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Thermal and dielectrical studies of acryolonitrile with isobornyl acrylate and methacrylate copolymers

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ABSTRACT

Copolymers of Acrylonitrile with Isobornyl acrylate (IBA) and Isobornyl Methacrylate (IBM) were synthesized by free radical polymerization using AIBN as initiator in dimethyl formamide (DMF) at 60 ± 1°C. Thermo gravimetric analysis of the copolymers was performed and their thermal stabilities were studied. Thermal stability of IBM copolymers is found to be more than that of IBA copolymers. The dielectric properties of the copoymers were studied. The dielectric loss of the copolymers is found to be shifting to a higher temperature from acrylate to methacrylate copolymers.

Key words: Acrylonitrile, isobornylacrylate, isobornylmethacrylate, copolymerization, thermal and dielectric properties.

INTRODUCTION

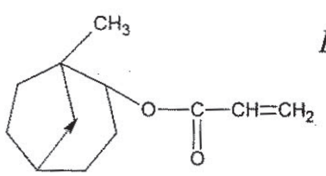
The copolymers of isobornylacrylate and methacrylate seem to show high tensile strength, elongation at break and upper service temperature[1]. Introduction of isobornylacrylate and methacrylate ito various copolymers seem to modify and improved the properties of a number of copolymers[1,2]. In our earlier communication[3], we have discussed the copolymer of isobornyl arcylate and methacrylate with acrylonitrile.

The present work was under taken to study the properties of copolymers of isobornylacrylate and methacrylate with acrylonitrile, in order to study the thermal and dielectric properties of the above synthesized copolymers.

EXPERIMENTAL

Acrylonitrile (AN), Isobornyl acrylate (Aldrich) and Isobornyl methacryalte (Lancaster) were purified by washing with 5% solution of sodium hydroxide twice and subsequently with distilled water for three to four times. Then they are dried over calcium chloride before distilling uder reduced pressure. The middle fraction of the distillate is collected and used for copolymerization. 2,2'-Azobisisobutyronitrile (AIBN) (Fluka) was crystallized from methanol. The solvent used in copolymerization as DMF which is a reagent grade chemical. This dried and purified by distillation before use.

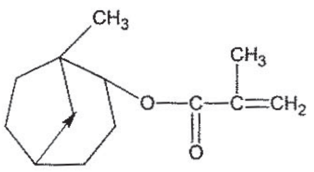
All Experimenta are performed in glass tubes with appropriate quantities of dry monomers,



Isobornyl acrylate (IBA)

$$H_2C-\underset{CN}{\overset{H}{C}}$$

Acrylonitrile



Isobornyl methacrylate (IBM)

The monomer unit structures

solvents and initator. The tubes are then sealed in an atmosphere of nitrogen and then they were introduced into the thermostat at 60 ± 1°C temperature. The reaction is allowed to go for less than 10% conversiton i.e. 90 min. After a given time, the polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered and washed thoroughly with water followed by ether and hexane for purification. Then it was dried under vaccum. Different samples were prepared by changing the initial monomer feed. The initiator is used at 2.5 g/l of solvent. The total monomer concentration was maitained at 1.5 M, while the feed ratio is varied.

Thermal studies

Thermal stability of the copolymers AN-IBA and AN-IBM are determined uisng V51A Dupont 2000 at a heating rate of 10/min. The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature at 50% weiht loss. In these copolymers, the factor that can influence therma stability are (a) backbone structure (b) nature of the acrylate and methacrylate and (c) nitrile content. To obtain a comparative picture of relative thermal stability, initial decomposition temperature, integral procedural decomposition temperature and decomposition temperature for 50% weight loss are summarised in Table 1.

The thermal stabilities of AN-IBM copolymers are found to be more than those of AN-IBA copolymers shown in Fig. 1 & 2. This is evident from IDT and IPDT values of these copolymers. This may be attributed to the stability of the radicals formed by the decomposition process[5-6]. It is also evident from the data that the acrylate copolymers are less stable than the corresponding methacrylate

Table 1: Thermal behaviour of acrylonitrile with IBA and IBM copolymers

Copolymer	IDT(°C)	IPDT(°C)	Temperature (°C) at wt. loss 10%	20%	50%
AN-IBA_1	149.20	269.14	190.00	235.14	350.89
AN-IBA_2	152.60	276.44	220.00	240.62	357.16
AN-IBA_3	169.58	291.80	248.57	259.44	367.41
AN-IBA_4	175.37	312.13	252.62	270.64	413.14
AN-IBA_5	202.00	366.56	258.89	308.24	432.10
AN-IBA_1	170.24	301.06	258.92	264.72	379.56
AN-IBA_2	185.13	305.26	262.54	270.89	382.37
AN-IBA_3	190.62	313.99	268.36	282.74	390.89
AN-IBA_4	215.24	325.47	272.18	289.62	425.62
AN-IBA_5	234.56	344.21	290.10	310.20	482.34

