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THE INFLUENCE OF N-BUTYL MERCAPTAN ON ACRYLIC COMPOUNDS OBTAINED WINDER γ-GAMA RADIATION

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ABSTRACT

The chain transfer agents play a key role in the production of polymers, as they allow better control of their molecular weight, among other functions. For this reason we performed this study to perform an analysis on the influence of n-butyl mercaptan in the reaction of compounds of ethyl methacrylate by varying the density and shrinkage of the samples. In the present study can be seen that n-butyl mercaptan, acts as transfer agent, which influences the reaction kinetics of composite acrylic, since it presence in the compound increased average density and contraction average. It is also possible to minimize the variability of the compound density, even if they are altered. Final products with improved properties homogeneously could be obtained.

1. INTRODUTION

Arkema (2000) has reported that the agents mercaptans or thiols are analogous substances to sulfur and alcohols with a low binding energy between atoms of hydrogen and sulfur (RSH), These substances present relevant reactivity. It is considered (Adamu (1999)] that thiols belong to widely used compounds in industrial applications controlling the molecular weight of polymers. The efficiency is related to the type of selected polymerization system adopted and the reaction conditions. Their presence changes in reaction kinetics, the mechanisms of absorption and adsorption, as well as particle nucleation. According to Coutinho and Oliveira (2006) the thiols are substances, which present the highest transfer rate constant, because of weak bond S-H.

$$R - M_{n*} + R' - S - H \rightarrow^{ktr} R{-}M_nH + R'S. \qquad \text{Transfer} \qquad (1)$$

$$R'S. + M \rightarrow^{ki} R'S - M. \qquad \text{Initiation} \qquad (2)$$

The transfer can be seen as a premature termination of the chain, where there is an induced decomposition of the mercaptan molecule under the influence of an active chain. This growing chain tends to scavenge the S atom from transfer agent, resulting in its termination, as the result after the abstraction of S is accomplished, the transfer agent becomes a highly reactive radical, which initiates a new chain.

The application of ionizing radiation in the modification of polymers has provided significant results in this field. In certain cases the radiation process improves functional properties, enlarging the range of applications. According to Coutinho and Oliveira (2006) ionizing radiation is an important energy source used in polymerization, because free radical are generally in a large concentration track.

With respect to the obtained compound, radiation treatment has become a proper alternative that allows minimizing the problems of time consuming waste and contamination. The thermal initiation self-acceleration may hinder the compound obtained by changing the properties and generation internal tensions. In the case of polymerizing compounds, properties such as density and contraction are of extreme importance for the efficiency of the molding process, as well as applicability and final product quality. For this reason, the present work seeks to identify the contribution of n-butyl mercaptan to the properties (density and contraction) for methyl methacrylate subject to polymerization by ionizing radiation.

2. METHODS AND EQUIPMENT

2.1. Methodologies used

The dose of 10 kGy was chosen for sample irradiation being starting for the results reported by Cardoso et al. (2005). The irradiations were performed in a radiator Gammacell provided by Co^{60} (IPEN / CNEN-SP).

Table 1 - Main composition of samples

Component	MMA	PMMA	TBPPI	ATH- Hidral 710
Parties	100	35	----	80
manufacturer	Rudnick	Resarbrás	Akzo Nobel	Almatis

Note: MMA (methyl methacrylate), PMMA (poly methyl methacrylate); TBPPI (peroxide tert-butyl pivalate); Hidral-710 ATH (aluminum hydroxide trihydrate)

Density measurements of formulations in Table 1, were performed with solid pycnometer to Brand (Gay Lussac type) and an analytical balance.

In the first set of tests the foreseen influence properties of of n-butyl mercaptan density and shrinkage of the samples was identified brought by mercapto compounds. There were separated two groups: Group 1 consisting on free- mercaptan and samples of Group 02 having 0.6 % w% of n-butyl mercaptan added in each sample. In Table 2 the composition of the samples prepared for this first step are listed.

