an effort has been done, to study the dispersion properties of alkali-modified SMA resins of varying characteristics. For this SMA, copolymers with different molar feed ratios were synthesized and characterized. The synthesized SMA copolymers were then modified by further reactions with different alkalis such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH) in order to generate modified SMA copolymers.

The dispersing ability of these copolymers of varying chemical nature have been studied for dispersion of inorganic pigment like TiO_2 in aqueous solution. The effect of variation in molar feed ratio on dispersing ability of copolymers were studied and correlated with their structure. These studies would be helpful in generating an efficient dispersing material based on copolymers of styrene and maleic anhydride for application in the leather, paint, and paper industries.

EXPERIMENTAL

Materials

These chemicals were used for synthesis of copolymers: maleic-anhydride (MAn) (SD's Lab Chem, Mumbai), styrene (E. Merck, Germany), methanol and scetone AR grade (SD's Lab Chem, Mumbai), N,N-dimethylformamide and tetrahydrofuran AR grade (Qualikems Chemicals, Delhi), benzoylperoxide (Qualikems Chemicals, Delhi), sodium hydroxide and potassium hydroxide (Qualikems Chemicals, Delhi), ammonia 25% aqueous solution (Qualikems Chemicals, Delhi), titanium dioxide powder with particle size < 5 μm and purity of 99.9% that is predominantly rutile (E. Merck, Germany).

Synthesis of copolymer

For polymerization, styrene was purified by alkaline wash method and maleic anhydride was recrystallized twice from methanol. The copolymer of styrene and maleic anhydride was prepared by radical polymerization. The monomer feed ratio of styrene to maleic anhydride (Sty : MAn) was taken as 1 : 1, 2 : 1, and 3 : 1. The reaction was carried out in a three-neck flask using an oil bath having its temperature
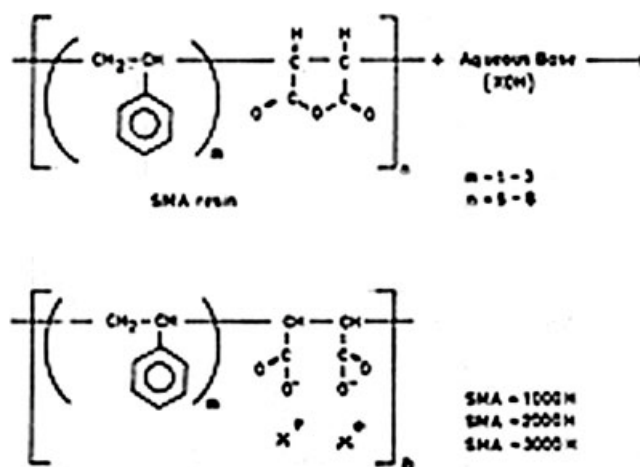

Figure 1 Neutralization of SMA resin with base.

accurately controlled. The N,N-dimethylformamide (DMF) was used as a solvent and Benzoylperoxide (BPO) was used as initiator. The reaction was carried out at 80°C for 4 h in a nitrogen atmosphere. The polymer was precipitated using methanol as a non-solvent. The homopolymer of polystyrene was removed by dissolving copolymer in benzene solution, then filtering and drying in oven at 50°C for 48 h. The SMA11 copolymers of varying molecular weight have been synthesized by varying the reaction conditions.

Characterization of the polymers

The molecular weights of SMA copolymers were determined by the Mark–Houwink equation using data from Ostwald Viscometery in tetrahydrofuran (THF) at 25°C. The acid value was determined by Volumetric Analysis. A Brookfield viscometer (Brookfield Synchro Lectric, Model RTV) was used to determine the apparent viscosity of 20% solids of SMA copolymers in ammonical solution at the temperature of 30°C and shear rate of 20 rpm.

Hydrolysis of SMA copolymers

The synthesized copolymers were hydrolyzed using three different alkalis, namely, sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH). The neutralization reaction of base is shown in Figure 1. The temperature for neutralization with NaOH, KOH, and NH_4OH was maintained at 40, 65, and 70°C, respectively. For this, 100 ml of distilled water were taken in a three-neck flask and the weighed amount of SMA resin was added to it with constant stirring. The appropriate amount of aqueous alkali required to dissolve the sample was added into it with constant stirring

TABLE I
Percentage Yield, Molecular Weight, and Acid Values of Synthesized
SMA Copolymer

S. no.	SMA copolymer	Percentage yield	Molecular weight	Acid values
1	SMA11	37%	1862	480
2	SMA21	29%	2015	357
3	SMA31	28%	2276	295

for 2 h. Then a few drops of concentrated H_2SO_4 were added to it until the pH of solution becomes less then 4. The product was collected as white powders by filtration and dried at 50°C for two days.

Fourier Transform infrared spectroscopic analysis of SMA copolymers

The infrared spectra of the SMA copolymers and modified SMA11 copolymer in KBr pellets were recorded on a high-resolution Bruker Model Vector 22 Fourier Transform infrared spectrophotometer with a DTGS detector (deuterated triglycerine sulfate).

Evaluation of the dispersing ability of the polymers

The abovementioned Brookfield viscometer was used to determine the dispersing ability of alkali-modified SMA resin synthesized by taking the molar feed ratio of styrene to maleic anhydride as 1 : 1 for dispersion of TiO_2. Aqueous solution of sodium-salt of SMA having concentration varying in the range of 0.5–5% was mixed with 50 gm of TiO_2 to make a paste and viscosity of the dispersion was measure at 20 rpm at 30°C using an SCS-6 spindle.

As the evaluation of dispersibility of any filler in a vehicle using the Brookfield viscometer is a complicated process and requires a large amount of sample, a simpler process, namely, the Daniel flow method, has also been used for assessing the dispersing efficiency. The data of Brookfield viscometry have been compared with the data of the Daniel flow method, and a procedure for investigating dispersing ability of other alkali-modified copolymers has been standardized. The Daniel flow method is a simple and useful method for evaluating the amount of vehicle required to produce a critical consistency, where just a sufficient additional vehicle is incorporated to produce a flow or falling off from the vertical blade of a horizontally held spatula. Aqueous solutions of all alkali-modified SMA copolymers of concentrations in the range of 0.5–5% were prepared in distilled water. These aqueous solutions of copolymer were taken in a burette and added to 20 gm TiO_2 dropwise with constant stirring and rubbing with a glass rod until a heavy and smooth paste was obtained. Then more aqueous solution was added gradually to

the paste until the mass achieved a consistency at which it could be stirred without significant resistance. A characteristic end point was reached when a thin and even film material remained on the glass rod and the last drop fell at an interval of 1–2 sec. These drops appear to break with an elastic snap back. A graph for the amount of aqueous solution of copolymer required to reach the above end point against the concentration of the dispersing agent was plotted to obtain a U-shaped curve having a minimum that corresponds to the optimum concentration of dispersant for efficient dispersion.