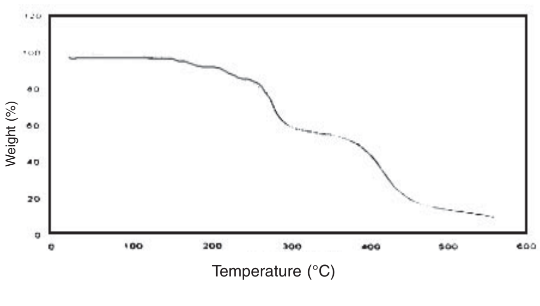


Fig. 1: Thermogram of AN-IBA_1 copolymer

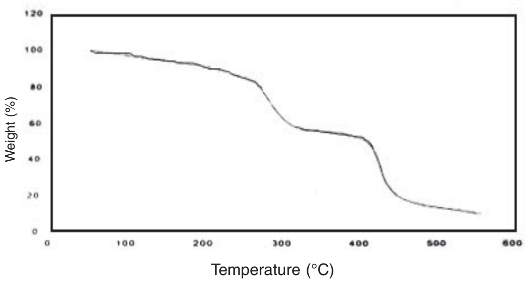


Fig. 2: Thermogram of AN-IBM_1 copolymer

copolymers . The thermal stability increase with the increasing in the nitrile content. This is also evident from the data given in Tables 1. All these copolymers are undergoing decomposition in two steps.

Dielectrial studies

A capacitance bridge model GR 1620(WG) is used to measure the dielectric constant and dielectric loss of the AN-IBA and AN-IBM Copolymes. All the samples are annealed prior to use for the measurements.

AN-IBA copolymers

For acrylonitrile-isobornyl acrylate (AN-IBA) copolymers the dielectric constant (ε') is found to vary with frequency. As the frequency is reduced from 100 to 5KHz the values of the dielectric constant are found to increase from 1.84 to 3.30 in case of AN-IBA_1, from 1.79 to 3.14 in case of AN-IBA_3 copolymers. These results are given in Table 2. The ε' values decrease slightly from AN-IBA_1 to AN-IBA_3 at any frequency. Fig 3 shows the variation of dielectric constant (ε') with frequency at room temperature for AN-IBA copolymer at different compositions.

Fig. 4 shows the frequency dependence of dieletric loss (tanδ) for AN-IBA copolymer at different compositions. It is seen from the curves that the tanδ values increase from 1×10^{-2} to 5×10^{-2} in the frequency range 100 to 5KHz for the two compositions studied namely AN-IBA_1 and AN-IBA_3. From the result given in Table 3, it is evident that the composition change is not having much influence on tanδ values increases slightly from AN-IBA_1 to AN-IBA_3.

The increase in ε' the copolymers AN-IBA_1 and AN-IBA_3 at low frequency is belived to be due to space charge polarisation. The space charge polarisation results from the carrier which are not locally boundto the material rather due to their migration on to the surface of the material or due to

Table 2: Variation of dielectric constant with frequency for AN-IBA copolymer

Frequency (f)(KHz)	Log frequency (log f) (1+logf)	'ε' AN-IBA_1	AN-IBA_3
100	3.00	1.84	1.79
50	2.70	2.01	1.99
30	2.47	2.32	2.13
20	2.30	2.88	2.41
10	2.00	2.17	2.99
5	1.69	3.30	3.14

Table 3: Variation of dielectric loss with frequency for AN-IBA copolymer

Frequency (f)(KHz)	Log frequency (log f) (1+logf)	tanδ AN-IBA_1	AN-IBA_3
100	3.00	0.010	0.016
50	2.70	0.028	0.031
30	2.47	0.037	0.042
20	2.30	0.048	0.051
10	2.00	0.054	0.059
5	1.69	0.056	0.062

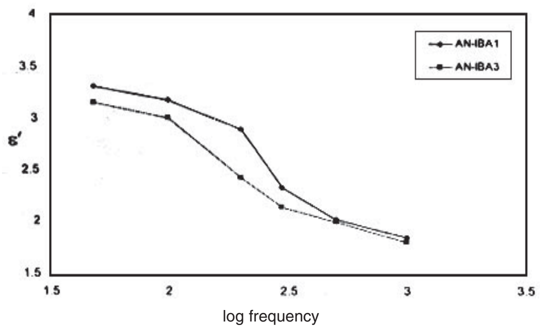


Fig. 3: Frequency dependence of ε' for AN-IBA copolymer at different compositions