Table 2 - Composition of the samples with / or without n-butyl mercaptan - stage 1

	Sample	N-Butyl %	TBPPI %
GROUP 01	A-1	-	0.1
	A-2	-	0.2
	A-3	-	0.3
	A-4	-	0.4
	A-5	-	0.5
GROUP 02	A-6	0.6	0.1
	A-7	0.6	0.2
	A-8	0.6	0.3
	A-9	0.6	0.4
	A-10	0.6	0.5

Note: TBPPI – (*t*-butyl peroxide pivalate.). Irradiation dosage 10 kGy

For the second step the concentration of the transfer agent (0.1, 0.2, 0.3, 0.4 and 0.5 w%) as the initiator (0.1; 0.2, 0.3 and 0.4 w%) was varied in order to assess the effect of each factor on the samples density. In Tab.3, the composition of each sample divided into four groups are presented.

Table 3 – Samples with variation of n-butyl mercaptan and initiator - stage 2

Group	Sample	Mercaptan - %	TBPPI - %
01	B-1	0.1	0.1
	B-2	0.1	0.2
	B-3	0.1	0.3
	B-4	0.1	0.4
02	B-5	0.2	0.1
	B-6	0.2	0.2
	B-7	0.2	0.3
	B-8	0.2	0.4
03	B-9	0.3	0.1
	B-10	0.3	0.2
	B-11	0.3	0.3
	B-12	0.3	0.4
04	B-13	0.4	0.2
	B-14	0.4	0.3
	B-15	0.4	0.4
05	B-16	0.5	0.2
	B-17	0.5	0.3
	B-18	0.5	0.4

Note: TBPPI – (*t*-butyl peroxide pivalate.). Irradiation dosage 10 kGy

3. RESULTS

3.1. Analysis of densities in the presence of n-butyl mercaptan

In the following tests, the effects of variation in material density due to different TBPPI concentrations for selected groups Group 1 and Group 2 were studied.

Table 4 - Characteristics of the samples with / or without n-butyl mercaptan - stage 1

	Sample	Density g/cm³	Mean Density g/cm³	CVP of Density %	shrinkage %	Mean shrinkage %	CVP of shrinkage %
GROUP 01	A-1	1.468			22.54		
	A-2	1.389			1.94		
	A-3	1.319	1.3632	4.90	10.1	13.79	40.43
	A-4	1.304			8.85		
	A-5	1.336			1.52		
GROUP 02	A-6	1.415			18.11		
	A-7	1.411			17.78		
	A-8	1.402	1.4018	0.84	17.03	17.01	5.78
	A-9	1.395			16.44		
	A-10	1.386			15.69		

Note: TBPPI – (*t*-butyl pivalate peroxide initiator) and the irradiation dose was of 10 kGy

The presence of n-butyl mercaptan according to the compositions listed in Tab.4 and Fig.1, the samples densities were modified. The presence of mercaptan according to the composition listed in Tab.2 the samples densities were modified by 2.85 % in average density from 1.36 to 1.40. Regardless of the concentration of TBPPI the variation of sample density was found low.