The aqueous solutions of potassium and ammonium salts of SMA copolymers of concentration in the range of 0.5–5% were also prepared in distilled water in a similar way and the dispersing ability of these for TiO_2 were determined by the Daniel flow method.

RESULTS AND DISCUSSION

Synthesis and Characterization of SMA and Hydrolyzed SMA

The SMA copolymers have been synthesized using N,N-Dimethylformamide (DMF) as a solvent and benzoylperoxide (BPO) as a free radical initiator, taking molar feed ratios of styrene and maleic anhydride as 1 : 1, 2 : 1, and 3 : 1 at 80°C. The above synthesized copolymers have been designated in this work as SMA11, SMA21, and SMA31, respectively. The percentage yield, molecular weight, and acid values of synthesized SMA copolymers have been determined as described above and the results are shown in Table I. It has been observed that the percentage yield of copolymer SMA11 is 37% which is 21% higher than the yield observed for SMA21 and 24% higher than that for SMA 31. Thus, as the molar concentration of maleic anhydride decreases in the feed, the copolymers yield also decreases. This indicates that the copolymer yield is determined by the concentration of MAn in the feed. It has also been found that in the synthesis of copolymer with a lower concentration of MAn in the feed, a mixture of homopolymer of styrene and the copolymer of SMA was obtained as a larger peak of polystyrene comes in the FTIR spectra when synthesized copolymer is analyzed without removing polystyrene by dissolution in benzene. When homopolymer has been re-

moved by dissolution in benzene, the percent yield of SMA21 and SMA31 becomes low.

It has also been observed that when an equimolar ratio of styrene to maleic anhydride is taken in the feed, a solid mass with almost quantitative yield is obtained immediately on precipitation. In case of other ratios large amount of nonsolvent is required for precipitation, and slurry type content is obtained Since in the synthesis of copolymer of styrene and maleic anhydride at 80°C, there are more chances of formation of an alternating copolymer.[18] The stichiometric imbalance in the feed may interfere with the precipitation of copolymer from solvent. This is also evident in the studies of Bhuyan et al.[19] on copolymers of styrene and maleic anhydride prepared by a charge transfer mechanism at 60°C. They have found that the percentage yield decreased with increase in styrene content in the feed and the copolymers prepared from a feed ratio higher than 5.5 did not dissolve in dilute alkali and swelled in acetone because of the formation of homopolymer of styrene along with the copolymers.

Molecular weight

Chow et al.[21] have determined the molecular weight and molecular weight distribution of styrene-maleic anhybride copolymers using gel-permeation chromotography, light-scattering photometry, membrane osmometry, and intrinsic viscosity and have proposed a dual-calibration method for SMA copolymers. According to them, a linear relationship of intrinsic viscosity (η) and weight average molecular weight (Mw) can be expressed for unfractionated SMA in THF at 25°C by the equation $\eta = 3.98 \times 10^{-4}$ Mw$^{0.596}$, which is valid for SMA having anhydride content in the range of 5–50 mol %.[17] The molecular weight of SMA copolymers, as obtained by the Mark–Houwink equation for SMA11, SMA21, and SMA31 are 1862, 2015, and 2276, respectively, and are given in Table I. The range of molecular weights of SMA which can be used efficiently as a dispersant has been reported as 1600–2000. Thus the molecular weights obtained for SMA11, SMA21, and SMA31 in this study are in a range such that these can be modified for use as a dispersant.

Kuo et al.[22] reported that an appropriate molecular weight is an important factor for polymer dispersant because the polymers having inadequate molecular weight could possibly act as a flocculants and interaction with dispersing particle is difficult. An appropriate molecular weight of copolymer of styrene and maleic anhydride can be obtained through alternating copolymerization under a controlled condition like temperature, because maleic anhydride is a type of monomer that does not undergo homopolymerization by the normal free-radical initiation

TABLE II
Brookfield Viscosity of 20% Solid in Ammonical Solution at 30°C for SMA Copolymers

S. no.	SMA copolymer	Brookfield viscosity of 20% solids in ammonical solutions (cP at 30°C)
1	SMA11	26
2	SMA21	136
3	SMA31	gel

process; it can only copolymerized with election donating monomers like styrene.

As can be observed from Table I, the molecular weight of copolymer SMA11 is the lowest among the three and molecular weight increases with an increase in styrene in the feed. The increase in molecular weight is 8.2% for SMA21 and 22.2% for SMA31. This increase in the molecular weight with the increase in styrene in molar feed may be due to formation of homopolymer at the propagating end of the chains once the maleic anhydride has been consumed.

It has been reported by Barb et al.[23] and Walling et al.[24] that styrene and maleic anhydride form alternating copolymer over all ranges of monomer feed ratios at moderate temperature (e.g., 80°C). Since SMA11, SMA21, and SMA31 have been synthesized in this study at 80°C, it is expected that the copolymers formed are alternating in nature and can be used as a dispersant. When these alternating copolymers are treated with alkalis, the charges on the modified copolymers are homogeneously distributed and these can be useful as pigment dispersants.

Acid value

The acid value of styrene-maleic anhydride for SMA11, SMA21, and SMA31 are 480, 357, and 295, respectively. These results are in good agreement with the SMA series reported in the literature.[20] Since acid value is a measure of number of acidic group present, the acid value of copolymer decrease with decrease in maleic anhydride content as the concentration of acidic groups available on polymer chains becomes lower. The copolymers with lower acid values would have less-functional groups for further reaction and thus less tendency to interact with dispersing particles. Thus, the acid value of SMA copolymer would be a factor which affects the efficiency of SMA to act as a dispersing agent.