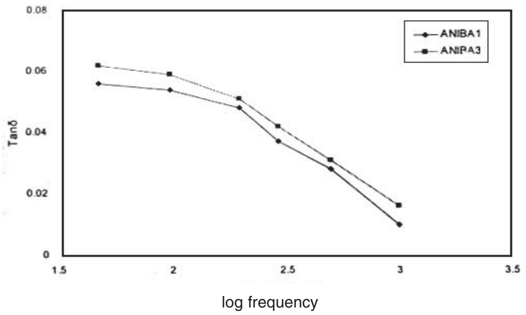


Fig. 4: Frequency dependence of tanδ for AN-IBA copolymer at different compositions

trapping themseleves in the material during their motion. The increase of tanδ values at lower frequencies may be due to the internal effects which may cause the macroscopic A.C. field distortions.

Effect of temperature on dielectric constant (ε') and dielectric loss (tanδ) has been explained by taking AN-IBA$_2$ copolymer at 1KHz. The values are given in Table 4. Fig. 5 gives a typical plot of ε' and tanδ against temperature for AN-IBA$_2$, copolymer at 1KHz frequency. With increase in temperature tanδ values increase reaches a maximum value and then decreases with further increases in temperature. A peak due to relaxation is observed in tanδ, known as α-relaxation, at a particular remperature in the rubbery state of polymer[7-11]. At lower temperatures molecular chains are not only immobile but also tightly bound at some points due to dipole-dipole interacations. As the temperature is increased more and more dipole groups are released and the mobility of polymer segments increases. For AN-IBA$_2$, tanδ$_{max}$ is occuring at 120 °C at a constant frequency of 1 KHz. The ε' value increase from 3.52 to 3.92 with increase in temperature.

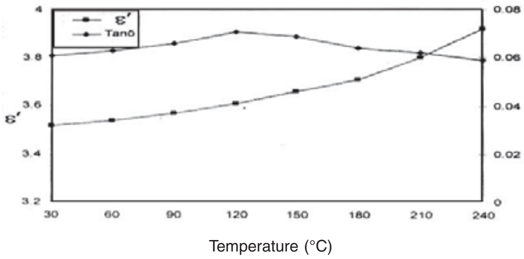


Fig. 5: Typical plot of ε' and tanδ against temperature for AN-IBA$_2$ copolymer

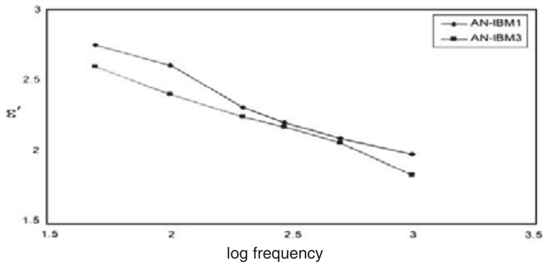


Fig. 6: Frequency dependence of tanδ for AN-IBM copolymer at different compositions

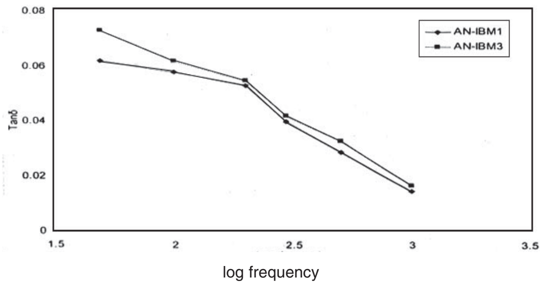


Fig. 7: Typical plot of tanδ' for AN-IBM copolymer at different compositions

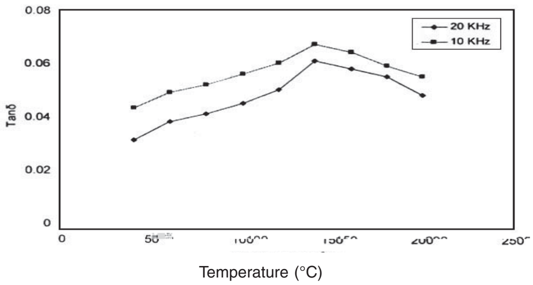


Fig. 8: Temperature dependence of ε' for AN-IBM$_2$ copolymer at different frequencies