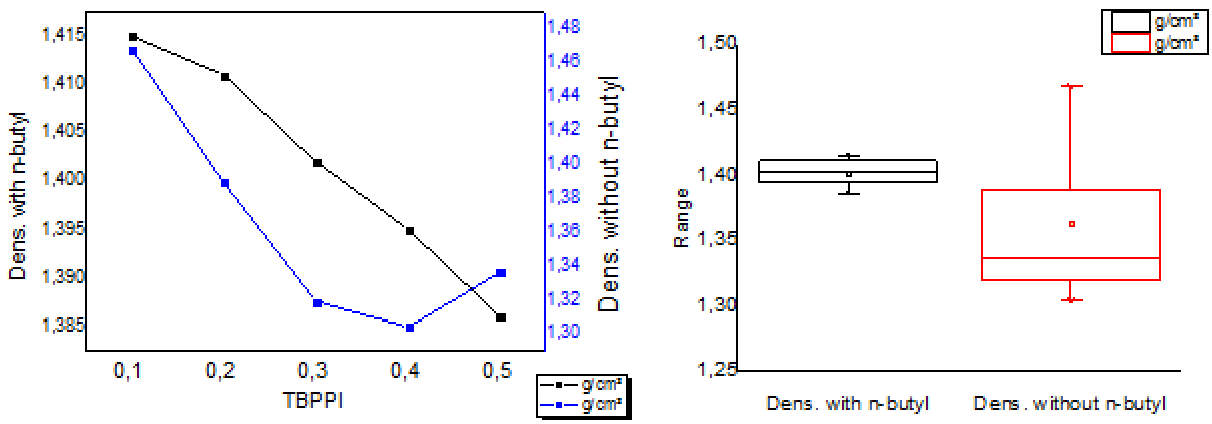

Figure 1 - Variations in density of the samples obtained with or without agent n-butyl mercaptan - stage 1

Mercaptan had a great influence on the reaction mechanism of the specimens cured by means of ionizing radiation minimizing the modification of the material characteristics. The chain transfer has a direct consequence on the rate of reaction and on the degree of polymerization. The decreased molecular weight and properties related to it can be obtained.

The properties of compounds namely density and contraction are determined by the entanglement of molecules during polymerization, so that a proper controlled reaction allows a more satisfactory organization of molecules. In this sense the mercaptan acts as break agent according to its reactivity. The influence of reactivity to molecular weight figures is attained by the variation in the loading of mercapto compounds.

The presence of n-butyl mercaptan in the formulation of Group 02 brings about a higher average contraction, 23% higher than for the compositions belong to Group 1, listed in Tab.4 and Fig.1. This result is due to the ability of n-butyl to bind and minimize variations in the material properties during the reaction: the FMC density of 0.84%, and CVP contraction with a value of 5.78%.

The n-butyl mercaptan is an important additive to control the properties of the compound, in view of decrease of both characteristics the density and the shrinkage of the samples present in Group 2 (Fig. 2). In this case, the densities of the samples containing the mercaptan cover the range from 1.386 to 1.415 g/cm ³, while the other density group varied between 1.336 and 1.468 g/cm^3.

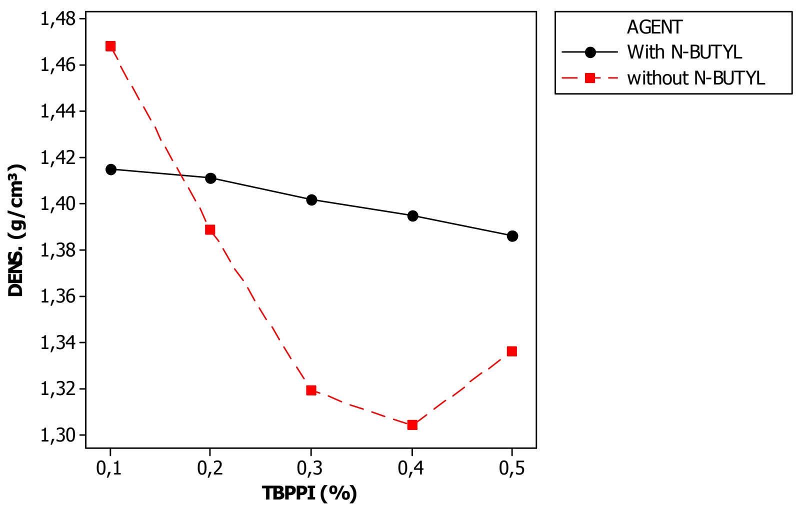

Figure 2 – Comparison of densities of samples with n-butyl mercaptan and without n-butyl mercaptan – stage 1

The change in concentration TBPPI is directly linked with initial generation of free radicals, and the number of chains in growth. The increase in the concentration of initiator (TBPPI) increases the rate of polymerization, but decrease in the molecular chain is obtained simultaneously.

N-butyl reduces the influence of the initiator TBPPI ability of the packaging chain during the reaction. It is assumed that products with higher densities and less shrinkage, respectively, are obtained by this way.