Brookfield viscosity

The typical viscosity of 20% solid in ammonical solution was observed on the Brookfield viscometer at 30°C for SMA11 and SMA21 and found to be 26 and 136 cp, respectively, as shown in Table II. This increase in viscosity of the copolymers formed by
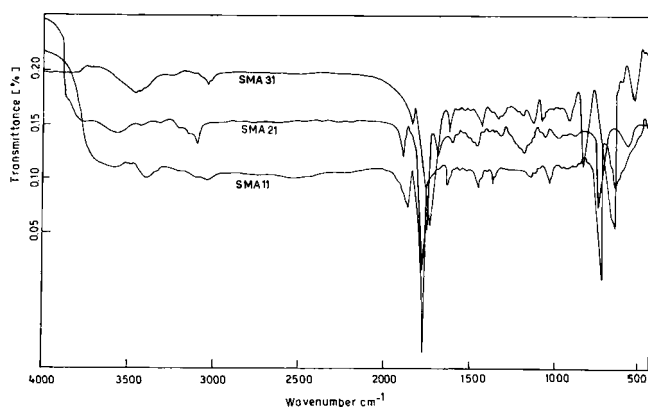
Figure 2 FTIR Spectra of SMA11, SMA21, and SMA31.

taking higher styrene in feed may be due to the higher molecular weight of the copolymer, which has also been observed by viscometry.

In case of copolymer SMA31 with a further higher homocopolymer content in the polymer, a gel is formed and viscosity could not be measured. This may occur because in this case anhydride groups present on polymer are insufficient for dissolution in ammonical solution and, due to the bridging effect of water-insoluble polystyrene molecules, a gel is formed and viscosity could not be measured.

Hydrolysis

The SMA copolymers are prepared by taking the mole ratio of styrene to maleic anhydride as 1 : 1. The ratios 2 : 1 and 3 : 1 have been synthesized in such a way so as to obtain copolymers having molecular weight in the same range. Since an alternative SMA is useful for acquiring the polycarboxylates of which charges are homogeneously separated, the reaction temperature during synthesis of SMA copolymers was kept at 80°C and the solvent used was N,N-dimethylformamide. According to Seymour et al.,[18] the SMA copolymers synthesized under these conditions was found to be an alternative copolymer. The synthesized copolymers have been hydrolyzed with sodium hydroxide solution and designated as SMAH11, SMAH21, and SMAH31. The

copolymers hydrolyzed with potassium hydroxide and ammonium hydroxide were designated as SMAK11, SMAK21, and SMAK31, and SMAN11, SMAN21, and SMAN31, respectively. The hydrolysis of SMA copolymers in all the three alkalis results in formation of ionic bonds between alkali metal and anhydride groups of SMA making SMA water soluble.

Characterization by Fourier Transform infrared spectroscopy

The infrared spectra of the copolymers obtained for polymers with different molar ratios of styrene and maleic anhydride, designated as SMA11, SMA21, and SMA31, were taken and their spectra are shown in Figure 2. In all the spectra, the prominent absorption bands in the ranges of 1840–1800 and 1778–1725 cm^{-1} represent asymmetrical and symmetrical $\nu_{C=O}$ of maleic anhydride moieties. The presence of two strong bands in the ranges of 1650–1640 and 1455–1440 cm^{-1} shows $\nu_{C=O}$ of phenyl groups on the backbone. The characteristic bands of five-membered cyclo anhydride, i.e., ν_{C-O-C} has been observed in the range of 1390–1380 cm^{-1}. The bands in the range of 765–700 cm^{-1} are the characteristic bands of the $\delta_{C=C}$ of the Phenyl groups. The broad absorption bands in the ranges of 3485–3400 and 3400–3000 cm^{-1} are due to the absorption of water from the air during preparation of KBr pellets. The details of bands from FTIR spectra for various SMA copolymers are shown in Table III. It has been observed from the spectra bands of different SMA copolymers that as the concentration of maleic-anhydride decreases in the molar feed ratios, the absorption peaks of the anhydride groups becomes broader. It has also been observed from the higher area under bands of phenyl groups that as the concentration of styrene is increased in the starting monomer mixture, the styrene content in copolymer increases. Similar peaks have been observed for SMA copolymers in the literature[22-28] Sadhir et al.[29] had also drawn similar conclusions from their studies in which they had varied the Sty : MAn ratio from 3 : 1 to 22 : 1 when there was a very low concentration of maleic anhydride in the feed (i.e., Sty : MAn was

TABLE III
Details of Bands from FTIR Spectra

| Copolymer	Bands at wave number (cm^{-1})			
SMA11	1846 and 1778	1644–1447	1383.68	702
SMA21	1847 and 1728.64	1645.62–1446.34	1385.17	762.38
SMA31	1848 and 1732.75	1646.57–1451.91	1386.06	700.40
Characteristic groups representing the band	Adsorption bands for asymmetrical and symmetrical $\nu_{C=O}$ of maleic-anhydride moiety	Absorption bands for $\nu_{C=C}$ Phenyl groups	Five membered cyclo anhydride ν_{C-O-C}	$\delta_{C=C}$ of the phenyl groups
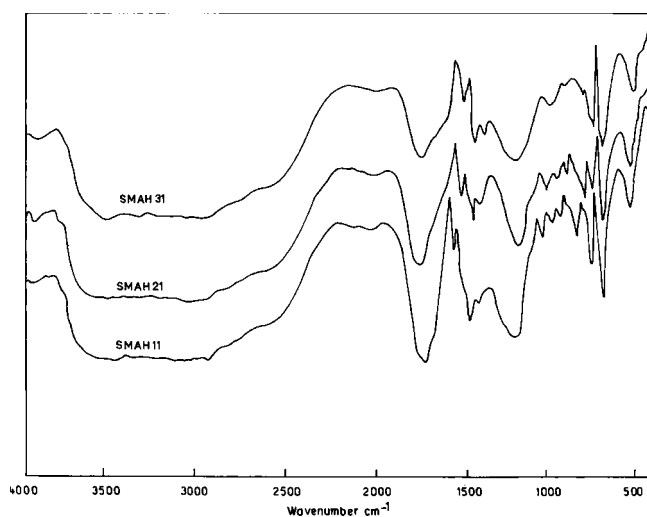
Figure 3 FTIR Spectra of SMAH11, SMAH21, and SMAH31.

22 : 1); a homopolymer mixture of styrene and co-polymer of styrene and maleic-anhydride was obtained.