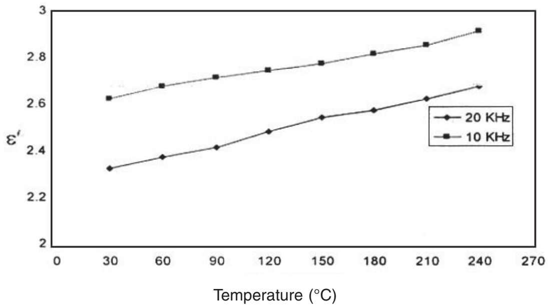


Fig. 9: Temperature dependence of tanδ for AN-IBM$_2$ copolymer at different frequencies

Table 4: Variation of dielectric constant and dielectic loss with temperature for AN-IBA copolymer at 1KHz

Temperature	ε'	tanδ
30	3.52	0.061
60	3.54	0.063
90	3.57	0.066
120	3.61	0.071
150	3.66	0.069
180	3.71	0.064
210	3.80	0.062
240	3.92	0.059

Table 5: Variation of dielectric constant with frequency for AN-IBM copolymer

Frequency (f)(KHz)	Log frequency (log f) (1+logf)	ε'	
		AN-IBM$_1$	AN-IBM$_3$
100	3.00	1.98	1.89
50	2.70	2.09	2.06
30	2.47	2.20	2.17
20	2.30	2.31	2.25
10	2.00	2.61	2.40
5	1.69	2.75	2.60

Table 6: Variation of dielectric loss with frequency for AN-IBM copolymer

Frequency (f)(KHz)	Log frequency (log f) (1+logf)	tanδ	
		AN-IBM$_1$	AN-IBM$_3$
100	3.00	0.015	0.017
50	2.70	0.029	0.033
30	2.47	0.040	0.042
20	2.30	0.053	0.055
10	2.00	0.058	0.062
5	1.69	0.062	0.073

Table 7: Variation of ε' with temperature at different frequencies for AN-IBM$_2$ copolymer

Temperature	tanδ	
	20 KHz	10KHz
30	2.32	2.62
60	2.37	2.67
90	2.41	2.71
120	2.48	2.74
150	2.54	2.77
180	2.57	2.81
210	2.62	2.85
240	2.67	2.91

Table 8: Variation of tanδ with temperature at different frequencies for AN-IBM$_2$ copolymer

Temperature	tanδ	
	20 KHz	10KHz
40	0.031	0.043
60	0.038	0.049
80	0.041	0.052
100	0.045	0.056
120	0.050	0.060
140	0.061	0.067
160	0.058	0.064
180	0.055	0.059
200	0.049	0.056

AN-IBM copolymers

For acrylonitrile-isobornyl methaacrylate (AN-IBM) copolymers the dielectric constant (ε') is found to vary with frequency. As the frequency is reduced from 100 to 5KHz the values of the dielectric constant are found to increase from 1.98 to 2.75 in case of AN-IBM$_1$, from 1.89 to 2.60 in case of AN-IBM$_3$ copolymers. These results are given in Table 5. Fig. 6 shows variation of dielectric constant (ε') with frequency at room temperature for AN-IBM copolymer.

Fig. 5 shows the frequency dependence of dieletric loss (tanδ) for AN-IBM copolymer at different compositions. It is seen from the curves that the tanδ values increase from 1×10^{-2} to 7×10^{-2} for two compositions studied namely AN-IBM$_1$ and

AN-IBM$_3$. in the frequency range from 100 to 5KHz. These variations are given in Table 6.

Fig. 8 shows the variation of dielectric constant (ε') for AN-IBM$_2$ copolymer at different frequencies as a function of temperature. The results are given in Table 7. It is observed that for any frequency as the temperature increases the value of dielectric constant increases. The ε' value increase from 2.32 to 2.67 at a frequency of 20KHz and from 2.62 to 2.91 at a frequency of 10KHz.

Fig. 9 shows the temperature dependence of dieletric loss (tanδ) for AN-IBM$_2$ copolymer at different frequencies. The results are given in Table 8. It is observed that for any frequency as temperature increases, the value of dielectric loss (tanδ) initially increases, reaches a maximum and then decreases with further increases in temperature. As the temperature increases from 40 to 200°C the tanδ reaches maximum value of 6×10^{-2} for a frequency of 10KHz at 140°C. At any given temperature, the tanδ value increases as the frequency decreases from 20 to 10KHz (Table 8).

The trend in the result of ε' and tanδ values for AN-IBM copolymer is similar to that of AN-IBA copolymers.

CONCLUSIONS

The copolymer of AN with IBA and IBM haves been synthesized using thermal initiator in DMF. Thermal properties like T_g, IDT and IPDT have been evaluated to find the stability of the copolymer. The thermal stability of IBM copolymer is more than that of IBA copolymers. The dielectric constant and dieletric loss of the copolymer were determined to find out molecular relaxations.

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