The reduction in the variation of the sample contraction is a positive factor for the preparation of composites, especially in the molding process where the modification in samples size is prevented.

3.2. Analysis of varying densities of the initiator and mercaptan

The variation in the concentration of both additives, mercaptan and TBPPI is applied for the qualification of effects. In tab. 3 it to be noticed the composition of each sample, gathered in 5 groups according with the concentration of mercaptan amount.

As it can be seen in the first part, the addition of mercaptan tends to minimize the influence of initiator concentration on the density of the composites. The composition with mercaptan lead to a higher polymer packaging and respectively greater density. In general, the average density corresponding to the five groups of samples that reach a value of 1.409 g/cm³, similar to the group 2.

Table 5 – Samples with variation of n-butyl mercaptan and initiator - stage 2

Group	Sample	Density g/cm³	Density Mean g/cm³	CVP of Density %	shrinkage %	shrinkage Mean %	CVP of shrinkage %
01	B-1	1.28	1.395	5.54	6.760	16.348	39.39
	B-2	1.44			20.10		
	B-3	1.44			20.10		
	B-4	1.42			18.43		
02	B-5	1.43	1.435	0.40	19.27	19.685	2.43
	B-6	1.43			19.27		
	B-7	1.44			20.10		
	B-8	1.44			20.10		
03	B-9	1.41	1.398	0.90	17.60	16.555	6.33
	B-10	1.40			16.76		
	B-11	1.38			15.10		
	B-12	1.40			16.76		
04	B-13	1.42	1.417	0.41	18.43	18.153	2.64
	B-14	1.41			17.60		
	B-15	1.42			18.43		
05	B-16	1.38	1.400	1.89	15.10	16.767	13.16
	B-17	1.43			19.27		
	B-18	1.39			15.93		

Note: TBPPI – (*t*- butyl pivalate peroxide). Irradiation dose of 10 kGy

Importantly, the increase in the concentration of mercaptan groups 03, 04 and 05 did not induce an increase in the average density of these groups, so that the samples show values close to the average. In the case of group 01, which has a concentration of 0.1%? The 75% of the average values obtained are above the average obtained for samples B-1.

This result demonstrates a trend to use low concentrations of n-butyl mercaptan to be achieve better results. It occurred in the samples from group 2 All values were above average, and this group had the highest average density of individuals densities. (Table 5)

In the case of group 2 (samples B-5 to B-8), their average density was 1.435 g/cm³, i e above the average of the other groups. This is a best result, with the variation (CPV) group of 0.40%, demonstrating that this concentration of mercaptan requires statistically lower initiator concentration. Both properties, density and contraction, exhibit better results in the Group 02 samples. In the case of Group 01 it is possible that the sample B-1 has present an atypical result due to experimental error. It can be consider that groups 01 and 02 presented the best results with higher mercaptan concentration. Otherwise, when the mercaptan concentration of 0.1 %, it would be interesting to use TBPPI concentrations greater than 0.2 %.

Table 6 - ANOVA Two-way and Tukey test samples contained in step 2

```
Source   DF         SS         MS     F      P
N-Butyl   4  0,0044933  0,0011233  4,62  0,032
TBPPI     2  0,0001200  0,0000600  0,25  0,787
Error     8  0,0019467  0,0002433
Total    14  0,0065600

S = 0,01560   R-Sq = 70,33%   R-Sq(adj) = 48,07%

Individual 95% CIs For Mean Based on Pooled StDev

N-Butyl     Mean   -+---------+---------+---------+--------
0,1%     1,43333                    (-------*--------)
0,2%     1,43667                     (--------*-------)
0,3%     1,39333   (-------*--------)
0,4%     1,41667             (--------*-------)
0,5%     1,40000       (-------*-------)
                   -+---------+---------+---------+--------
                   1,375     1,400     1,425     1,450
```

For the application of Two-Way ANOVA for the samples of Table 6 it is identified a strong influence of n-butyl mercaptan to the variables density and contraction, with a significance level of 95%. This analysis also can identify the reduction of the influence by the concentration of TBPPI previously raised, and a high order interaction effects TBPPI and mercaptan, which can be seen as swelling of the error.