The infrared spectra of the SMA copolymers modi-fied with sodium hydroxide are shown in Figure 3. During the hydrolysis, the anhydride groups of the SMA copolymers open to give anionic carboxylate salts, as shown in Figure 1, and these polycarboxy-late salts are soluble in all proportions with water and act as a dispersing agent. In all the spectra of the sodium salts of SMA, namely, SMAH11, SMAH21, and SMAH31, the reduction in the characteristic peaks of anhydride present in the range of 1840–1800 cm^{-1} as compared to the respective peaks in the IR plots of unmodified SMA (given in Fig. 2.) indicates that most of the anhydride groups have reacted with alkalis. The peaks in the range of 1500–1400 cm^{-1} in the IR plots of modified SMA in Figure 3 are the characteristic absorption peaks of carboxylate anion stretching[30] type. Similar observations had been made by Susmer et al.[31] while studying the active and selective transport of K^+ and Na^+ ions through poly (styrene-alt-maleic acid) membrane crosslinked with tetraethylene glycol. They found the complete disappearance of peak at 1860 cm^{-1} after one week of dipping in the dilute alkalis. They suggested that this is because all the maleic anhy-dride residues had been opened in presence of alkali to form carboxylates.

From the IR spectra of SMAH11, SMAH21, and SMAH31 given in Figure 3, it is obvious that the bands for carboxylate anion became slightly broader from SMAH11 to SMAH31. This may be because the anhydride groups present on polymer chain, which are required to form strong complexes with multiva-lent cations, decrease with an increase in styrene

content in the feed. The variation observed in the absorption of peak of carboxylate anion of the hydro-lyzed SMAH is not very prominent from SMAH11 to SMAH31. This is because in the copolymerization of styrene and maleic anhydride variation in the feed ratio has little effect on polymer compositions, and there is a strong tendency of these monomers to form alternating copolymer. When excess of styrene is taken in the feed, these monomers have a tend-ency to form homopolymer at the terminal ends, which causes only a slight variation in the number of anhydride groups present on the polymer chain. Nguyen et al.[32] have reported SSS triad sequence distribution along with MSS, SSM, and MSM triads in ^{13}C-NMR analysis of SMA even when styrene homopolymer had been removed.

Dispersibility of TiO_2 particles

Apparent viscosity is always used to characterize a non-Newtonian fluid that shows different viscosities under a different shear rate.[33,34] For a well-dispersed system, the aggregate of particles is small, so that the spindle senses a smaller hindrance from aggre-gates under a given shear rate and, consequently, detects a smaller shear stress and a lower viscosity.

In contrast, the agglomerate of a poorly dispersed system forms a network that hinders the spindle and results in a higher shear stress and there by showing a higher viscosity. In this study, a low-shear-rate viscometer (the abovementioned Brookfield Synchro Lectric, Model RTV) with a spindle of SCS-6 was used to measure the apparent viscosity so that the effectiveness of the synthesized alkali-modified SMA copolymers as dispersant for TiO_2 can be assessed. For this, a paste of 50 gm of TiO_2 was prepared and varying amounts of SMAH11, SMAK11, and SMAN11 in the range of 0.5–5% was added. The Brookfield data of these pastes were plotted as a function of fractional concentration of copolymer in the paste, as shown in Figure 4. When TiO_2 was dis-persed in water without any copolymer, the appa-rent viscosity of the paste was too high, as compared to those which contain alkali-modified SMA copoly-mers. Due to the charges on the surfaces of TiO_2 particles when dispersed in water, an interparticle repulsion develops which leads to an increase in viscosity. Upon the addition of any of these modi-fied copolymers, the paste viscosity was reduced and could be determined using the Brookfield viscometer, as is obvious from Figure 4. The appa-rent viscosity of the paste containing 0.5% sodium-modified SMA11 was 164 cps, while when same amount of potassium and ammonium-modified SMA11 was added, the viscosity was found to be 180 and 222 cps, respectively. This may be due to the anionic nature of alkali-modified SMA copoly-
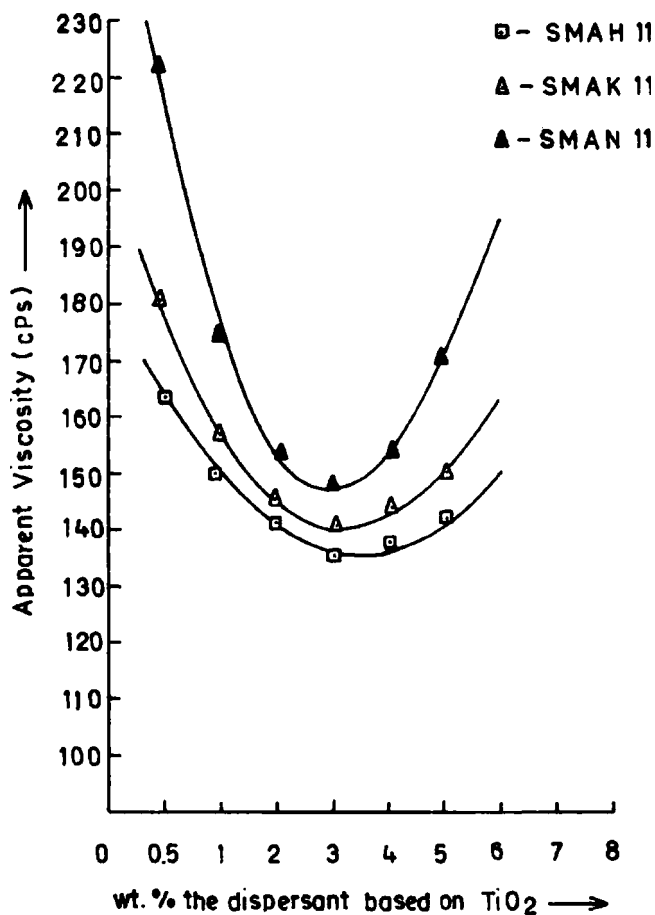
Figure 4 Relationship between viscosity and dispersant concentration of SMAH11, SMAK11, and SMAN11 for dispersion of TiO$_2$ determined using a Brookfield viscometer.

mers; the relative balance of positive and negative charges on the surface of TiO$_2$ is altered and so the isoelectric pH value is altered as well. This decreases the separation of pigment particles due to repulsion of ionic charges present on the surfaces.

It is obvious from Figure 4 that the increase in the concentration of dispersant results in the lower viscosity, and at a particular concentration the viscosity inversion is exhibited. This concentration can be taken as optimum concentration of dispersant copolymer. The dispersant concentration excess to this can be considered to be counter productive only. Thus these results show that the alkali-modified SMA copolymers can be used as dispersant for dispersion of TiO$_2$ particles in water.

Kuo et al.[22] also have studied dispersing ability of styrene-maleic anhydride for dispersion of polar and nonpolar particles and found that the apparent viscosity after an optimum concentration increased. The dispersing ability of various synthesized alkali-modified SMA11 copolymer has also been studied using a simpler method, namely, the Daniel flow method. For this the aqueous solution having frac-

tional concentration varying in the range of 0.5–5% of alkali-modified SMA in distilled water has been used for dispersion of 20 gm of the TiO$_2$ particles. The amount of dispersant solution required to disperse the TiO$_2$ pigment particles have been plotted as a function of fractional concentration of dispersant in solution. Such plots obtained for copolymers SMAH11, SMAK11, SMAN11 are shown in Figure 5. The amount of aqueous solution required to disperse the TiO$_2$ pigment in absence of any dispersant is as high as 36.2 ml, as shown in Figure 5, and on addition of sodium salt of SMA11 (i.e., SMAH11), the aqueous solution required to disperse the same amount of TiO$_2$ reduces. It drops to 15.2 ml in the presence of 0.5% of SMAH11 and decreases as the concentration of SMAH11 increases in the solution. It keep on decreasing until the concentration of SMAH11 in aqueous solution reaches at some minimum concentration beyond which, when the concentration of modified SMAH11 in the solution is increased, the amount of aqueous solution required to disperse 20 gm of pigment particles starts increasing.

As per the principle of the Daniel flow method, the least concentration at which the amount of aque-
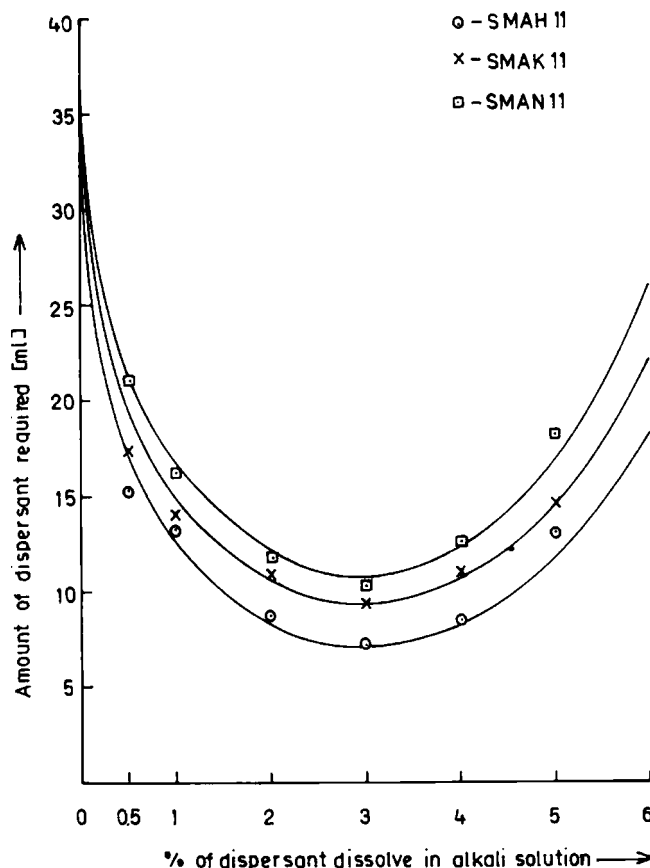

Figure 5 Daniel flow curve of SMAH11, SMAK11 and SMAN11 for dispersion of TiO$_2$.

TABLE IV
Dispersing Ability of Alkali-Modified SMA Copolymers for Dispersion of TiO_2

S. no.	SMA copolymers	Molecular weight SMA copolymer used for modification	Optimum concentration of aqueous solution of modified SMA for dispersion of 20 gm TiO_2
1	SMAH11	2180	7.2
2	SMAH21	2205	9.4
3	SMAH31	2276	11.0
1	SMAK11	2180	9.2
2	SMAK21	2205	10.4
3	SMAK31	2276	13.0
1	SMAN11	2180	10.2
2	SMAN21	2205	11.2
3	SMAN31	2276	14.4

ous solution required to disperse the TiO_2 is termed the optimum concentration of that dispersant. The optimum concentration for NaOH-modified SMA11 is 7.2 ml, which is about 80% less than the aqueous solution required for dispersion of 20 gm of TiO_2 when no copolymer is present in it. A similar behavior has been observed for KOH- and NH_4OH-modified copolymers, as shown in Figure 5. The optimum concentration observed in this way for SMA11 copolymers modified with different alkalis have been found to be 3%. The amount of aqueous solution of these copolymers required to disperse the same amount of TiO_2 at optimum concentration is given in Table IV. For SMAH11, the volume is about 7.2 ml of dispersant at optimum concentration and for SMAK11 SMAN11, it is 9.4 and 10.2 ml, respectively. Thus, it is obvious from the above results that alkali-modified SMA resins can improve dispersion of TiO_2 in the water. The reason for this better dispersion with the addition of alkali-modified copolymer is the presence of reactive ionic carboxylic groups on the SMAH, SMAK, and SMAN copolymers, which are formed between the anhydride groups of maleic anhydride present on the polymer chains and the alkali metals. The formation of carboxylic groups can be confirmed by comparing the IR spectra of sodium-modified SMA copolymers with that of unmodified SMA11, wherein reduction of anhydride peak as well as characteristic peak of carboxylic group has been observed in the later. Due to the presence of these groups, the water-insoluble SMA resin becomes water-soluble polymer having a unique anionically charged chemical structure. When hydrophilic anionically charged SMA copolyme (i.e., SMAH, SMAK, or SMAN) is added for dispersion of TiO_2, it becomes adsorbed on the surface of particles of TiO_2 by anchoring through carboxylic groups. Thus, it may be presumed that the presence of ionic groups directing outside the surface makes the overall surface of the pigment particles hydrophilic in nature; these particles interact in such a way to prevent agglomerations, hence making dispersion more efficient.