By performing the Tukey analysis, it was found that the samples belonging to groups 03, 04 and 05 exhibit the same statistical population distribution with not significant contribution from mercaptan concentration. But the samples of groups 01 and 02 stand out from the others (03, 04 and 05) presenting a strong influence caused by the presence of mercaptan. Their densities and contractions became higher as mercaptan concentration is higher.

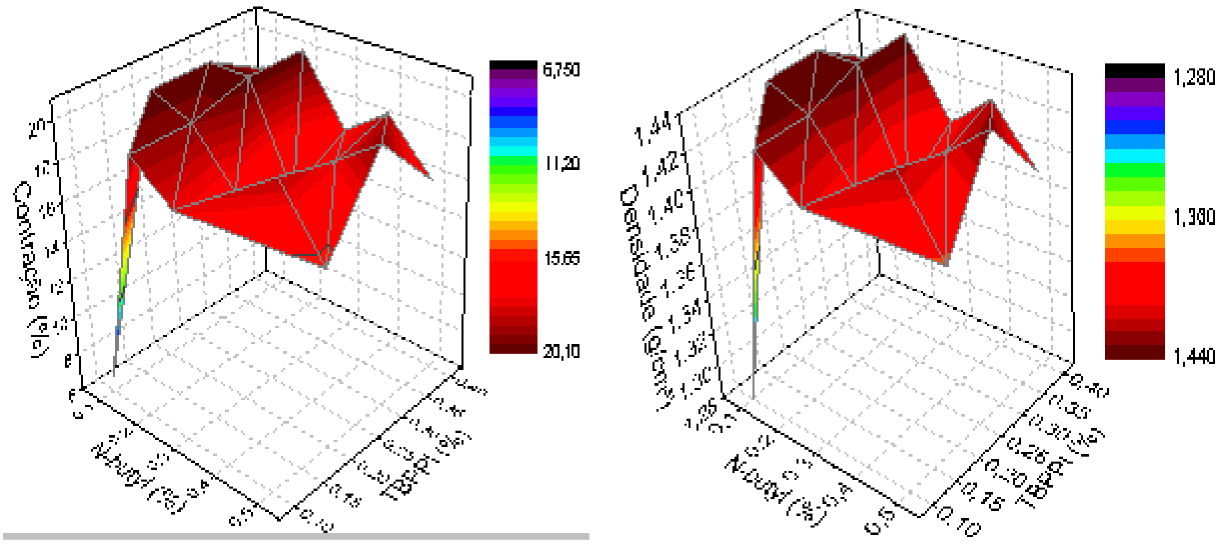

Figure 3 - Response surface variation TBPPI and n-butyl mercaptan to contraction (left) and density (right) – stage 2

A limited concentration of mercaptan improves the functional properties of the material. The exceeding in its concentration becames the material less applicable. Maintaining the concentration of mercaptan in the range of 0.1 % to 0.2 %, it is possible to obtain products with higher densities and contractions. But increasing the concentration of mercaptan reduces the density and contraction of compounds (Fig. 3). However, as the varying results, the presence of n-butyl mercaptan tends to minimize this behavior, homogenizing the values obtained in an average.

4. CONCLUSION

In the present study we can remark that n-butyl mercaptan transfer agent exerts a noticiable influence on the reaction kinetics of the polymerization in acrylic composite subject to ionizing radiation, promoting a better organization of the chains, and also a reduction in its size resulting in an increased density.

The insertion of mercaptan compounds resulted in three effects. First the composite increased in average density and average contraction, making it possible to obtain denser materials. Secondly, it minimize the variability of density of the compound, even if it is altered the initiator concentrations. Thirdly, has a direct influence on the action of initiator. For future work, it is possible to analyze if the presence of mercaptan also influences other thermal and mechanical properties such as glass transition temperature, and tensile strength.

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