Shenoy et al.[35] synthesized alphamethyl styrene-maleic anhydride copolymer having molecular weight as 8000 and modified it using dibutyl amic acid and diethanolamic acid. On the basis of their studies for dispersion of 20 gm of TiO_2 in water, they concluded that diethanolamic acid-modified copolymer gives better dispersion, as diethanolamic acid is more hydrophilic in nature. The reason for this behavior has been attributed to the presence of hydroxyl group on copolymer modified by diethanolamic acid, which is directed outside the surface. Wang et al.[36] had synthesized four kinds of SMA copolymers derived with different charged forms containing carboxylic acid groups and exhibiting characteristic indicative of anionic cationic, zwitterionic, or nonionic surfactants, as the pH was changed. Their result showed that the dispersing abilities are the function of the pH of the system and found that degree of aggregation observed by fluorescence spectroscopy for all dispersants at high concentration increases in the order: SMA-Na < SMA-B [poly(styrene-Co-B-iminoproply-N-trimethyl ammonium acetate) maleic acid, disodium salt] < SMA-N < SMA-Q [poly(styrene-Co-B-iminoproply-N-trimethyl ammonium sulfate.) maleic acid, sodium salt]. In their studies of influence of SMA copolymer on the stability and flocculation of quinacridone red-pigment suspension, Zhou et al.[37] observed that the SMA copolymer improved the dispersion, and the system with an intrinsic viscosity of 0.2438 Lg^{-1} gave the best dispersing ability. Apart from pigment dispersion, alkali-modified SMA copolymers have also been used for dispersion in suspension ion and emulsion copolymers. Nolken et al.[38] have studied modification of SMA with ammonium hydroxide to generate polymers which were found to be efficient dispersing agents for suspension and emulsion polymerization.[39] Thus, by incorporation of the alkali group on SMA copolymers, the polymer becomes
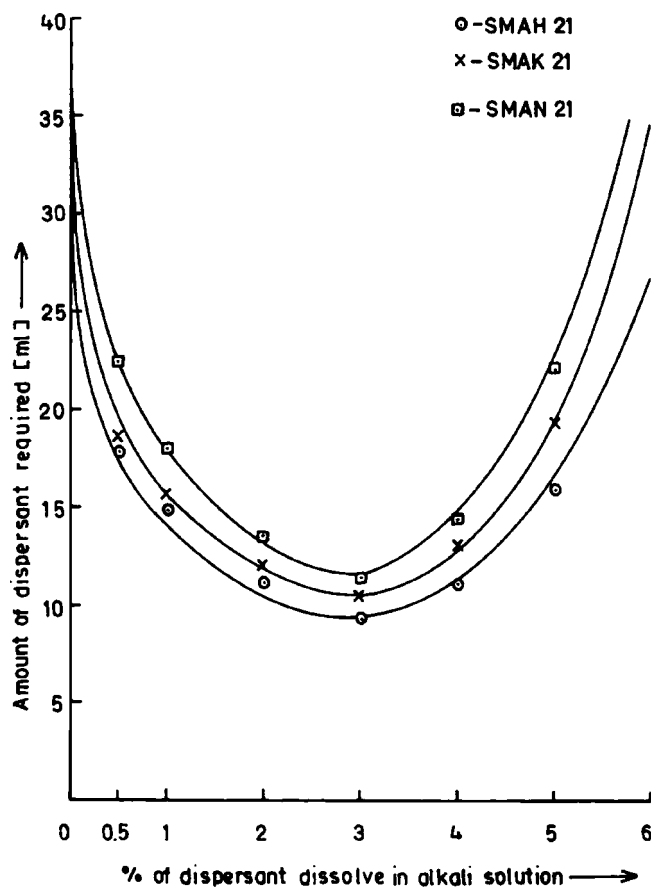
Figure 6 Daniel flow curve of SMAH21, SMAK21, and SMAN21 for dispersion of TiO$_2$.

water soluble and can act as an efficient dispersant for TiO$_2$.

Effect of alkali used for modification

The efficiency of alkali-modified SMA depends on the compound which is used for its modification. In order to study this, the SMA has been modified by three alkalis, namely, NaOH, KOH, and NH$_4$OH. On comparing the results the amount of 0.5% of aqueous solution of SMAK11 and SMAN11 required to disperse 20 gm of TiO$_2$ is 17.2 ml and 21 ml, respectively as compared to 15.2 ml for 0.5% SMAH11 containing aqueous solution. Similarly at 1% concentration of SMAK11 and SMAN11 copolymers the amount of aqueous solution required to disperse 20 gm of TiO$_2$ is 14 ml and 16.2 ml as compared to 13.2 ml for SMAH11 copolymers. The optimum concentration also varies with alkali used for modification as it has been shown in Figures 5–7. For SMAK11 and SMAN11 the optimum concentration is 9.4 ml and 10.2 ml, respectively as compared to 7.2 ml for SMAH11 copolymers. Similarly, in case of using the Brookfield viscometer, the apparent viscos-

ity at 0.5% of dispersants of SMAK11 and SMAN11 required to disperse 50 gm of TiO$_2$ is 180 cps and 222 cps, respectively, as compared to 164 cps for 0.5% SMAH11 containing aqueous solution. Similarly, at 1% concentration of SMAK11 and SMAN11 copolymers, the apparent viscosity of the dispersants required to disperse TiO$_2$ is 158 and 175 cps, as compared to 150 cps for SMAH11 copolymer. At the optimum concentration for SMAK11 and SMAN11 it is 142 and 149 cps, respectively, as compared to 136 cps for SMAH11 copolymer, as is obvious in Figure 4.

Thus, among the three alkalis studied, the sodium-modified SMA copolymers (i.e., SMAH copolymers) have been found to give the best dispersion, as the amount of aqueous solution required for dispersing the same amount of TiO$_2$ particles at optimum concentration (in this case) is minimum, as compared to the KOH- and NH$_4$OH-modified SMA copolymers studied.

The dispersion, which is actually the reduction of agglomerate size, is governed by a simple balance between the hydrodynamic forces actively pulling the minor component (i.e., fine particle clusters) apart verses cohesive forces acting to hold the minor com-
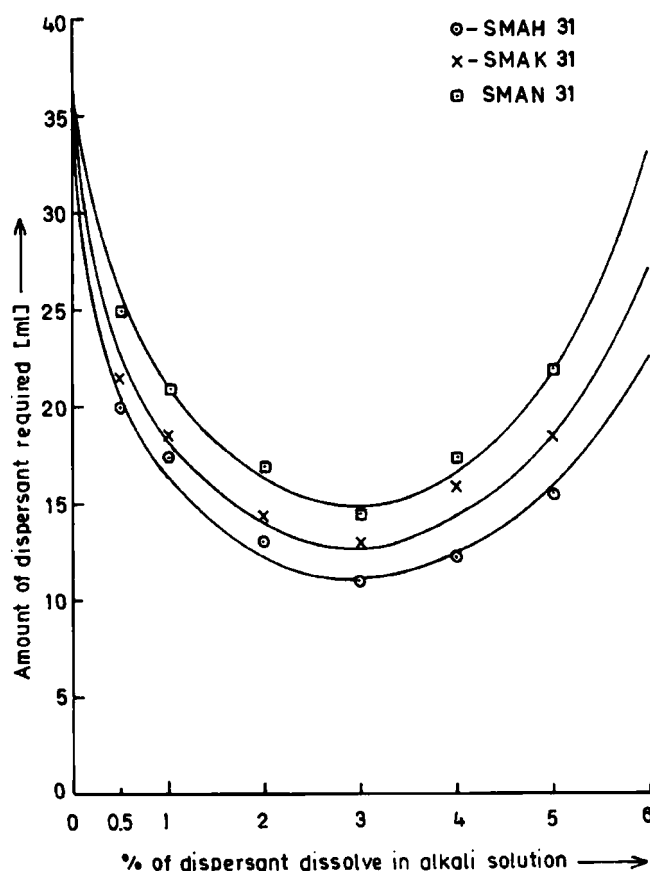

Figure 7 Daniel flow curve of SMAH31, SMAK31, and SMAN31 for dispersion of TiO$_2$.

ponent together. The hydrodynamic forces are dependant upon the strength of the flow field, which can be varied by the presence of a modifier. If the modifier is ionic in nature, an ionic field is developed which, if stronger than the cohesive forces of agglomerate, results in reduction in cluster size. This is because of the difference in basicity of sodium hydroxide, potassium hydroxide, and ammonium hydroxide; thus, the tendency for ionization is higher in case of NaOH, as compared to KOH and NH$_4$OH, and due to the presence of stronger concentration of ions on sodium-modified SMA anchoring TiO$_2$ particles, their agglomeration is prevented to a greater extent and better dispersion is formed with lower amount of aqueous solutions of sodium-modified copolymers, as compared to that with other two alkali-modified copolymers. Zhou et al.[39] studied the effect of ammonium salt of styrene-maleate copolymer on the rheology of quinacridone red pigment and found that the flow curve of the quinacridone pigment dispersion with SMA-NH$_4$ copolymer showed a nearly Newtonian behavior. They also found that the rheological properties of aqueous quinacridone pigment dispersion with SMA-NH$_4$ were strongly affected by both pH and ionic strength. Lung-Pin Chen et al.[40] studied the dispersing ability of the Amphoteric water-soluble copolymer, polyacrylamide/[α-N,N-dimethyl-N-(3-(β-carboxylate) acryl amino)propyl] ammonium ethanate (PAM/DAE), as a dispersing agent for Barium titanate (BaTiO$_3$) particles. They found that this copolymer could uniformly disperse the particles and the resulting suspensions were less viscous, more stabilized, and contained powder with smaller particle size. They also found that the dispersing/stabilizing ability of PAM/DAE is close to or slightly better than that of a commercial dispersants, ammonium salt of poly(methacrylic acid).

After comparing the results of dispersion studies of alkali-modified SMA11 for TiO$_2$ particles observed using the Brookfield viscometer and the Daniel flow method, it was observed that both exhibit inversion of dispersibility at same concentration and thus the optimum concentration value is the same for a dispersant copolymer, whether studied using the Brookfield viscometer or the Daniel flow method. This is because the lowered viscosity of well-dispersed solution is associated with a decrease in resistance to flow, which can be compared to the lower volume requirement of dispersant to achieve drops, with an elastic snap back considered an end point in the Daniel flow method. Since the Daniel flow method is a simpler method and the quantities of copolymer and TiO$_2$ required are less in this case; thus, the dispersion analysis of rest of the copolymer (i.e., those based on SMA21 and SMA31) were done only by using the Daniel flow method.

Effect of maleic anhydride content

After comparing the result of Daniel Flow studies of sodium-modified SMA11, SMA21, and SMA31 for dispersibility given in Figures 5, 6, and 7, respectively, it was observed that the efficiency of a dispersant is very much dependent on the extent of active groups present on the polymer, as these are responsible for dispersion. In order to study this effect of SMA copolymers on dispersion, the copolymers of varying compositions were studied. For this purpose, three copolymers having the Sty/MAn molar feed ratios of 1 : 1, 2 : 1, and 3 : 1 were synthesized. The anhydride content of these copolymers, as determined by elemental analysis, was found to be 48, 46, and 41%, respectively. These copolymers were modified with three different alkalis and used for studying dispersion of TiO$_2$. The plots for the Daniel Flow studies for the modified copolymers having SMA molar feed ratios of 2 : 1 and 3 : 1, as referred to SMAH21, SMAK21, SMAN21 and SMAH31, SMAK31, and SMAN31, are given in Figures 6 and 7, respectively. After comparing the results shown in these plots, it was observed that for all the copolymers studied, SMA11 exhibits better dispersibility as compared to SMA21 and SMA31. It was found that when 0.5% of SMAH11 copolymer was used for dispersion, the amount of aqueous solution required to disperse 20 gm of TiO$_2$ particles is 15.2 ml and when 1% SMAH11 is used, it is 13.0 ml. On the other hand, the amount of 0.5% of modified SMAH21 required to disperse the same amount of TiO$_2$ is 18.0 ml and that of 1% of SMAH21 it is 15 ml. When SMAH31 is used at same concentrations, the amount of aqueous solution required was found to be 20.0 and 17.4 ml, respectively. These results show that the amounts of aqueous solution required at optimum concentration observed for sodium-modified SMAH21 and SMAH31 copolymers are 9.4 and 10.8 ml, respectively, as compared to 7.2 ml observed for SMAH11. A similar behavior has been observed for SMA copolymer modified with KOH and NH$_4$OH, as the minimum optimum concentration value was observed for SMAK11, as compared to SMAK21 and SMAK31, and for SMAN11 as compared to SMAN21 and SMAN31. The amount of aqueous solution of these copolymers at optimum concentrations is given in Table IV. Thus, it is obvious from these results that among the various copolymers studied, the minimum amount of aqueous solution is required in the case of sodium-modified copolymer, synthesized with a mole feed ratio of styrene to maleic anhydride as 1 : 1. Denis et al.[41], while preparing emulsion copolymer by a semicontinuous process, added SMA copolymer in a second stage as a comonomer to produce coagulum-free latex, and found SMA11

having a 1 : 1 ratio of styrene to maleic anhydride in its copolymers to be the preferred resin, as opposed to SMA21 and SMA31, respectively. This was because it interacted least with the conventional surfactant, which allowed its ready incorporation into coagulum-free recipies.

Thus, all SMA11 copolymers are giving better results in dispersing 20 gm of TiO_2 particles, as compared to SMA21 and SMA31, when modified with any of three alkalis studied. This is because, in the case of SMA11, the number of carboxylic groups required for bond formation with various alkalis is present in higher concentration, as compared to SMA21 and SMA31. This is evident from the higher acid value for SMA11, which is 480 and suggests the presence of larger number of carboxylic groups on SMA11, as compared to SMA21 and SMA31, the acid values for which are 357 and 295, respectively. The broadening of bands in the IR spectra of SMAH21 and SMAH31, as compared to SMAH11, confirms this (see Fig. 3). Thus, the presence of a large number of carboxylic groups on modified SMA11 would lead to a higher probability of interacting with dispersing particles and it would act as a more efficient dispersing agent, as compared to modified SMA21 and SMA31. The lower number of carboxylic groups present on SMA21 and SMA31, as compared to SMA11 polymer chains, causes the anti-bridging effect to be more prominent, which would make them less effective as a dispersing agent.

Effect of molecular weight on the dispersing ability of SMA

The SMA copolymers having molar feed ratios of styrene and maleic anhydride of 1 : 1 have been synthesized by adjusting the reaction conditions to obtain resins of molecular weight varying in the range of 1770–2710 and acid values in the range of 475–490. The optimum concentrations were observed for these modified copolymers for dispersion studies by the Daniel flow method, as given in Table V and Figure 7. Figure 8 shows a plot between the optimum concentration observed for SMA of varying
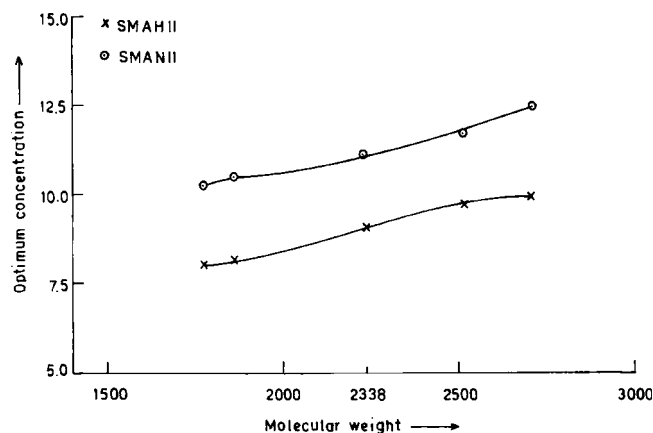
TABLE V
Dispersing Ability of Alkali-Modified SMA11 Copolymers for Dispersion of TiO₂

| | Optimum concentration of aqueous solution of modified SMA11 for dispersion of TiO_2 | | | |
S. no.	Molecular weight	Acid value	SMAH11	SMAN11
1	1770	475	8.0	10.2
2	1860	480	8.2	10.5
3	2240	486	9.1	11.1
4	2520	485	9.8	11.7
5	2710	490	9.9	12.4

Figure 8 Optimum concentration of alkali-modified SMA11 as a function of its molecular weight for dispersion of TiO_2 determined using the Daniel flow method.

molecular weight as a function of molecular weight, which demonstrates that there is not much variation in the optimum concentration of modified SMA required to disperse 20 gm of TiO_2 when the molecular weight of SMA has been varied in the above mentioned range, although it tends to increase with molecular weight. Thus, the dispersing ability of SMA decreases with an increase in the molecular weight of the resin. This may be attributed to the increased size of molecules that restrict the anchoring process and, subsequently, the adsorption of polymer on TiO_2 particles. Thus, the molecular weight of SMA resins should be kept in the range of 1800–2200.

CONCLUSIONS

1. Styrene-maleic anhydride (SMA) copolymer of molecular weight in the range of 1800–2200 can be synthesized using benzoylperoxide (BPO) as an initiator and N,N-dimethylformamde (DMF) as a solvent at the temperature of 80°C.
2. The percentage yield achieved is higher when the styrene to maleic anhydride ratio in the feed is 1 : 1, as compared to feed ratios of 2 : 1 and 3 : 1.
3. The characteristic bands of SMA observed in the FTIR spectra of all the types of SMA copolymers synthesized confirm the formation of SMA copolymer.
4. The reduction in the peaks of anhydride groups and presence of carboxylate anion peaks in the FTIR spectra of the alkali-modified SMA indicates that the most of the anhydride groups reacts with alkali to form alkali-modified SMA resin.
5. The SMA copolymer modified with alkalis such as NaOH, KOH, and NH_4OH, becomes soluble in water.

6. The effectiveness of the synthesized alkali-modified SMA copolymer as dispersant for TiO$_2$ can be assessed using a Brookfield viscometer and the Daniel flow method.

7. The amount of aqueous solution required to disperse 20 gm of TiO$_2$ decreases when these alkali-modified SMA copolymers are added in the solution and thus these copolymers have the ability to function as dispersing agents.

8. Among the three alkalis used for modification of SMA, the sodium-modified SMA copolymer of all three types of copolymers, namely, SMA11, SMA21, and SMA31, have been found to give the best dispersion among the three different modified copolymers studied.

9. Among the three copolymers synthesized by taking varying monomer ratios, the SMA11 copolymer modified by any of the three alkalis has exhibited the best dispersion. This is because of the presence of a higher number of carboxylic groups present on SMA11, which is required for hydrogen bonding with hydroxyl groups of alkalis, as compared to those present on SMA21 and SMA31.

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